THE ENVIRONMENTALLY BENIGN PULPING PROCESS OF NON-WOOD FIBERS

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Abstract

The increasing demand for paper has raised the need for low-cost raw materials and also for the development of new processes in order to boost production. Non-wood fibers, for example agricultural residues and annual plants, are considered an effective alternative source of cellulose for producing pulp and paper sheets with acceptable properties. This paper reviews some physical and chemical properties of non-wood pulps which have effects on the making of paper. The less polluting pulping processes that use organic solvents are of interest for pulp production. The delignification of the Organosolv pulping process depends on the type of Organosolv methods and cellulosic sources used. The chemicals and cooking conditions, such as the catalysts, solvent concentration, cooking temperature, cooking time, and liquor to raw material ratio, all influence the properties of the pulp and paper.

Keywords: Non-wood fiber, organosolv, alcohol pulping, solvent-based pulping, delignification

Introduction

Pulp and paper production is one of the high demand sectors in the world of industrial production. The total global consumption from paper-making was projected to increase from 316 million tons in 1999 and 351 million tons in 2005 to about 425 million tons by 2010 (García et al., 2008). Progress in pulp and paper technology has overcome most of the related environmental problems. The environmental problems have brought forth the cleaner technology now involved in paper making. New raw materials have replaced traditional wood raw materials with non-wood and residual materials, and less polluting cooking and pulp bleaching processes have been evolved.

Cleaner technology is applied to achieve increased production with minimum effect on the environment, and to save, utilize, and recycle expensive and scarce chemicals and raw materials. This technology is also called low and non-waste technology (Müller, 1986). The technology lessens the disposal costs, stability risks and resource costs results in a reduced burden on the natural environment and increases profits. New technology is essential for a clean industry, but this option is largely suppressed because of the costs of the technology required. Some studies have looked specifically into the environmental problems.
consequences of pulp and paper production using wood as the feedstock (Young and Akhtar, 1998; Thompson et al., 2001; Environment Canada, 2003; Sadownic et al., 2005; Aysar and Demirer, 2008).

Wood is the most widely used raw material for production of pulp and paper in the world. It is used as part or all of fiber composition in practically every type of paper and constitutes approximately 90% of virgin pulp fiber used by the world’s paper and board industry (Feng and Alén, 2001). Wood pulp is pulp manufactured either by mechanical or chemical means or both from softwood or hardwood trees.

Pulping is the process by which wood is reduced to a fibrous mass. It is the means of rupturing the bond within the wood structure. The commercial processes are generally classified as mechanical, chemical or semichemical pulping.

**Mechanical Pulping**

The most common method of mechanical pulping is the groundwood process, where a block (or bolt) of wood is pressed lengthwise against a roughened grinding stone revolving at peripheral speeds of 1000 to 1200 m/min. Fibers are torn out of the wood, abraded, and washed away from the stone surface with water. A recent development in mechanical pulping involves shredding and grinding chip of wood between the rotating discs of a device called a refiner. The product of this process is known as refiner mechanical pulp (RMP). RMP usually retains more long fibers than stone groundwood and yields stronger paper. Most new installations now employ thermal (and/or chemical) presoftening of the chips to modify both the energy requirement and the resultant pulp properties, e.g., thermomechanical pulp (TMP). TMP is usually much stronger than RMP and contains very little screen reject materials.

Mechanical pulping processes have the advantage of converting up to 95% of the dry weight of the wood into pulp, but require prodigious amounts of energy to accomplish this objective. Mechanical pulps are most often produced from softwood sources, such as spruce and pine. The smaller, thinner hardwood fibers are more severely damaged during mechanical pulping and yield a finer, more flour-like material that forms an exceedingly weak sheet.

**Chemical Pulping**

The two principal methods of chemical pulping process are the alkaline process, such as kraft process (Figure 1), and the acidic process, such as sulfite process (Figure 2). The pulping processes used over the years, both for woody and non-woody fibers, have been mainly chemical based (Wegener, 1992). The world pulp production statistics reveals that most of the chemical pulps produced today are made by the kraft process (Dahlmann and Schroeter, 1990). Kraft pulping produces a stronger pulp, but it too is feeling the pressure of environmental regulations on emissions from manufacturing plants, such as total reduced sulfur compound (TRS), sulfur dioxide, suspended solids, and wastewater pollution (UNEP, 1997). Sulfite pulping has been in a steady decline for many years due to the environmental concerns and the inferior physical properties of the pulp.

The increasing of environmental concerns, uncertain future availability of wood fiber and potential increases in wood costs have caused the pulp and paper industry to search for alternative fiber sources, such as non-wood fibers.

**Non-wood Fibers**

There is a growing interest in the use of non-wood such as annual plants and agricultural residues as a raw material for pulp and paper. Non-wood raw materials account for less than 10% of the total pulp and paper production worldwide (El-Sakhawy et al., 1996). This is made up of 44% straw, 18% bagasse, 14% reeds, 13% bamboo and 11% others (Figure 3). The production of non-wood pulp mainly takes place in countries with a shortage of
wood, such as China and India (Oinonen and Koskivirta, 1999). China accounts for more than two thirds of the non-wood pulp produced worldwide (Hammett et al., 2001).

The utilization of non-wood fibers is an ethically sound way to produce pulp and paper compared to the clear-cutting of rain forests or primeval forests. The benefits of non-wood plants as a fiber resource are their fast annual growth and the smaller amount of lignin in them that binds their fibers together. Another benefit is that non-wood pulp can be produced at low temperatures with lower chemical charges. In addition, smaller mill sizes can be economically viable, giving a simplified process. Non-wood pulps are also more easily refined. Moreover, non-food applications can give additional income to the farmer from food crops or cattle production (Rousu et al., 2002; Kissinger et al., 2007; Rodríguez et al., 2007).

Non-wood fibers are used for all kinds of paper. Writing and printing grades produced from bleached non-wood fiber are quite common. Some non-wood fibers are also used for packaging. This reflects the substantially increased use of non-wood raw materials, from 12,000 tons in 2003 to 850,000 tons in 2006 (FAO, 2009; López et al., 2009). Given that world pulp production is unlikely to increase dramatically in near future, there is a practical need for non-wood pulp to supplement the use of conventional wood pulp (Diesen, 2000).

According to their origin, non-wood fibers are divided into three main types: (1) agricultural by-products; (2) industrial crops; and (3) naturally growing plants (Rowell and Cook, 1998; Svenningsen et al., 1999). Agricultural by products are the secondary products of the principal crops (usually cereals and grains) and are characterized by low raw material price and moderate quality, such as rice straw and wheat straw (Navaee-Ardeh et al., 2003; Deniz et al., 2004). Industrial crops, such as hemp, sugarcane and kenaf, can produce high quality pulps with high expense cost of raw materials. However, the source of the pulp is limited and these materials come from crops planted specifically to yield fiber (Kaldor et al., 1990; Zomers et al., 1995). Naturally growing plants are also used for the production of high quality pulps. This includes bamboo and some grass fibers, such as elephant...
The Environmentally Benign Pulping Process of Non-wood Fibers

grass, reed and sabai grass (Walsh, 1998; Poudyal, 1999; Shatalov and Pereira, 2002; Salmela et al., 2008). The specific physical and chemical characteristics of non-wood fibers have an essential role in the technical aspects involved in paper production. On the other hand, the technical issues involved are related to the economic, environmental and ethical contexts and vice versa.

Properties of Non-wood Fibers

The chemical compositions of non-wood materials have tremendous variations in chemical and physical properties compared to wood fibers (Gümuşkaya and Usta, 2002; Rezayati-Charani et al., 2006). They vary, depending on the non-wood species and the local conditions, such as soil and climate (Bicho et al., 1999; Jacobs et al., 1999). The non-wood materials generally have higher silicon, nutrient and hemicellulose contents than wood (Hurter, 1988). Some parts of the non-fibrous materials may be removed by the pre-treatment of the raw material, which has a positive influence on the ash content and the pulp and paper properties. Table 1 shows the average results of the chemical and physical analyses of some non-wood fibers (Hurter, 1988; Chen et al., 1987; Rodríguez et al., 2008). The standard deviations of the three replicates in each test with respect to the means were always less than 10%.

Short fiber length, high content of fines and low bulk density are the most important physical features of non-wood raw materials (Oinonen and Koskivirta, 1999; Paavilainen, 2000). The large amount of fines and the short fiber length (< 2 mm.) especially affect the drainage properties of pulp. Apart from the operation of the pulp mill itself, these properties also affect dewatering in the paper machine. Due to the wide range of different non-wood species and their different physical properties, substantial differences in dewatering behavior may arise. (Cheng and Paulapuro,

Table 1. Physical and chemical properties of some non-woods used for Papermaking

<table>
<thead>
<tr>
<th>Properties</th>
<th>Unit</th>
<th>Rice straw</th>
<th>Wheat straw</th>
<th>Bagasse</th>
<th>Reed grass</th>
<th>Bamboo</th>
<th>Jute</th>
<th>Hemp (bast)</th>
<th>Kenaf (bast)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. fiber length</td>
<td>mm</td>
<td>1.41</td>
<td>1.48</td>
<td>1.70</td>
<td>1.5</td>
<td>1.36-</td>
<td>2.5</td>
<td>20</td>
<td>2.74</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avg. diameter</td>
<td>μm</td>
<td>8</td>
<td>13</td>
<td>20</td>
<td>20</td>
<td>8-30</td>
<td>18</td>
<td>22</td>
<td>20</td>
</tr>
<tr>
<td>L/D ratio</td>
<td></td>
<td>175:1</td>
<td>110:1</td>
<td>85:1</td>
<td>75:1</td>
<td>135-</td>
<td>139:1</td>
<td>1000:1</td>
<td>135:1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>175:1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alpha cellulose</td>
<td>%</td>
<td>28-36</td>
<td>29-35</td>
<td>32-44</td>
<td>45</td>
<td>26-43</td>
<td>61</td>
<td>55-65</td>
<td>31-39</td>
</tr>
<tr>
<td>Lignin</td>
<td>%</td>
<td>12-16</td>
<td>16-21</td>
<td>19-24</td>
<td>22</td>
<td>21-31</td>
<td>11.5</td>
<td>2-4</td>
<td>15-18</td>
</tr>
<tr>
<td>Pentosan</td>
<td>%</td>
<td>23-28</td>
<td>26-32</td>
<td>27-32</td>
<td>20</td>
<td>15-26</td>
<td>24</td>
<td>4-7</td>
<td>21-23</td>
</tr>
<tr>
<td>HWS</td>
<td>%</td>
<td>7.3</td>
<td>12.27</td>
<td>4.4</td>
<td>5.4</td>
<td>4.8</td>
<td>3.7</td>
<td>20.5</td>
<td>5.0</td>
</tr>
<tr>
<td>ABS</td>
<td>%</td>
<td>0.56</td>
<td>4.01</td>
<td>1.7</td>
<td>6.4</td>
<td>2.3</td>
<td>2.4</td>
<td>2.6</td>
<td>2.1</td>
</tr>
<tr>
<td>SS</td>
<td>%</td>
<td>57.7</td>
<td>43.58</td>
<td>33.9</td>
<td>34.8</td>
<td>24.9</td>
<td>28.5</td>
<td>-</td>
<td>28.4</td>
</tr>
<tr>
<td>Ash</td>
<td>%</td>
<td>15-20</td>
<td>4-9</td>
<td>1.5-5</td>
<td>3</td>
<td>1.7-5</td>
<td>1.6</td>
<td>5-7</td>
<td>2-5</td>
</tr>
<tr>
<td>Silica</td>
<td>%</td>
<td>9-14</td>
<td>3-7</td>
<td>0.7-3</td>
<td>2</td>
<td>1.5-3</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>-</td>
</tr>
</tbody>
</table>

HWS: hot water solubility, ABS: alcohol benzene solubility, SS: 1%sodium hydroxide solubility
The low bulk density affects the logistics of non-wood raw materials. This would make the amount of cellulose handled comparable to wood.

The production of pulp from non-wood resources has many advantages such as easy pulping capability, excellent fibers for the special types of paper and high-quality bleached pulp. They can be used as an effective substitute for the forever decreasing forest wood resources (El-Sakhawy et al., 1995; 1996; Jiménez et al., 2007). In addition to their sustainable nature, other advantages of non-wood pulps are their easy pulping and bleaching capabilities. These allow the production of high-quality bleached pulp by a less polluting process than hardwood pulps (Johnson, 1999) and the reduced energy requirements (Rezayati-Charani et al., 2006). However, some mineral substances in their composition, including K, Ca, Mn, Cu, Pb, and Fe, may have negative effects on the different steps of pulp and paper manufacturing, especially the bleeding process. Metals may interfere during the bleaching with hydrogen peroxide or ozone. The transition elements form radicals that react unselectively with the pulp when the pulp is bleached without chlorine chemicals (Gierer, 1997). Furthermore, bleeding is accompanied by the formation of oxalic acid. Calcium reacts with oxalic acid to form calcium oxalate, which deposits easily. Thus, effluent-free bleeding will obviously be difficult to achieve in the bleeding plant (Dexter and Wang, 1998).

Non-wood Pulping

Traditionally, non-wood material is cooked with hybrid chemimechanical and alkali-based chemicals (Goyal et al., 1992; Jahan et al., 2007). Hybrid chemimechanical pulps, which were once thought of as a logical replacement for chemical pulps, simply do not provide the purity necessary for high grade and dissolving pulps. Chemimechanical pulps cannot be used in grades that do not allow fiber-containing furnishes due to brightness reversion, brightness levels, or simply customer insistence. Much more money is spent each year on environmental projects in an attempt to resolve some of the problems associated with the pulping process. Solving these motivates much the research and development in relation to new pulping technologies.

In chemical pulping, the raw materials are cooked with appropriate chemicals in an aqueous solution at an elevated temperature and pressure. The objective is to degrade and dissolve away the lignin and leave behind most of the cellulose and hemicelluloses in the form of intact fibers. In practice, chemical pulping methods are successful in removing most of the lignin; they also degrade and dissolve a certain amount of the cellulose and hemicelluloses (Smook, 1994).

Non-wood pulping processes generate large volumes of black liquor as by-products and wastes. Black liquor wastewater is a mixture of organic and inorganic materials, with very high amounts of total dissolved solids (TDS). The total dissolved solids in the black liquor are composed of lignin derivatives, low molecular weight organics, and the rest being made up of chemicals from the digesting liquor (Huang et al., 2007). In delignification, the relatively high amount of silicon present in non-wood material is dissolved together with lignin into cooking liquor, This has led to difficulties in the recovery of cooking chemicals. This situation makes black liquor one of the most difficult materials to handle in wastewater treatment processes.

Generally, alkaline non-wood pulps contain much hemicellulose while their fibers are short. This impairs the dewatering properties in different unit processes, the adhesive forces in the paper machine, and paper quality. Then the hemicellulose content of the pulp should be controlled to avoid these problems. However, when using the alkaline pulping processes, the hemicellulose content of the pulp cannot be easily controlled without losses in pulp quality (Rousu et al., 2002).

The conventional alkaline pulping process is not suitable for many non-wood raw materials and caused serious environmental problems. Therefore, throughout the world many alternative pulping processes have been
introduced. One group of the most promising alternative processes is called the Organosolv processes. These cooking methods are based on cooking with organic solvents such as alcohols or organic acids. Methanol and ethanol are common alcohols used and the organic acids are normally formic acid and acetic acid. High cooking temperatures and associated high pressures are needed when alcohols are used in cooking. However, organic acids require lower temperatures and the pressure is closer to atmospheric pressure. Other more unusual solvents include various phenols, amines, glycols, nitrobenzene, dioxane, dimethylsulfoxide, sulfolane, and liquid carbon dioxide (Sunquist, 2000).

**Organosolv Pulping of Non-wood**

The Organosolv process has certain advantages. It makes possible the breaking up of the lignocellulosic biomass to obtain cellulosic fibers for pulp and papermaking, high quality hemicelluloses and lignin degradation products from generated black liquors, thus avoiding emission and effluents (Aziz and Sarkanen, 1989; Hergert, 1998; Paszner, 1998; Sidiras and Koukios, 2004).

The Organosolv processes use either low-boiling solvents (for example methanol, ethanol, acetone), which can be easily recovered by distillation or high-boiling solvents (for example ethylene glycol, ethanolamine), which can be used at a low pressure and hence at available facilities currently used in classical pulping processes. Thus, it is possible to use the equipment used in the classic processes, for example the soda and Kraft processes, hence saving capital costs. (Muurinen, 2000; Lavarack et al., 2005; López et al., 2006; Rodríguez and Jiménez, 2008). Using this process, pulps with properties such as high yield, low residual lignin content, high brightness and good strength can be produced (Shatalov and Pereira, 2004; Yawalata and Paszner, 2004). Moreover, valuable byproducts include hemicelluloses and sulphur-free lignin fragments. These are useful for the production of lignin-based adhesives and other products due to their high purity, low molecular weight, and easily recoverable organic reagents (McDonough, 1993, Dapía et al., 2002; Pan et al., 2005).

In recent years, research into the Organosolv pulping processes has led to the development of several Organosolv methods capable of producing pulp with properties near those of Kraft pulp. Prominent among the processes that use alcohols for pulping are those of Kleinert (Aziz and Sarkanen, 1989), Alcell (Lönnberg et al., 1987; Aziz and Sarkanen, 1989; Stockburger, 1993), MD Organocell (Lönnberg et al., 1987; Aziz and Sarkanen, 1989; Stockburger, 1993), Organocell (Lönnberg et al., 1987; Dahlmann and Schroeter, 1990; Stockburger, 1993), ASAM (Lönnberg et al., 1987; Black, 1991), and ASAE (Kirci et al., 1994). Other processes based on other chemicals also worthy of special note are ester pulping (Aziz and McDonough, 1987; Young, 1989), phenol pulping (Aziz and Sarkanen, 1989; Funaoka and Abe, 1989), Acetocell (Neumann and Balser, 1993), Milox (Poppius-Levlin et al., 1991, Sundquist and Poppius-Levlin, 1992; Sundquist and Poppius-Levlin 1998), Formacell (Saake et al., 1995) and NAEM (Paszner and Cho, 1989).

Organosolv pulping processes, by replacing much or all of the water with an organic solvent, delignify by chemical breakdown of the lignin prior to dissolving it. The cleavage of ether linkages is primarily responsible for lignin breakdown in Organosolv pulping. The chemical processing in Organosolv pulping is fairly well understood (McDonough, 1993). High cooking temperature and thus high pressures are needed when alcohols are used in cooking. However, organic acids require lower temperatures and the pressure is closer to atmospheric.

The ethanol Organosolv process was originally designed to produce clean pulping and was further developed into the Alcell® process for pulp production (Pye and Lora, 1991). The Alcell® process is a solvent-pulping process that employs a mixture of water and ethanol (C₂H₅OH) as the cooking medium.
The process can be viewed as three separate operations: extraction of lignin to produce pulp; lignin and liquor recovery; and by-product recovery (Stockburger, 1993). The raw materials are cooked in a 50:50 mixture of water and ethanol at around 175-195°C for 1 hour. The typical liquid to biomass solid ratio is 4-7 and a liquor pH of about 2-3. The system employs liquor-displacement washing at the end of the cooking to separate the extracted lignin. The sulfur-free lignin produced with this process has very high purity and has the potential of high-value applications. Furthermore, this process generates the furfural which is used as the solvent for lubricating oil production. It is claimed that the process produces pulps with a higher yield that bleach more easily and are free of sulfur emissions. The Alcell® process enjoys a significant capital cost advantage compared with the Kraft process, since it does not require a recovery furnace or other traditional chemical recovery equipment (such as lime kilns and causticators).

The methanol Organosolv process has been used in the alkaline sulphite-anthraquinone-methanol process (ASAM) and the soda pulping method with methanol (Organocell). The ASAM process is basically alkaline sulphite pulping with the addition of anthraquinone (AQ) and methanol (CH₃OH) to achieve a higher delignification level (Stockburger, 1993). The process has been successful in the pulping of softwood, hardwood and also non-wood material. The active cooking chemicals of the ASAM process are sodium hydroxide, sodium carbonate and sodium sulphite. The addition of methanol to the alkaline sulphite cooking liquor considerably improves delignification, and the process produces pulp with better strength properties, higher yields and better bleachability compared to the Kraft process.

The ASAM process utilizes sodium hydroxide, sodium carbonate, sodium sulfite (Na₂SO₃), methanol, and small amounts of the catalyst anthraquinone. ASAM cooking liquor normally contains about 10% methanol by volume. The anthraquinone dose is 0.05%-0.1% by weight for fibrous materials. The liquor-to-raw material ratio is 3-5:1, and the cooking temperature and time are 175°C and 60-150 min, respectively. Anthraquinone serves as a catalyst to increase the reaction rate. Methanol is added to assist in dissolving the lignin and acts as a buffer, prevents lignin from condensing and stabilizes the carbohydrates (Muurinen, 2000). Methanol also improves the solubility of the anthraquinone. The strength properties of ASAM pulps have been found to be equivalent to Kraft pulps while at a higher yield and lower residual lignin content. It is more environmentally benign, since the process is free of the reduced sulfur compounds produced in the Kraft process. Unbleached ASAM pulps also have higher initial brightness and thus lend themselves well to totally chlorine-free bleaching sequences. Methanol improves the impregnation of the chemicals.

The Organocell process is a solvent pulping process that uses sodium hydroxide, methanol, and catalytic amounts of anthraquinone as the pulping chemicals (Stockburger, 1993). The Organocell process was originally a two-stage process. The first stage is cooking with aqueous methanol, a 50% methanol solution, at 190°C for 20-50 min. This stage operates at a mildly acidic condition due to a deacetylation of the raw material. The main part of the sugars and 20% of lignin is dissolved in this stage. The second stage involves the addition of sodium hydroxide at an 18-22% concentration at temperatures of 160-170°C (Kinstrey, 1993).

For the new Ogancell pulping process, the first stage was eliminated from the process. The resultant single stage process is operated with sodium hydroxide, methanol, and catalytic amounts of anthraquinone as cooking chemicals. The concentration of methanol in the cooking liquor is in the range of 25-30%. The one stage process is easier to control and the elimination of the first stage results in stronger fibers than those from the two stage process (Leponiemi, 2008). Methanol improves the capacity of the cooking liquor to penetrate into the fibrous materials and renders the lignin more soluble. Anthraquinone functions in the same way as
in soda cooking by stabilizing polysaccharides and accelerating lignin dissolution (Sundquist, 2000). Methanol is recovered by evaporation and distillation. Lignin is precipitated in evaporation by decreasing the pH of the liquor and it can be separated using a centrifuge. Organocell pulps produced at a pilot operation are almost as good as the corresponding Kraft pulps in yield and physical characteristics. The organocell pulps were also found to bleach more easily. The process is suitable for hardwood, softwood and non-wood species. The process also is entirely free of the sulfur emissions found in the traditional Kraft and sulfite processes (Aziz and Sarkanen, 1989).

Organic acid processes are alternative methods of organosol pulping to delignify lignocellulosic materials to produce pulp for paper (Poppius et al., 1991; Jiménez et al., 1998; Lam et al., 2001; Kham et al., 2005a,b). Typical organic acids used in the acid pulping methods are formic acid and acetic acid. The process is based on acidic delignification to remove lignin, a necessary part of the hemicellulose and nutrients, while silicon remains in the pulp. The pulping operation can be carried out at atmospheric pressure. Acid used in pulping can be easily recovered by distillation and re-used in the process (Muirinen, 2000). Cellulose, hemicellulose and lignin can be effectively separated by degradation in aqueous acetic acid or formic acid. The cooking liquor is washed from the pulp, and both cooking chemicals and water are recovered and recycled completely. Formic acid can also be used to enhance acetic acid pulping. The temperature and pressure can be lower when formic acid is used in pulping compared to those used in alcohol or acetic acid pulping. Organic acid lignin is an optimal feedstock for many value-added products, due to its lower molecular weight and higher reactivity (Kubo et al., 1998; Cetin and Ozmen, 2002). Another advantage of organic acid pulping is the retention of silica on the pulp fiber that facilitates the efficient recovery of cooking chemicals (Seisto and Poppius, 1997). The Organosolv pulping processes based on organic acid cooking are the Milox, Acetosolv and Formacell processes.

The Milox process is an Organosolv pulping process which uses peroxyformic acid or peroxyacetic acid as the cooking chemical (Leponiemi, 2008). Peroxyformic or peroxyacetic acids are simple to prepare by equilibrium reaction between hydrogen peroxide and formic or acetic acids. These are highly selective chemicals that do not react with cellulose or other wood polysaccharides in the same way as formic acid. The hydrogen peroxide consumption is reduced by performing the process in two or three stages. The two-stage formic acid/peroxyformic acid process can be used to produce high viscosity (> 900 dm³/kg SCAN) and fully bleached (90 % ISO) pulp with a reasonable yield (40-48 %). The pulping stages are carried out at atmospheric pressure and at temperatures below 100°C. The resulting pulps have kappa numbers between 5 and 35. (Muirinen, 2000).

The hydrogen peroxide charge needed can be reduced by using a three-stage cooking method. In the first stage, the temperature increases from 60°C to 80°C. The peroxyformic acid that forms is allowed to react with the cellulosic material for 0.5-1 hours. The temperature is raised to the boiling point of the formic acid (ca. 105°C) and the cooking proceeds for 2-3 h. The softened chips are then blown into another reactor, and the pulp is washed with pure formic acid. The washed pulp is then reheated with peroxyformic acid at 60°C at about 10% consistency. Peroxide is applied to the liquor at 1%-2% of the original dry weight of the chips. After cooking, the pulp is washed with strong formic acid, pressed to 30%-40% consistency, and washed under pressure with hot water at 120°C. This removes the chemically bonded formic acid. After washing and screening, the pulp is ready for bleaching.

Unlike with wood species, the two-stage Milox pulping of agricultural plants is more effective than three-stage cooking. The two-stage process uses cooking with formic acid alone, followed by treatment with formic acid and hydrogen peroxide (Sundquist, 2000). When the Milox method is used to delignify
agricultural plants, the resulting pulp contains all the silicon present in the plant. This enables the use of a similar chemical recycling system as in a corresponding wood pulping process. The silica is dissolved during the alkaline peroxide bleaching. (Muurinen, 2000). The two stage peroxyacetic acid process gives higher delignification than three-stage process and vice-versa with peroxyformic acid. The Milox process is a sulphur free process and bleaching can be achieved totally without chlorine chemicals (Sundquist, 2000).

Acetic acid was one of the first organic acids used for the delignification of lignocellulosic raw material to produce pulp for paper. Processes based on the use of acetic acid as an organic solvent have been applied with success to hard and softwoods, and even to non-wood materials (Pan and Sano, 2005). It can be used as a pulping solvent in uncatalyzed systems (Acetocell method) or in catalyzed systems (the Acetosolv method) (Young and Davis, 1986; Kin, 1990; Parajó et al., 1993; Vázquez et al., 1995; Pan et al., 1999; Abad et al., 2003; Ligero et al., 2005). The Acetosolv process is a hydrochloric acid catalysed (0.1%-0.2%) acetic acid process. The cooking temperature is 110°C and the process can be conducted at atmospheric pressure, or above (Nimz, 1989).

Acetic acid used in pulping can be easily recovered by a stilling operation and reused in the process. Acetic acid lignin is an optimal feedstock for many value-added lignin products due to its lower molecular weight and higher reactivity. The sugars from hemicellulose are readily convertible to chemicals and fuels. It has already been reported by a number of researchers that the acetic acid pulping properties of woods are comparable to conventional chemical processes. They also have some advantages in comparison to other Organosolv processes (Groote et al., 1993; Sahin and Young, 2008).

The Formacell process was developed from the Acetosolv process. It is an Organosolv pulping approach in which a mixture of formic and acetic acid is used as the cooking chemical (Leponiemi, 2008). Nimz and Schone (1993) have invented a process where lignocellulosic material is delignified under pressure with a mixture of acetic acid (50-95 w-%), formic acid (< 40 w-%) and water (< 50 w-%). The pulping temperature is between 13°C and 190°C. Pulps with very low residual lignin contents are produced and they can be bleached to full brightness using ozone and peroxyacetic acid. Azeotropic distillation with butyl acetate is used to separate water from the acids. Low pulping temperatures and high acetic acid concentrations should be used in the Formacell process in order to preserve hemicelluloses for paper grade pulps. The use of higher temperatures and water concentrations in the pulping liquor results in dissolving pulps with hemicellulose contents below 3% (Saake et al. 1995). Formacell pulps produced from annual plants have better strength properties than corresponding soda pulps (Sundquist, 2000).

Factors of Delignification

Important parameters controlling the delignification of the Organosolv pulping processes are the types of raw materials, the solvent properties, the chemical properties of catalysts and pulping conditions. The chemical composition of non-wood materials varies, depending on the non-wood species. Non-wood materials generally have higher silicon, nutrient and hemicellulose contents than wood (Hurter, 1988). By pre-treatment of the raw materials, part of the leaves and non-fibrous materials may be removed. This has a positive influence on the ash content and the pulp and paper properties; the chemical composition of the fibers, however, still remains different from paper processed from woods.

The solvent properties have effects on the delignification and pulp properties of non-wood fibers. In Organosolv pulping, alcohols promote solvolysis reactions (Sarkanen, 1990; Schroeter, 1991; McDonough, 1993) but they also reduce the viscosity of the pulping liquor. This makes possible a better penetration and the diffusion of chemicals
into fibrous materials (Balogh et al., 1992; Bendzala et al., 1995). Ethanol and methanol are normally used as the pulping solvents. Both alcohols show similar selectivity when pulp total yield is considered, but higher screened yield values can be obtained in ethanol pulping. Methanol shows better lignin dissolution on average. However, ethanol pulping produces pulps with less lignin at high-intensity cooking conditions, where Kappa numbers lower than 10 can be obtained. The extent of delignification increases as the ethanol concentration is decreased (Oliet et al., 2002). The selectivity towards lignin dissolution is similar for ethanol and methanol.

The most important differences are those observed for pulp viscosity. Although ethanol pulps have a higher viscosity on average, the best results are obtained from methanol pulping. Thus, viscosity values well over 1000 ml/g are obtained for pulps with Kappa numbers between 20 and 30 in the methanol system. These pulps, which are obtained under mild cooking conditions, are of special interest since they can be bleached and are obtained at a good screened yield. Ethanol provides lower viscosity pulp but at a slightly higher screened yield. In both cases, acceptable pulp Kappa numbers can be reached.

The interest in ethanol and methanol pulping is not only justified in terms of cost. The acceptable quality of the pulp produced and the ease of recovery of the solvent by rectification also make the use of ethanol and methanol attractive. Furthermore, some valuable by-products, such as lignin and carbohydrates, can be obtained during solvent recovery. The ethanol solvent has mainly been used in autocatalyzed pulping, the ALCELL process, and antracquinone catalyzed pulping (Aziz and Sarkanen, 1989; Pye and Lora, 1991). The focus of methanol use has been alkaline pulping (Stockburger, 1993). However, it has been shown that pulps with low lignin content and acceptable viscosity can be obtained in an acidic medium by methanol autocatalyzed pulping (Gilarrazz et al., 1999). Methanol has some interesting features, such as easy recovery by distillation, and has a lower material cost than ethanol. However, the use of methanol may be hazardous since methanol is a highly flammable and toxic chemical (Oliet et al., 2002).

Aranovsky and Gortner (1936) found that primary alcohols were more selective delignifying agents than secondary or tertiary alcohols. The monovalent and polyvalent alcohols had higher pulping efficiencies in the presence of water. The use of methanol resulted in less hemicellulose loss than with η-butanol. The higher pulping efficiency (better fiber separation) was associated with increased hemicellulose losses in the aqueous alcohol mixtures.

When using organic acid solvents, the typical organic acid used as the pulping solvents are acetic and formic acid. Formic acid can also be used to enhance acetic acid pulping. Temperature and pressure can be lower when formic acid is used in pulping compared to that used in alcohol or acetic acid pulping (Rousu et al., 2002). The major influence was the acidity or acid concentration. Increasing acetic acid concentration reduced yield and lignin content. The solvent concentration had effects on the various mechanical properties (breaking length, burst, tear index and folding endurance) of paper sheets obtained from each pulping process. The extent of delignification was found to be associated with the system’s hydrogen ion content.

Hydrogen ion concentration plays a very important role in solvent pulping. This is because lignin dissolution is expected to be preceded by the acid-catalyzed cleavage of α-aryl and β-aryl ether linkages in the lignin macromolecule, and becomes soluble in the pulping liquor (Goyal et al., 1992). Delignification in cooking in high-alcohol concentration can be improved by the addition of mineral acids. A lower alcohol concentration favored faster delignification by virtue of a higher hydrogen ion concentration. Acidity increases at lower alcohol concentrations and at lower liquor-to-raw material ratios, but this
did not translate into enhanced delignification, probably because of some lignin redeposition. Acidity also increased with increasing cook time. There are clear signs for the recondensation and deposition of lignin that is common in the Organosolv processes. However, organic acids, especially formic acid, are highly corrosive and cause severe corrosion problems in the processing equipment (Leponiemi, 2008).

Operating conditions that lead to the best pulp quality are important to the Organosolv pulping of non-wood fibers. The actual cooking condition required is a function of solvent concentration, cooking temperature, cooking time, type of non-wood being cooked and the type of organosolv pulping process. Table 2 shows a range of pulping conditions from the literature and the pulp properties of Organosolv pulping processes.

Chemical catalysts is a critical factor in accelerating delignification in the Organosolv pulping processes. Paszner and Cho (1989) discovered that salts of alkaline earth metals, such as calcium and magnesium chlorides, are effective catalysts in Organosolv liquors with high methanol and ethanol contents. They have applied these catalysts to the Organosolv pulping of several softwood and hardwood species as well as bagasse. Bleachable-grade pulps with exceptionally high yields were obtained in each case. The reported bleached pulp yields are 54-57% for softwoods, 57-62% for hardwoods, and 55% for bagasse. The strength properties of these pulps were essentially equal to those of corresponding bleached Kraft processes.

Orth and Orth (1977) recommended the use of aluminium chloride (AlCl₃ * 6 H₂O) as the preferred catalyst in solvents of aqueous glycol or glycol ether. They further indicated that organic acids such as formic, acetic, propionic, oxalic, malic, citric or phthalic acids were suitable catalysts, as did Paszner and Chang (1983). The use of these organic acids has proved to be a great improvement over the use of mineral acids because they facilitate pulping. In the presence of an acid catalyst, many high-boiling solvents allow the pulping process to be performed at ambient pressure, thus eliminating the need for a pressurized reactor. A brief review of the pH effects on solvent pulping will help in understanding the effect of catalysts to control delignification and fiber quality. The solvent type and pH control are both important factors. A drop in pH during solvent cooking is considered to be responsible for a number of effects. These include the condensation of the solvolytically liberated lignin, the extensive hydrolytic dissolution of hemicelluloses, degradation of the cellulose, and formation of solvent insoluble condensation products in the cooking liquor (Aziz et al., 1988).

The Organosolv pulping conditions have effects on the delignification of fibrous materials. Acidic Organosolv pulping is facilitated by the hydrolysis of ether linkages between lignin and carbohydrate. The dissolved lignin decreases with increasing cooking time when the fibrous materials are pulped with organic acids, indicating that lignin condensation occurs during cooking. Condensation during pulping occurs to a greater extent with formic acid than with acetic acid, and to a greater extent with acetic acid than with propionic acid. Propionic acid was also observed to delignify more effectively than either of the other two acids. Lignin precipitation occurs in the ethanol pulping process due to either the reduction of the ethanol concentration in the washing process or the drop in temperature which causes a decrease in lignin solubility, or both.

The influence of cooking conditions, as mentioned previously, have effects on the properties of paper obtained from each Organosolv pulping process. Sahin and Young (2008) found that the pulping of jute in acetic acid results in strength losses at higher temperatures and prolonged cooking. The severe pulping conditions cause the depolymerization reactions of the carbohydrates. The extended delignification, with increasing temperature, strongly affected the strength properties of paper. Increasing temperature and extending cooking time usually brings about 10–50% reduced tear strength.
Table 2. Some Organosolv pulping conditions of non-wood fibers

<table>
<thead>
<tr>
<th>Title</th>
<th>Unit</th>
<th>ASAM (Bagasse)</th>
<th>ASAE (Wheat straw)</th>
<th>Acetic Acid (Jute)</th>
<th>LCELL (Kenaf)</th>
<th>Autocatalyzed EtOH (Core Hemp)</th>
<th>CIMV (Wheat straw)</th>
<th>CIMV (Bagasse)</th>
<th>CIMV (Rice straw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L:M ratio</td>
<td></td>
<td>3-5:1</td>
<td>7:1</td>
<td>7-10:1</td>
<td>12:1</td>
<td>15:1</td>
<td>10:1</td>
<td>12:1</td>
<td></td>
</tr>
<tr>
<td>Cooking temp.</td>
<td>°C</td>
<td>170-180</td>
<td>170</td>
<td>195</td>
<td>200</td>
<td>195</td>
<td>107</td>
<td>107</td>
<td>107</td>
</tr>
<tr>
<td>Cooking Time</td>
<td>min</td>
<td>60-150</td>
<td>60</td>
<td>60</td>
<td>120</td>
<td>120</td>
<td>180</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>Organic solvent</td>
<td>%</td>
<td>20 (MtOH)</td>
<td>50 (EtOH)</td>
<td>90 (AA)</td>
<td>60 (EtOH)</td>
<td>60 (EtOH)</td>
<td>60:20:20</td>
<td>30:55:15</td>
<td>20:60:20</td>
</tr>
<tr>
<td>Na_2SO_4 charge</td>
<td>%</td>
<td>16-18</td>
<td>14</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NaOH charge</td>
<td>%</td>
<td>-</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Anthraquinone(AQ)</td>
<td>%</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Kappa No.</td>
<td>%</td>
<td>3-6</td>
<td>16.4</td>
<td>42-56</td>
<td>30</td>
<td>31.4</td>
<td>50.4</td>
<td>28.2</td>
<td>45.8</td>
</tr>
<tr>
<td>Screened Yield</td>
<td>%</td>
<td>61-63</td>
<td>56.1</td>
<td>76</td>
<td>60</td>
<td>47.7</td>
<td>43</td>
<td>49.4</td>
<td>52.9</td>
</tr>
<tr>
<td>Tensile index</td>
<td>Nm/g</td>
<td>-</td>
<td>-</td>
<td>24</td>
<td>-</td>
<td>87.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Burst index</td>
<td>kPa.m^2/g</td>
<td>-</td>
<td>3.2-4</td>
<td>1.1</td>
<td>4.4</td>
<td>4.6</td>
<td>2.14</td>
<td>3.21</td>
<td>2.52</td>
</tr>
<tr>
<td>Tear index</td>
<td>mN.m^2/g</td>
<td>-</td>
<td>7.3</td>
<td>8.0</td>
<td>9.9</td>
<td>3.1</td>
<td>3.27</td>
<td>4.23</td>
<td>4.38</td>
</tr>
<tr>
<td>Reference</td>
<td></td>
<td>Shukry et al., 2000</td>
<td>Usta et al., 1999</td>
<td>Sahin and Young, 2008</td>
<td>Winner et al., 1997</td>
<td>Zomers et al., 1995</td>
<td>Kham et al., 2005</td>
<td>Lam et al., 2004</td>
<td>Delmas et al., 2003</td>
</tr>
</tbody>
</table>

L:M : liquor to raw material ratio, MtOH: Methanol, EtOH: Ethanol, FA: Formic acid, AA: Acetic acid
For alkali ethanol pulping of rice straw (Navae-Ardeh, et al., 2004), the breaking length, burst index and folding endurance of paper sheets were more affected by ethanol concentration than temperature. This was after a cooking time of 150 minutes. At a high cooking temperature, these dependent variables were much more sensitive to changes in time than in an ethanol concentration. Sabatier et al. (1989) found that the acid catalyzed ethanol pulping process is less selective than the alkaline process. Soda ethanol pulping can produce paper-grade pulps of good strength with a saving of 50% of the sodium hydroxide or more, compared with plain soda pulping. The pulps obtained by the alcohol soda (NaOH-EtOH–H₂O) method had a better quality and lower kappa number than those from ethanol solvent (EtOH-H₂O). Adding anthraquinone (AQ) as a catalyst to the pulping by aqueous alcohol soda gave higher yields, lower kappa number and better strength (Physico-mechanical) properties. (El-Skhawy et al., 1995).

Conclusions

The increasing demands for paper and environmental concerns have increased the need for non-wood pulp as a low-cost raw material for papermaking. This has also led to the developing of alternative pulping technologies that are environmentally benign. Annual plants and agricultural residues appear to be well suited for papermaking due to them being an abundant and renewable resource. However, many factors influence the suitability of raw materials for use in papermaking. These include: the ease of pulping; the yield of usable pulp; the cost of collection and transportation of the fiber source; the presence of contaminants; and the availability of the fiber supply. Additional factors include fiber morphology, such as its composition and strength, the fiber length and diameter.

The Organosolv pulping processes are alternatives to conventional pulping processes, and have environmental advantages. Organosolv pulping features an organic solvent in the pulping liquor which limits the emission of volatile sulfur compounds into the atmosphere and gives efficient chlorine-free bleaching. These processes should be capable of pulping all lignocellulose species with equal efficiency. Another major advantage of the Organosolv process is the formation of useful by-products such as furfural, lignin and hemicelluloses. However, there are inherent drawbacks to the Organosolv pulping methods. The dilution of pulping liquor with water tends to reprecipitate the dissolved lignin on the pulp fibers. The digester leaks in Organosolv pulping can be inherent fire and explosion hazard.

References

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ruminant animals from wood and/or woody products. U.S. Patent no. 4,017, 642


