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INFLUENCES OF THE OPERATING VARIABLES OF ACETOSOLV PULPING ON PULP PROPERTIES OF OIL PALM FROND FIBRES

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ABSTRACT

The effect of acetosolv pulping variables viz. pulping time, temperature, catalyst (HCl) and acetic acid on oil palm frond fibres was investigated. The following conditions were found to be optimum to pulp frond fibres: 140 ºC, 0.5% HCl, 75% acetic acid, and 1/10 solid/liquor ratio. Under these conditions we could obtain these properties: Kappa number 13-16, zero-span tensile breaking length – 83 km, sheet density – 0.57 g cm^{-3}, tensile index – 48 N m g^{-1}, tear index – 5.4 mN m^2 g-1, brightness – 16% ISO and opacity – 98%. Higher values of these operating parameters would degrade the fibre characteristics such as zero-span tensile breaking length, tensile index, and sheet density.

Keywords: Elaeis guineensis, oil palm fronds, acetosolv pulping, acetic acid, pulp properties

INTRODUCTION

Wood is the main raw material for the production of pulp and paper in the world. However, increasing concerns over future fibre supplies and potential increases in wood costs encourage the pulp and paper industry to search for alternative fibre sources such as nonwood fiber plants. Within the mixed portfolio of nonwood fibres, oil palm *(Elaeis guineensis)* is one that has great potential in papermaking, particularly for Indonesia and Malaysia where oil palm biomass is abundantly available (Fuad *et al.* 1999). In Malaysia alone, the palm oil industry generates, in 2006, massive amounts of lignocellulosic residues such as trunks, fronds and the empty fruit bunches (EFB), approximately 70 million tonnes (Yacob 2007). The suitability of this abundant, inexpensive and renewable raw material for papermaking has been explored using a variety of pulping methods (Akamatsu *et al.* 1987, Khoo and Lee 1991, Wan Rosli *et al.* 1988, Mohd. Yusoff 1997). An earlier work Wan Rosli *et al.* (1988), reported that soda pulping of EFB appears to be the most interesting process in terms of efficacy and environmental friendliness.

In this study we used an organic acid hydrolysis to produce chemical pulp fibres from oil palm frond. This organosolv technique (Kleinert 1971, Kleinert 1974), which is an environmentally friendly, can selectively fractionate the raw material into pulp fibres, lignin and water soluble sugars, permitting us to recover the lignin and water soluble components containing sugars, oligosaccharides and organic acids. Various types of organic acids are being employed, for example formic acid (Formacell) (Tu *et al.* 2008), acetic acid without catalyst (Acetocell) (Sahin and Young 2008) and acetic acid (AcOH) with catalyst, e.g. HCl (Acetosolv) (Vázquez *et al.* 1997, Nimz *et al.* 1984). These acid based processes are capable of achieving selective delignification in a single-step operation.

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Acetosolv pulping has been successfully applied to various species of softwood, hardwood and non-wood raw materials. For example, researchers had conducted studies on *Pinus pinaster* (Vázquez *et al.* 1995) and *Pinus sylvestris* (Nimz *et al.* 1984), and recommended a concentration of 90% acetic acid for the delignification of pine wood and pointed out the significant effect of lignin condensation. The hardwoods that had been investigated include *Fagus sylvatica* (Nimz *et al.* 1984), *Eucalyptus globulus* (Vázquez 1995, Dapia *et al.* 2003), and aspen *(Populus tremula x Populus tremuloides)* (Dapia *et al.* 2003). Significant lignin condensation and precipitation at high temperature (160 ºC) were also observed in these works. Acetosolv pulping of nonwoody materials had also been exploited by other researchers. For instance, bagasse (Tu *et al.* 2008), jute bast (Sahin and Young 2008), cardoon *(Cynara cardunculus)* stalks (Ligero *et al.* 2007), bark (Ligero *et al.* 2005), and wheat straw (*Triticum vulgare* CV. Horoshiri) (Pan and Sano 1999).

The aforementioned investigations suggested that acetosolv pulping is capable of fractionating the lignocellulosic material into cellulose (pulp fibres), acid lignin and monosaccharides. It was confirmed that the acid delignification process was attributed to the hydrolysis of α-aryl ether bonds (Gierer 1980, Ljunggren 1980). A suggested kinetic model comprises of two consecutive processes that is lignin solubilization followed by lignin condensation (Davis *et al.* 1986, Parajó *et al.* 1995). Therefore, in extended delignification (e.g. prolonged reaction time and/or at elevated temperature) lignin condensation and deposition on fibre surface could occur in acid pulping, which has detrimental effect on inter-fibre bonding potential and bleaching cost. Additionally, partial removal of hemicelluloses from the cellulosic structure may have negative impact on the papermaking properties of the resulting pulps because hemicelluloses could help hydrate the cellulose structure. Despite these possible undesirable side effects, a project was initiated to examine the influence of operating parameters (i.e. dosages of AcOH and HCl and temperature) of acetosolv pulping on oil palm frond fibres.

EXPERIMENTAL

Raw Materials

Fresh oil palm fronds used in this study were obtained from a local palm oil plantation in Perak, Malaysia. This material had the following chemical composition: 14.81% lignin, 86.53% holocellulose, 62.34% alpha-cellulose, and 1.8% extractives (on oven-dry weight basis). The fronds were chopped by means of a cleaver into small sizes of about 4 cm (length) x 2 cm (width) with variable thickness, (5 mm - 10 mm). The chips were air dried to an average moisture content of 12.5% and stored in polyethylene bags until further chemical treatment.

Pulping

The frond chips (200 g, o.d. basis) were delignified in a 4-L stationary stainless steel digester (NAC Autoclave Co. Ltd., Japan) fitted with a computer-controlled thermocouple under these conditions: temperature: 110 – 170 ºC; HCl: 0 – 1% ; AcOH: 65 - 95%; and solid/liquor ratio (S/L): 1/10. Both the acetic acid and HCl were volume percentage (v/v) with respect to the cooking liquor.

At the end of reaction time, the cook material was washed once with acetic acid and three times with running tap water to remove the residual acetic acid from the treated chips. The thoroughly washed chips were disintegrated in a commercial blender (Waring, 4-liter capacity) at 5% consistency, for three min at room temperature followed by screening on a flat-plate screen with 0.15 mm slits (a 6-cut slot screen).

Pulp characterization

Kappa number of the screened pulps was determined using Tappi method T 236 cm-85. Handsheets of 60± 2 g/m^2 were prepared using the Standard British Laboratory handsheet former and were conditioned at 23ºC and 50% RH for at least 24 h before testing. Sheet properties were characterized in accordance

with the appropriate Tappi standard methods, such as: Tensile index (T 494 om-01), Tear index (T 414 om-98), Burst index (T 403 om-97), Zero-span (T 231 cm-96), Brightness (T 452 om-98) and Opacity (T425 om-91). (TAPPI 1996-1997)

RESULTS AND DISCUSSION

Figs. 1-4 show the effect of cooking temperature on various properties. As seen from these figures, 140 ºC was probably the most desirable temperature because beyond this point the intrinsic fibre strength (Fig. 1, zero-span tensile) and inter-fibre bonding strength (Fig. 3, tensile index) began to fall off with further degrees of delignification (Fig. 1, Kappa Number).

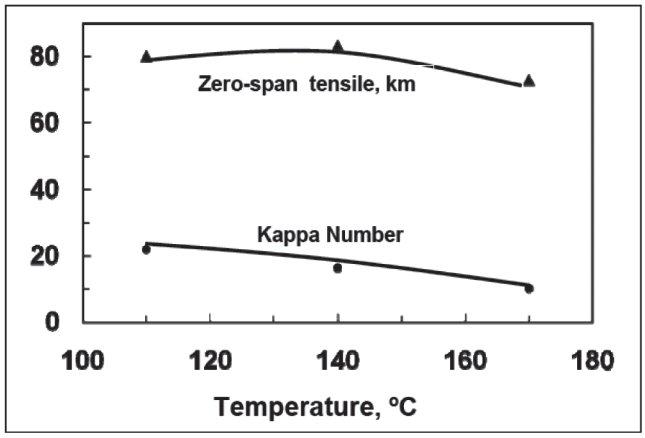

Figure 1. Effect of cooking temperature on Kappa number and Zero-span tensile under constant conditions of 75% AcOH, 0.5% HCl, and 120 min

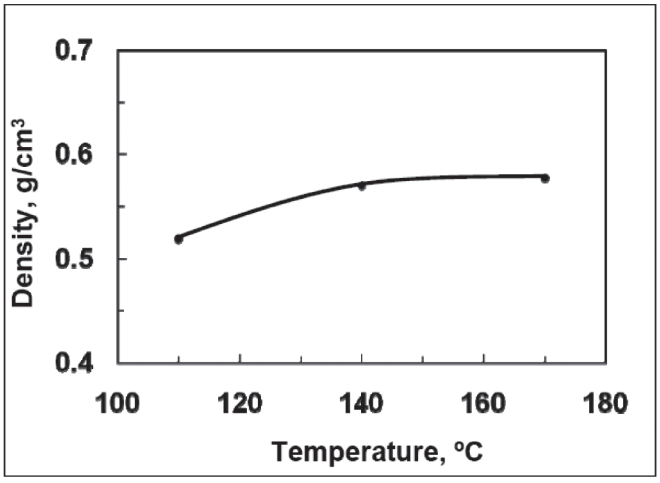

Figure 2. Effect of cooking temperature on sheet density under constant conditions of 75% AcOH, 0.5% HCl, and 120 min

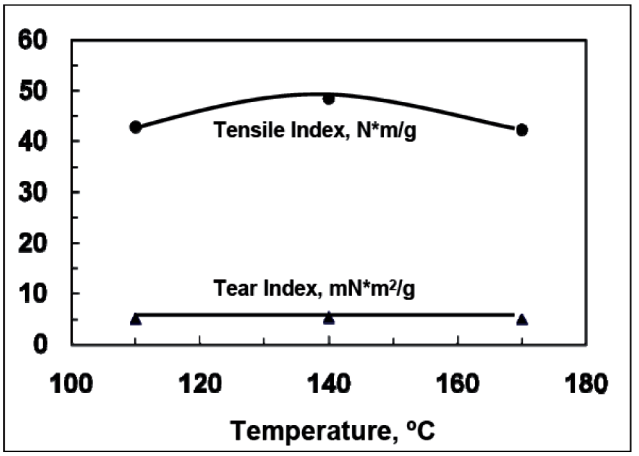

Figure 3. Effect of cooking temperature on tensile and tear indices under constant conditions of 75% AcOH, 0.5% HCl, and 120 min

This means that fibre degradation became significant when the temperature was > 140ºC. Besides, the handsheet density increased only marginally (Fig. 2) while the tear index (Fig. 3) and sheet opacity (Fig. 4) remained unchanged. On the negative side, the sheet brightness (Fig. 4) continued to drop with increasing reaction temperature, despite the fact more lignin was dissolved beyond 140ºC (Fig. 1, Kappa Number). The drop in brightness beyond 140ºC was probably attributed to the effect of lignin condensation and precipitation, as discussed earlier in the introduction section. However, Vázquez *et. al.* (1995) found that the selectivity of acetosolv pulping of *Eucalyptus globulus* was effectively independent of the operating temperature for pulp yields > 50%.

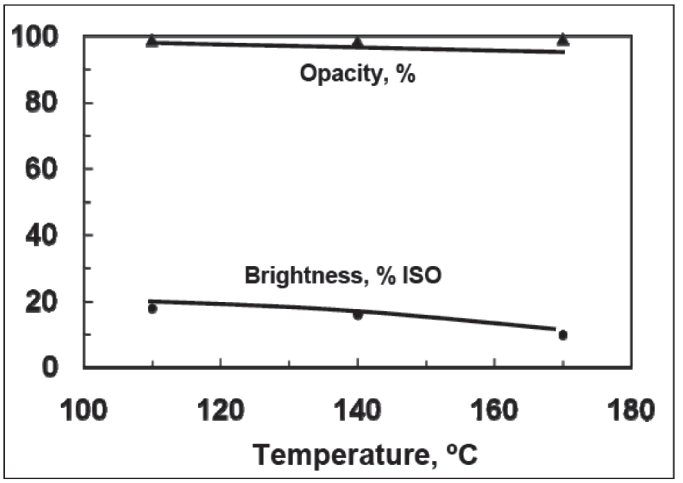

Figure 4. Effect of cooking temperature on brightness and opacity under constant conditions of 75% AcOH, 0.5% HCl, and 120 min

Fig. 5-8 show the influence of HCl charge on various properties under the conditions of 75% AcOH, 140ºC and 120 min. The addition of HCl as a catalyst in acetic acid pulping of oil palm fronds improved somewhat the delignification process when its charge was > 0.5% (Fig. 5, Kappa Number), indicating that H+ is needed to catalyze the solvation of the lignin fragments as shown by others (Lundquist and Hedlund 1967, Lundquist 1976). Interestingly, in comparison to the auto-catalyzed process where the HCl charge was 0%, the introduction of 0.5% had increased remarkably the Zero-span tensile (Fig. 5), sheet density (Fig. 6) and tensile index (Fig. 7) but had no noticeable changes in tear index (Fig. 7) and optical characteristics (Fig. 8). It was reported that the selectivity of acetosolv pulping of *Eucalyptus globulus* was effectively independent of HCl concentration for pulp yields > 50% (Vázquez *et al.* 1995). However, the present investigation revealed that the addition of 0.5% HCl improved the physical properties of frond pulps and that higher dosage of HCl could have detrimental effects on these properties.

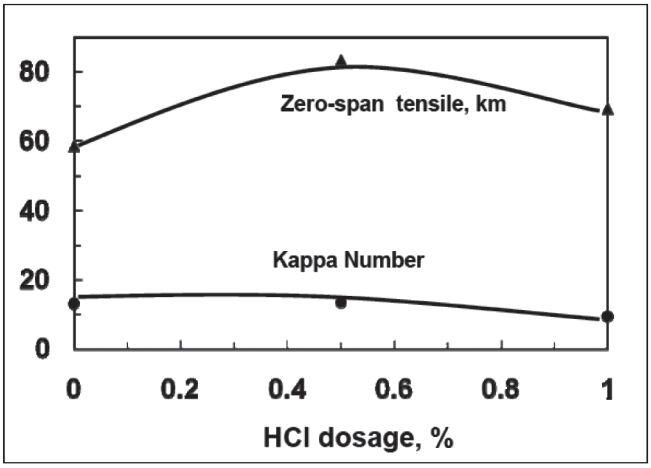

Figure 5. Effect of HCl dosage on Kappa number and Zero-span tensile under constant conditions of 75% AcOH, 140ºC and 120 min

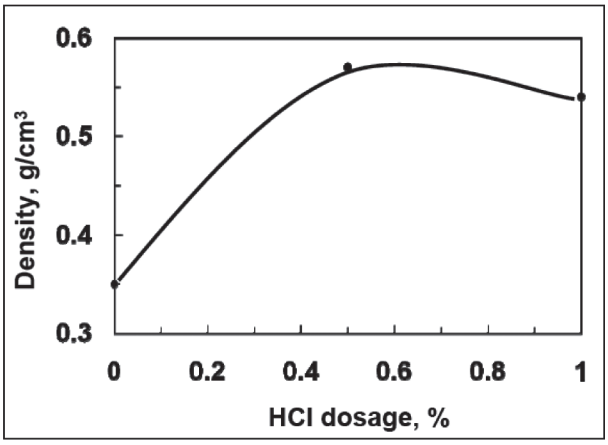

Figure 6. Effect of HCl dosage on sheet density under constant conditions of 75% AcOH, 140ºC and 120 min

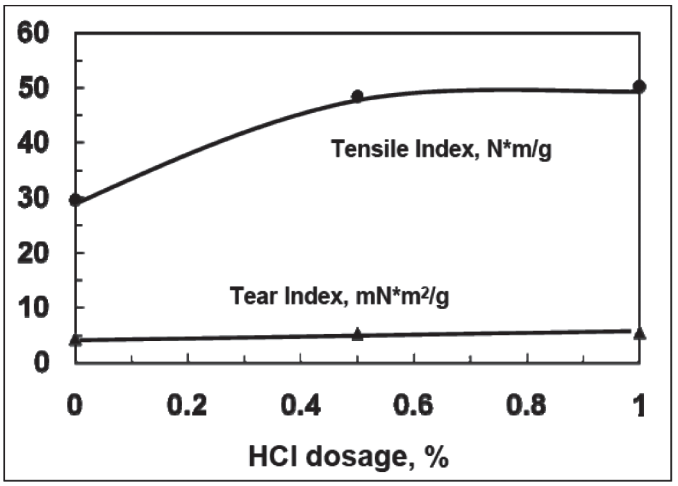

Figure 7. Effect of HCl dosage on tensile and tear indices under constant conditions of 75% AcOH, 140ºC and 120 min

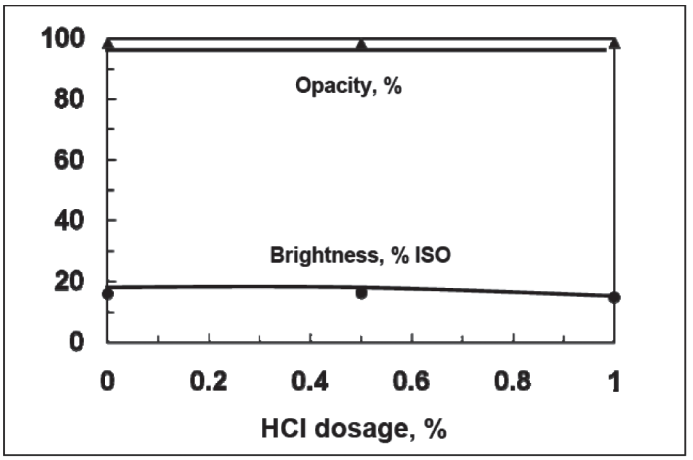

Figure 8. Effect of HCl dosage on brightness and opacity under constant conditions of 75% AcOH, 140ºC and 120 min

In acetosolv pulping the acetic acid is the main driving force in delignification. The effect of AcOH concentration on pulp characteristics, under constant conditions of 0.5% HCl, 140ºC and 120 min, are presented in figs. 9-12. As indicated in these figures, there exists an optimum dosage of AcOH in pulping of oil palm frond at Kappa number of about 16 (Fig. 9). The optimum value was 75%, which is lower that the values employed by most of the studies discussed in the introduction section. It had been reported that at high concentrations, the acetic acid protects carbohydrates from hydrolysis (Young *et al.* 1986). However, our study here suggested that a concentration of acetic acid higher than 75% could considerably degraded the frond fibre properties such as zero-span tensile (Fig. 9), sheet density (Fig. 10) and consequently tensile index (Fig. 11). When 95% acetic acid was used, the pulp brightness (Fig. 12) fell significantly, which is probably due to severe lignin condensation.

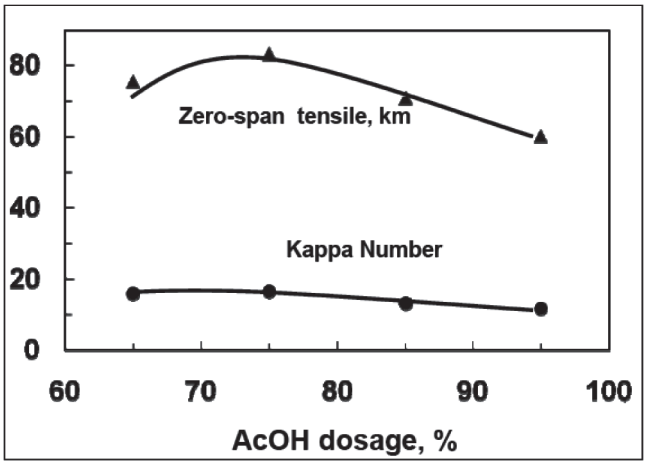

Figure 9. Effect of AcOH dosage on Kappa number and Zero-span tensile under constant conditions of 0.5% HCl, 140ºC and 120 min

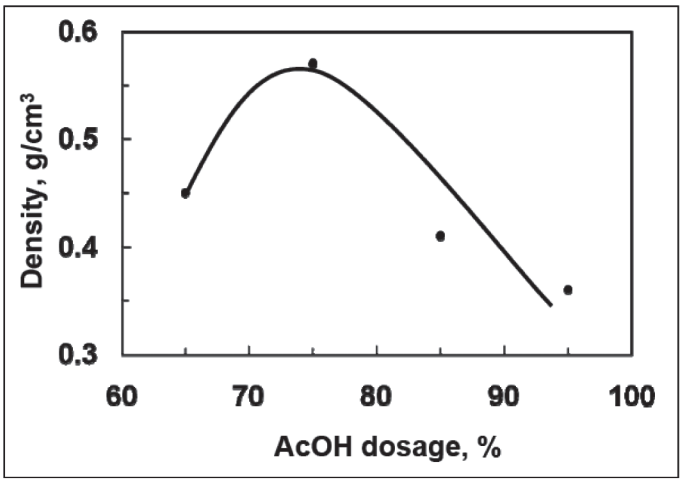

Figure 10. Effect of AcOH dosage on sheet density under constant conditions of 0.5% HCl, 140ºC and 120 min

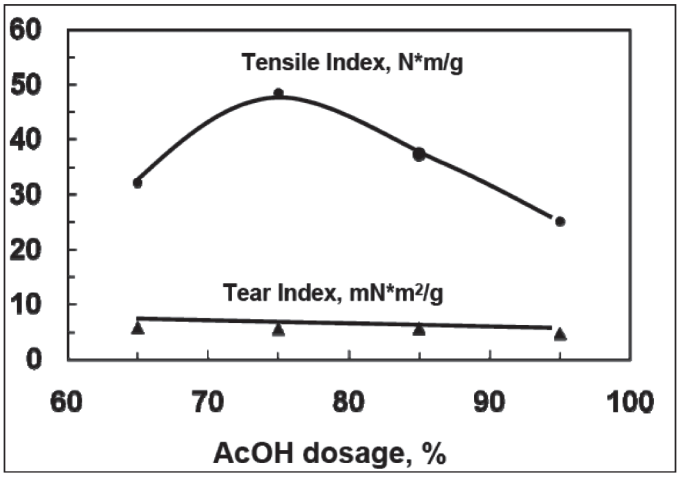

Figure 11. Effect of AcOH dosage on tensile and tear indices under constant conditions of 0.5% HCl, 140ºC and 120 min

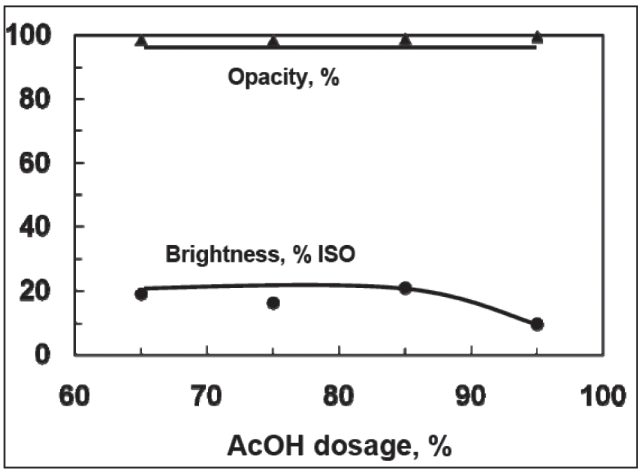

Figure 12. Effect of AcOH dosage on brightness and opacity under constant conditions of 0.5% HCl, 140ºC and 120 min

CONCLUSIONS

This study on acetosolv pulping of oil palm frond chips reveals that satisfactory pulp properties (save brightness) can be obtained at Kappa number between 13 and 16 when the following optimum conditions are employed: 140ºC, 0.5% HCl, 75% acetic acid, and 1/10 solid/liquor ratio. The pulp properties obtained under these conditions are as follows: zero-span tensile breaking length – 83 km, sheet density – 0.57 g/cm^3, tensile index – 48 N m/g, tear index – 5.4 mN m^2/g, brightness – 16% ISO and opacity – 98%. Higher values of the optimum operating parameters would degrade the fibre characteristics such as zero-span tensile breaking length, tensile index, and sheet density. In terms of sheet characteristics the main drawback of acetosolv delignification is to produce pulps with particularly low brightness, which would certainly incur high bleaching cost if the pulps are destined for the manufacture of printing and writing grades.

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