CHEMICAL AND THERMAL STABILITY OF RICE HUSKS AGAINST ALKALI TREATMENT

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Chemical and thermal stability of rice husks against alkali treatment with 2 to 8% w/v NaOH are presented and discussed in this paper. The thermal stability of the rice husks was examined by using a thermal gravimetric analysis instrument. Chemical stability was evaluated by examining the organic components of rice husks using proximate analysis. The results indicated that the proportion of lignin and hemicellulose in rice husks treated with NaOH ranging from 4 to 8% decreased significantly by 96% and 74%, respectively. The thermal stability and final degradation temperatures of the alkali-treated rice husks were also lowered by 24-26°C due to degradation of hemicellulose and lignin during alkali treatment. Absence of the onset degradation zones in the alkali-treated rice husks was a further indication that hemicellulose and other volatile substances degraded during alkali treatment. This leads to a conclusion that alkali treatment of rice husks with more than 4% NaOH causes a substantial chemical degradation of rice husks, which subsequently decreases their thermal stability.

INTRODUCTION

Rice husks, which are by-products of the rice hulling industry, are amongst the few agricultural residues that can be readily obtained in huge amount at one location. Researchers have made use of this advantage and have addressed the disposal nuisance caused by rice husks by developing various products from rice husks. Rice husks, like other agricultural residues, are quite fibrous and require relatively little input energy to be processed into various products, including panel boards. However, because of inconsistent properties of rice husks compared, for example, to wood particles, manufacture of panel boards from these residues has yielded undesirable properties (Chen 1979). Rice husks contain a high proportion of lignin, and about 20% of their outer surfaces are covered with silica (Houston 1972; Juliano 1985), which is deposited onto this surface as monosilicic acid to form a silicon-cellulose membrane (Yoshida et al. 1962).

Adhesion of agricultural fibres with thermosetting resins involves either or both chemical and physical interactions. Chemical interaction can be achieved through hydrogen or covalent bonding between the reactive OH groups available on the cellulosic fibres and compatible functional groups on the thermosetting resins. A high proportion of

reactive hydroxyl groups on cellulosic fibres can be attained by modifying the fibre surfaces (Ndazi et al. 2007). Alkali treatment is viewed as one of the widely employed chemical treatment techniques for surface modification of cellulosic fibres for the purpose of improving their adhesion properties with various thermosetting binders (Ndazi et al. 2007; Ray and Sarkar 2001; Bisanda and Ansell 1991; Mwaikambo and Ansell 2002; Albano et al. 2001). This treatment involves partial removal of the cementing materials (hemicellulose and lignin) and other impurities from the fibre surfaces (Albano et al. 2001). A similar change due to alkali treatment at limited concentrations of NaOH has also been reported to improve some of the mechanical properties of phenol formaldehyde bonded composites (Ndazi et al. 2007). Since the main goal is to generate these changes without causing significant effects on the properties of fibres, it was imperative to understand the effect of variation of alkali concentration on the properties of rice husks. In this paper, therefore, the stability of rice husks components against alkali treatment between 2 to 8% NaOH are presented and discussed.

EXPERIMENTAL

Materials

The main raw material for this study was rice husks, which were obtained from Morogoro Tanzania. A general laboratory reagent NaOH (~97%) used for alkali treatment of rice husks was supplied by a local chemical dealer.

Treatments of Rice Husks

Alkali treatment involved soaking different portions of rice husks in 2%, 4%, 6%, and 8% w/v solutions of NaOH maintained at 27°C for 24 hours. After alkali treatment the rice husks were rinsed thoroughly in water to remove unreacted NaOH before drying under the sun for about 2 days.

Proximate Analysis

The proximate analysis based on methods outlined in Allen (1989: chapter 6) was used to assess the chemical stability of rice husks against alkali treatment. Percentage changes in cellulose, hemicellulose, lignin, and silica based on ash content were examined due to variations of the concentration of NaOH from 2% to 8% w/v. The method starts with delignification of crude fibre to obtain holocellulose, which is then fractionated to hemicellulose and cellulose. Hemicellulose and cellulose are obtained by hydrolyzing with caustic potash and other reagents reported in Allen (1989). Lignin was hydrolyzed from crude fibre using 72% sulfuric along other reagents as described in Allen (1989, p 169-171).

Thermal Analysis

A Mettler Toledo TGA/SDTA 851^e Thermal Gravimetric Analyzer available at KTH in Sweden was used to establish the influence of alkali treatment on the thermal stability of rice husks. The samples were heated at 10°C/min under N_2 gas at a flow rate of 55 ml/min between 25 to 700°C.

RESULTS AND DISCUSSION

Proximate Chemical Contents

The proportions of organic cell wall components of rice husks, based on proximate analysis after alkali treatment, are presented in Figs. 1 to 4. The α-cellulose content indicated a relative increase by 400% over other components with increase of alkali concentration between 4 and 8% NaOH (Fig. 1). The increase was probably attributable to a relative percentage decrease of the more labile rice husk components such as hemicellulose and lignin during alkali treatment at these concentrations. It demonstrates that lignin and hemicellulose were more sensitive to alkali treatment than cellulose (Ray and Sarkar 2001; Sarkar et al. 1948; Gassan and Bledziki 1999; Ndazi et al. 2005). This is revealed in Figs. 2 and 3, where the proportion of lignin and hemicellulose in rice husks decreased substantially with increase of alkali concentration from 4 to 8% NaOH. Lignin content in rice husks decreased by 96% when the rice husks were treated between 4 and 8% with NaOH. However, the α-cellulose obtained by the fractionation method is not completely pure (Allen 1989). It is possible that some of hemicelluloses (mannose and xylose) retained during fractionation of hollocellulose to prevent attacking the cellulose structure may have contributed to this relative percentage increase.
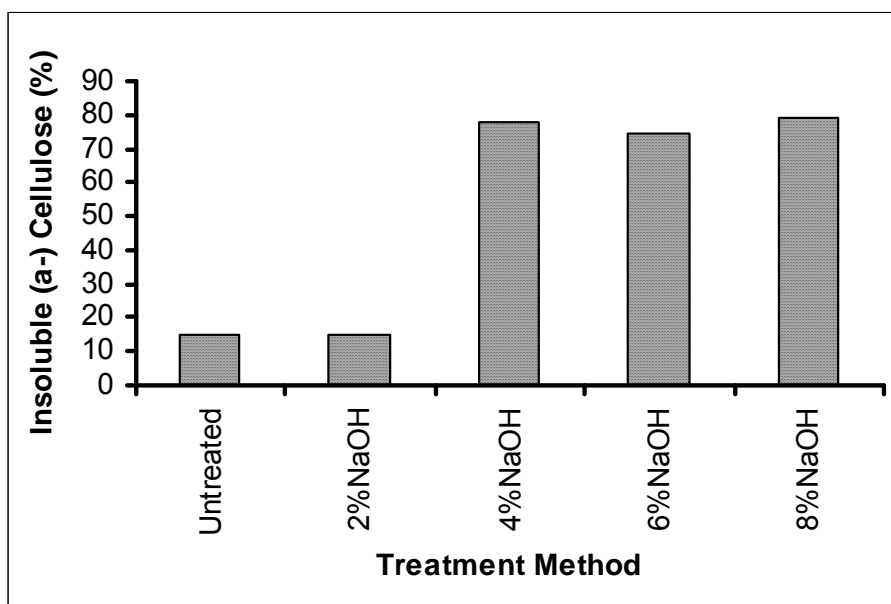

Fig. 1. Effect of alkali treatment of rice husks on cellulose content

It has also been reported that alkali treatment of lignocellulosic fibres leads to degradation of lignin. Although the fraction of lignin isolated by hydrolysis with 72% sulfuric acid could vary from species to species, it still contains the true amount of lignin suitable for most purposes (Allen 1989). Thus, as reported in previous studies, decomposition of lignin in cellulosic fibres becomes more profound at higher concentrations, higher temperatures, and longer treatment times (Ray and Sarkar 2001; Albano et al. 2001; Rajulu et al. 2002). But if the treatment is carried out under cold

alkali conditions, lignin might not degrade (Sarkar et al. 1948, Gassan and Bledziki 1999; Ray and Sarkar 2001). However, the results obtained from proximate analysis of the alkali-treated rice husks have revealed that degradation of lignin is certain and becomes very significant at room temperatures when the concentration of NaOH is at least 4%.
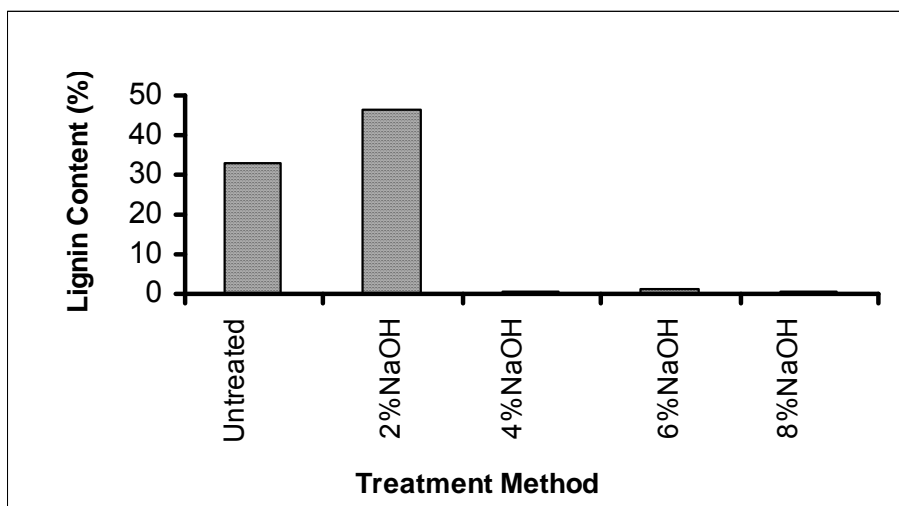

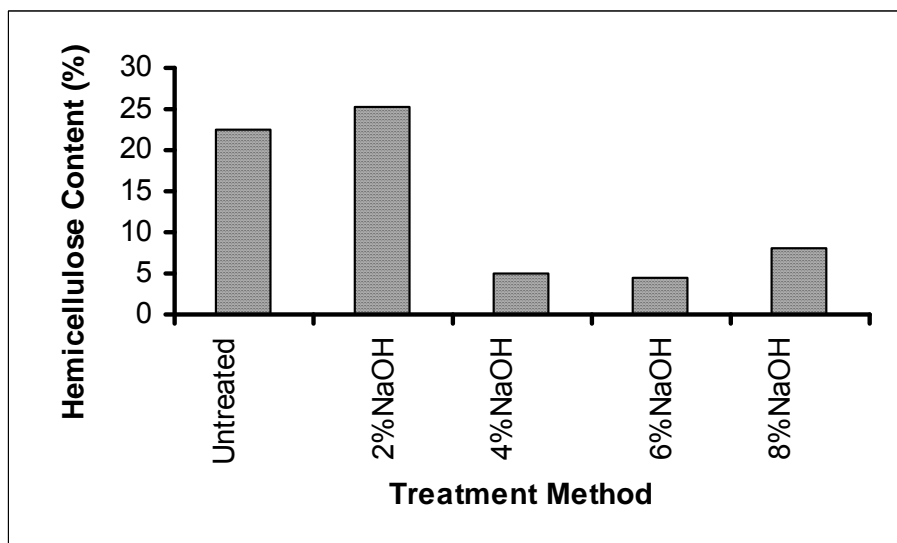**Fig. 2.** Effect of alkali treatment of rice husks on lignin content

Fig. 3. Effect of alkali treatment of rice husks on hemicellulose content

Hemicellulose was also observed to decrease by more than 74% after treating the rice husks with 4 to 8% NaOH. Hexoses are believed to be the most readily degradable form of hemicellulose (Gassan and Bledzki 1999; Sarkar et al. 1948). The large amount of hemicellulose removed from the rice husks during alkali treatment between 4 and 8% suggests further that other forms of hemicellulose, including pentoses, might have been also decomposed. Hydrolysis of hemicellulose from hollocellulose is normally expected to yield both pentoses and hexoses, although a fraction of hemicellulose could remain in

the solution (Allen 1989). Removal of hemicellulose and lignin has been reported to make the particles split and crack, as revealed by scanning electron microscopy (Ndazi et al. 2007). It also leads to fibre swelling, formation of new hydrogen bonds between cellulose chains, and loss of weight (Gassan and Bledzki 1999). A slight increase in lignin and hemicellulose contents in rice husks treated with 2% NaOH could be associated with the limitation of the method to isolate completely all hemicellulose from hollocellulose. It could also be influenced by a fraction lignin (2-4%) which is retained during delignification of holocellulose to protect attack against hemicellulose (Allen 1989).

It is further observed in Fig. 4 that alkali treatment of rice husks slightly reduced the ash content, despite the anomaly observed at the concentration of 2% NaOH, which was also noted during determination of lignin and hemicellulose contents. Reduction of ash content, which contain up to 97% silica (Mansaray and Ghaly 1999), in rice husks treated with higher concentrations of NaOH could be a possible indication of partial decomposition or transformation of silica on the outer surface of rice husks by NaOH into another form. This proposition needs to be justified in further studies. However, the reaction of silica and alkali to form alkali-silicate at different condition involving heat has been reported (Kurtis and Monteiro 2004) and patented, e.g. patent number EP19890310193 filed 04/11/1990. It is there possible that during alkali treatment part of the alkali reacted with silica to form sodium silicate despite operating at room temperature.
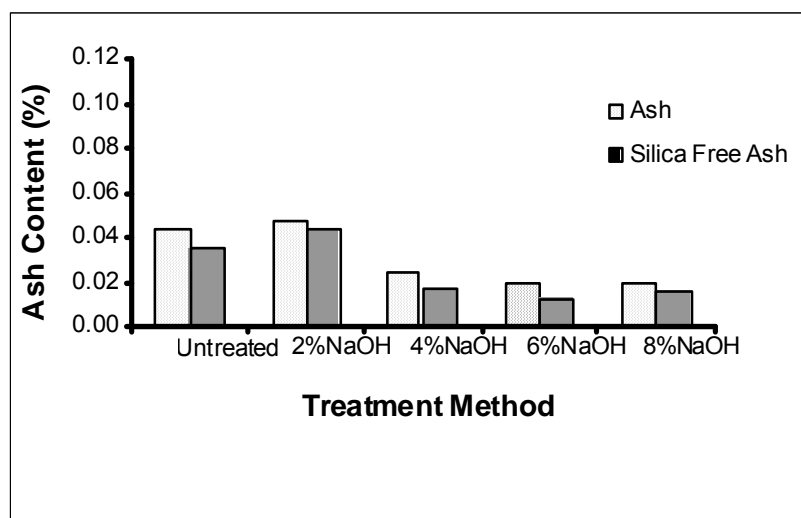

Fig. 4. Effect of alkali treatment of rice husks on ash content

Thermal Stability

The results of TGA of untreated and alkali-treated rice husks shown in Fig. 5 reveal that all the rice husks started to undergo initial weight losses between 60 and 134°C, irrespective of their treatment condition. This step involved elimination of water and other primary volatile substances. Initial degradation started at 229°C, involving decomposition of secondary volatile products such as various forms of hemicellulose.
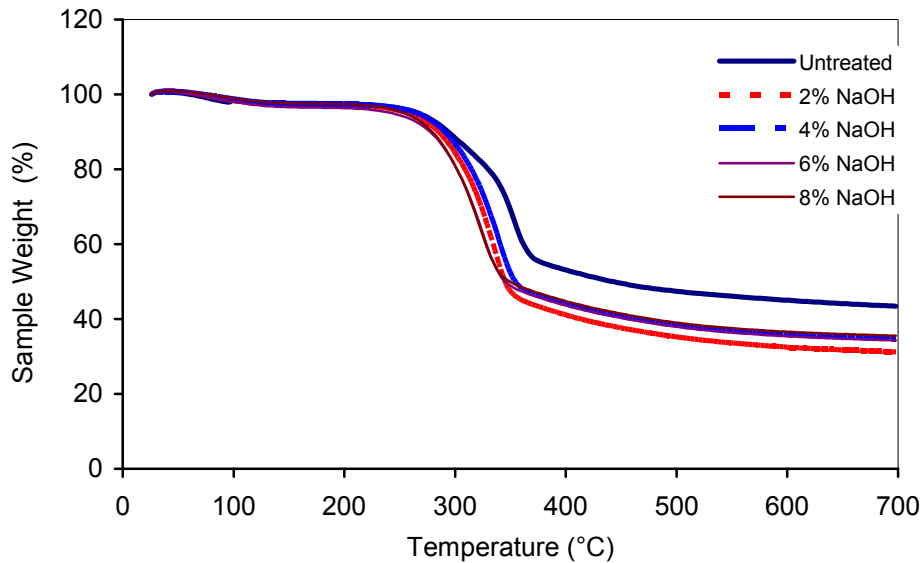
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Fig. 5. Effect of alkali treatment on thermal stability of rice husks

Degradation of alkali-treated rice husks was more significant from 229°C to around 330-344.5°C, as shown by sharp peaks on the derivative thermal gravimetric curves (DTG) in Fig. 6. The decomposition of alkali-treated rice husks involved only one step, in contrast to that of untreated rice husks, which was preceded by decomposition of volatile products up to around 341°C before undergoing a transition to further substantial weight losses thereafter.
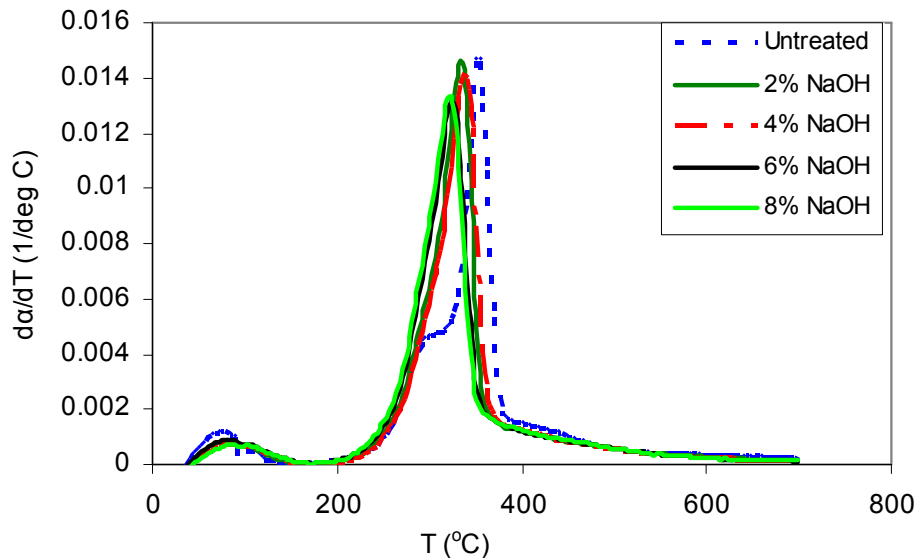

Fig. 6. Effect of alkali treatment on the decomposition rate of rice husks

The two-step decomposition observed on the untreated rice husks curve represent two main reaction zones, which involve degradation of at least two different components. Similar degradation patterns have also been reported on untreated rice husks (Mansaray and Ghaly 1999) and other plant fibres (Alvarez and Vázquez 2004). The single decomposition stage of alkali-treated rice husks shown in Figs. 5 and 6 implies that the components that decomposed in the first stage of untreated rice husks were not present in the alkali-treated rice husks. The first reaction zone of untreated rice husks was terminated at around 341°C, which is slightly above the final degradation temperature of hemicellulose (Alvarez and Vázquez 2004), and the temperatures of evolution of volatile products (Mansaray and Ghaly 1999) or splitting of aliphatic chain and carbon-carbon of lignin from the aromatic ring (Le Van 1989) in lignocellulosic fibres. Absence of the first reaction zone in alkali-treated rice husks was therefore associated with removal of waxy substances, natural fats, hemicellulose, and aliphatic chains of lignin during alkali treatment of rice husks at higher concentrations of NaOH.

The second decomposition step of untreated rice husks was between 351°C and 376°C. This zone falls within the region of α-cellulose and lignin degradations (Alvarez and Vázquez 2004; Le Van 1989). As observed in Fig. 5, this interval represents the temperature at which maximum weight loss of the sample occurred, corresponding to degradation of both α-cellulose and lignin. The maximum weight loss of alkali-treated rice husks occurred between 229 and 344.5°C. Since most of lignin, hemicellulose, and volatile components were removed during alkali treatment, these peaks correspond to decomposition of α-cellulose. Removal of the cementing material, predominantly lignin, during alkali treatment is what probably reduced the temperature of maximum weight losses of rice husks and α-cellulose by at least 26°C.

Table 1 summarizes the variation of alkali concentration with TGA parameters of rice husks. The amount of residue formed at the final decomposition temperature (700°C) was relatively higher for untreated rice husks and increased slightly with increase of alkali concentration. Char, which is part of this residue, has been attributed to formation condensed polycyclic aromatic structure from cellulose as the solid residue undergoes a chemical transformation and rearrangement (McGrath et al. 2003). However, the residues formed after heating the rice husks to 700°C also include silica, which makes the highest proportion of ash. Alkali-treated rice husks depicted the lowest amount of residue due to decomposition lignin and probably part of silica during alkali treatment. Thus, with a significant removal of lignin at higher alkali concentrations, the small amount of residues generated at the final temperature in the alkali-treated rice husks were predominantly char from condensed polycyclic aromatic structure of cellulose and silica. This increased slightly with the absence of lignin and dominance of cellulose at higher alkali concentrations (Table 1).

The activation energies which measure the minimum energies involved in the sample decomposition were also used to asses the relative thermal stability of rice husks due to alkali treatment. The Freeman-Carrol method which has been used extensively (Bolbukh et al., 2006) was applied to study this behavior by transforming the rate equation (Eq. 1) into Eqs. (2) and (3).

Table 1. Effect of Alkali Treatment on TGA Parameters of Rice Husks

Treatment	Main decomposition step (°C)		Activation E_a (kJ/Mol)		Reaction order n		Residues at 700°C
			Step 1	Step 2	Step 1	Step 2	
Untreated	229-341	351.5-376	26.12	-151.12	0.56	-1.79	43.43
2% NaOH	229-341		37.74		0.75		31.20
4% NaOH	229-344.5		37.88		0.75		34.79
6% NaOH	229-330.5		38.31		0.76		34.26
8% NaOH	229-330.5		38.06		0.76		35.52

$$-\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(\frac{-E_a}{RT}\right)[1-\alpha]^n \tag{1}$$

$$\ln\left(-\frac{d\alpha}{dT}\right) = \ln(A) - \frac{E_a}{RT} + n\ln(1-\alpha) \tag{2}$$

$$\frac{\Delta\ln\left(-d\alpha/dT\right)}{\Delta\ln(1-\alpha)} = n - \left(\frac{E_a}{R}\right)\left(\frac{1}{\Delta\ln(1-\alpha)}\right)\left(\Delta\frac{1}{(T)}\right) \tag{3}$$

where: the normalized sample weight $\alpha = (w_i - w)/(w_i - w_f)$, R is the gas constant, T is the temperature (K). w_i and w_f are initial, and final sample weights, w is the sample weight at any time t. Equation (3) is a linear equation of the form $y=mx+c$, where the apparent activation energy (E_a) and the order of reaction (n) can be obtained from the slope $(m = E_a/R)$ and the intercept $((c = n)$ of the linear graph Y vs. $1/T$ for $Y = \Delta\ln\left(-d\alpha/dt\right)/\Delta\ln(1-\alpha)$. The non-isothermal single heating rate $\beta = 10^o C/\min$.

No significant differences were observed relative to the variation against $1/T$ with alkali concentration, as shown in Fig.7. A lower activation energy observed in untreated rice husks in the first decomposition region (Table 1) confirms that less energy was required to decompose untreated rice husks than alkali-treated rice husks. This is due to the presence of more susceptible hemicellulose and lignin, whose degradations start earlier than cellulose in the same region. Reaction orders (n) of the first step of untreated rice husks and all alkali-treated rice husks were between 0.5 and 0.8. However, the second degradation region of untreated rice husks, which terminated at a higher temperature, involved higher negative activation energy and reaction order. The transition from positive to negative activation energies has been attributed to a two-step decompo-

sition process (Muenchi et al. 1996). It is possible that untreated rice husks involved endothermic and exothermic reactions of cellulose (Sergeeva and Vaivads 1954) and lignin (Kifani-Sahban et al. 1997) in this region. It appears that after removal of the amorphous phase during alkali treatment and probable transformation of cellulose (Mwaikambo 2002), the decomposition was predominantly endothermic. Negative activation energies have also been reported on Arrhenius plots of the rate of inactivation (killing) of mammalian cells and Drosophila (Muenchi et al. 1996).
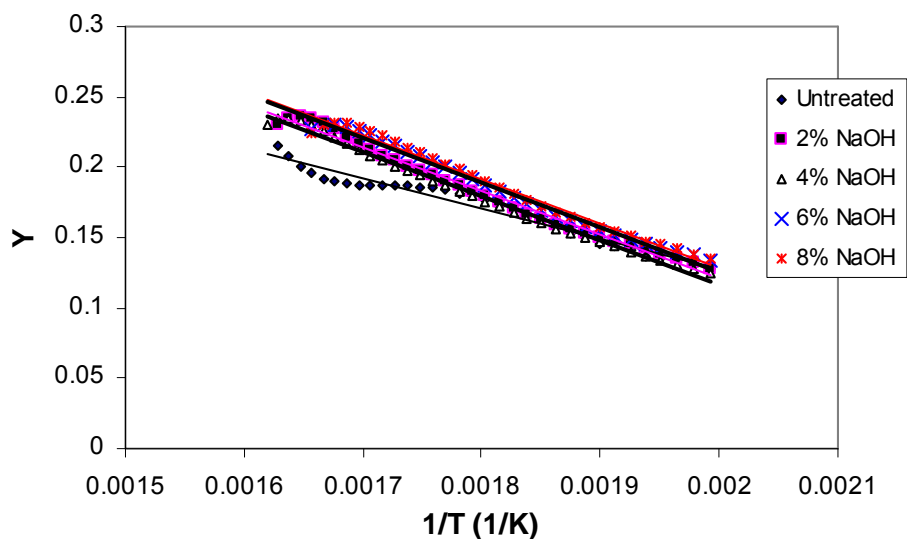

Fig. 7. Effect of alkali treatment on the decomposition rate over the degree of conversion (Y) of rice husks

CONCLUSIONS

Proximate analysis based on the fractionation of organic components of plant fibers can be used to examine chemical stability of rice husks against alkali treatment. Alkali treatment of rice husks causes substantial degradation of lignin and hemicellulose when the concentration of NaOH is at least 4%. Silica ash content also drops slightly with alkali treatment, suggesting possible degradation of silica upon alkali treatment.

Thermal stability of rice husks decreases due to chemical degradation of hemicellulose, lignin, and part of silica during alkali treatment. This is indicated by decrease of the temperatures of main degradation zones and increase of the activation energies with alkali concentrations. Lower activation energy during decomposition of untreated rice husks is an evidence of early thermal decomposition of hemicellulose and lignin, which require less activation energy than cellulose. Absence of the first peak on the TGA curves of alkali-treated rice husks affirms further degradation of hemicellulose and part of lignin during alkali treatment.

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