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NH_4OH–KOH pulping mechanisms and kinetics of rice straw

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Abstract

The mechanisms and kinetics of NH_4OH–KOH mixture pulping rice straw were studied. When aqueous ammonia was mixed with a small amount of caustic potash (ratio of 1:5), three distinct delignification phases were observed in the pulping process: a bulk delignification phase from the beginning of the cooking period to 100 °C, a supplementary delignification phase from 100 °C to 155 °C lasting a further 45 min, and a residual delignification phase until the end of the cooking period. There were two silica removal phases; the first phase was from the beginning of the cooking period to 100 °C and the second phase was from 100 °C to the end of the cooking period. The rate of delignification reaction was first order with respect to residual lignin and 0.3 order with respect to $[OH^-]$. The silica removal was pseudo-first-order with respect to residual silica and 0.6 order with respect to $[OH^-]$. The activation energies of the delignification and removal of silica reactions were 35.6 and 30.9 kJ/mol, respectively.

Keywords: NH_4OH–KOH pulping; Mechanisms; Kinetics; Rice straw; Delignification; Silica removal

1. Introduction

Wood is the preferred and dominant raw material for the paper industry. Non-wood raw materials account for only 5–7% of total pulp and paper production worldwide (Navaee-Ardeh et al., 2004). There has been an increase in paper and board production and consumption in recent decades. Data from FAO (2003) indicate that the total paper and board production in the world increased from 160 million tonnes in 1978 to 324 million tonnes in 2002. Paper and board consumption in China alone has grown by 10.7 million tonnes (130%) from 1998 to 2002 (Wright, 2004). Due to the strong growth in demand in recent years, it is predicted that the forecasted demand for wood materials may exceed the potential supply.

The environmental consequences for unlimited wood consumption (leading to increased tree logging) are significant, with particular implications for the recent debate about global warming. Non-wood raw materials such as rice straw, wheat straw, bagasse and bamboo have attracted more interest as partially replacements for traditional wood raw materials (Alaejos et al., in press; Jiménez et al., 1999, 2002; Hammett et al., 2001). Production of pulp from non-wood resources has several advantages compared with wood, such as easy pulping capability, excellent fibers for special types of paper and high-quality bleached pulp (Navaee-Ardeh et al., 2004). Because of limited forest resources and plentiful supplies, non-wood pulping materials, such as rice and wheat straw, mulibamboo, reed and bagasse, have been used for a long time as raw materials for pulp and papermaking in China.

Studies on rice straw pulping has been a relatively recent area of activity. Navaee-Ardeh et al. (2003, 2004) studied the so-called organosolv pulping process; they used soda–ethanol–water as the pulping agent to pulp rice straw and found optimum values for the cooking time, ethanol concentration and cooking temperature. Nassar (2003) studied acid and neutral sulfite pulping of rice straw to produce high opacity paper and stiff paperboard, with the process

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Nomenclature

a	reaction order of removal of silica
b	reaction order of $[OH^-]$
C_1	weight of KOH to the weight of oven-dry rice straw (g/g)
C_2	weight of NH_3 to the weight of oven-dry rice straw (g/g)
E	activation energy (kJ/mol)
K	reaction rate constant ($L^{0.30}/mol^{0.30}$ min for delignification; $Si^{0.60}/mol^{0.60}$ min for removal of silica)
k_0	frequent factor ($L^{0.30}/mol^{0.30}$ min for delignification; $Si^{0.60}/mol^{0.60}$ min for removal of silica)
L_t	remaining lignin at time t (g/g)
L	average L_t in times region (g/g)
$L{:}S$	the volume of cooking liquid to the weight of oven-dry rice straw (mL/g)
m	reaction order for $[OH^-]$
n	reaction order for delignification
$[OH^-]_t$	concentration of OH^- at time t (mol/L)
$[OH^-]$	average $[OH^-]_t$ in times region (mol/L)
r	reaction rate (min^{-1})
r_{exp}	delignification rate and removal of silica rate obtained by experiment
r_{mod}	delignification rate and removal of silica rate obtained by kinetics model
Si_t	remaining silica at time t (g/g)
Si	average Si_t in times region (g/g)
T	cooking temperature or maximum temperature (°C)
t	reaction time (min)
t_1	time to reach maximum temperature (min)
t_2	time at maximum temperature (min)

giving high yields. Singh et al. (1998) studied the kinetics and mechanisms of wheat straw, rice straw and bagasse pulping process with sulfite ions.

Huang and Shi (1986) studied rice straw pulping kinetics and mechanisms and suggested that delignification during soda-based cooking in the presence of anthraquinone could be divided into three phases: (1) a bulk phase of delignification at less than 90 °C, in which 72% delignification was attained, (2) a supplementary phase between 90 °C to 150 °C, in which 20% delignification occurred, and (3) a final phase at 150 °C. The delignification reaction of rice straw was a first-order reaction, with an activation energy of 49.7 kJ/mol. Gonzalo et al. (1998) found that about 90% of the lignin was dissolved in the rapid initial phase. The delignification reaction was first order with respect to residual lignin, and the activation energy for the bulk delignification was found to be 93 kJ/mol. Baosman et al. (1994) found similar results on the dissolution of lignin during caustic soda pulping of wheat straw in the temperature range of 25 °C to 170 °C. The activation energy for the delignification reaction, however, was much lower (14 ± 3 kJ/mol). Singh et al. (1998) studied the delignification process of wheat straw by sulfite ions buffered with sodium hydroxide, and found the kinetics of delignification to be second order with respect to lignin. Abdul-Karim et al. (1995) studied the kinetics of kraft pulping of Hungarian wheat straw and found that delignification was controlled by a chemical reaction, which was first order with respect to residual lignin and the activation energy of the reaction was 131 kJ/mol.

Park et al. (1999) systematically studied the mechanisms and kinetics of delignification and silica removal of rice straw soda pulping in the temperature ranges from 30 °C to 70 °C, and from 100 °C to 140 °C. Both delignification and silica removal reaction were suggested to be pseudo-first-order reactions. It was confirmed that silica removal is a kinetically easier process than delignification under alkali pulping conditions. They concluded that complete delignification from rice straw without serious silica removal cannot be achieved if sodium hydroxide was employed as a cooking reagent. The aim of this work was to study the pulping of rice straw with NH_4OH–KOH mixture as cooking liquor.

2. Methods

2.1. Materials and pulping conditions

Rice straw from Zhuhan, a suburban in Shanghai, China was used as the pulping raw material. It was dried in an oven at 105 °C and was cut into 2–3 cm lengths for the experiments. The typical chemical compositions of the rice straw were analyzed by China National Standards (GB). On a dried basis it contained 35.39% cellulose (GB5515 – 1985), 16.51% pentosan (GB745 – 78), 24.02% lignin (GB2677.8 – 81), 11.23% silica (GB2677.3 – 81) and 8.90% moisture (GB2677.2 – 81).

A stainless steel reactor, fitted with a stirrer, an electrical heating element and a temperature controller, was used for the experiment. 25.0 g of pre-dried and cut rice straw sample were presoaked in the cooking liquor for 2 h and then fed into the reactor. The cooking temperature was increased from room temperature to the preset temperature, and then kept constant for a given period of time. After cooking, the black liquor was separated from the pulp by filtration, and the pulp was washed thoroughly with water. Then the pulp and the black liquor were both analyzed. The lignin and silica contents in pulp were also analyzed by China National Standards (GB2677.8 – 81 and GB2677.3 – 81, respectively). The effective alkali content in black liquor was analyzed with a pH meter using an electrical potential titration method, with the pH end