

Role of KOH in the One-Stage KOH Activation of Cellulosic Biomass

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Abstract

The role of KOH in the one-stage KOH-activation of rice straws was studied using FTIR, XPS, TGA, and DTG techniques. It was found that at the impregnation, KOH extracts to some extent the lignin component from rice straw and reacts with hydroxyl groups. On heat-treatment, the impregnated KOH facilitates intermolecular condensation reaction on one hand but retards the thermal degradation of cellulose molecules on the other hand. The oxygen-containing surface functional groups newly created by oxidation of KOH may facilitate the bulk, not controlled, consumption of carbon atoms so that the effective porosities may not be able to be developed by the one-stage activation process.

Keywords : *one-stage KOH-activation, rice-straw, surface functional groups, bulk consumption of carbon*

1. Introduction

There have been two different processes for the preparation of activated carbons, i.e. gas (or conventionally called physical) activation and chemical activation. Gas activation usually involves the carbonization of a carbonaceous precursor, followed by activation of resulting char in the presence of some activating gas such as carbon dioxide [1-4] or steam [3-5]. Generally chemical activation, on the other hand, is one-stage preparation of activated carbons where carbonization and activation are accomplished concurrently during heat treatment. The chemicals used in the chemical activation are normally alkali and alkaline earth metal containing substances and some acids such as KOH [5-8], K₂CO₃ [9, 10], KNO₃ [11], NaOH [12], Na₂CO₃, AlCl₃, ZnCl₂ [8, 13-15], MgCl₂ and H₃PO₄ [16-18]. As precursor materials, coal [1-2, 13, 15, 18, 19] and cellulosic biomasses (or lignocellulosic materials [17]) that include various types of shells [7-9, 20, 21], stones of olive, peach, apricot and cherry, others like grape seeds, rice hulls [22], and palm-tree cobs [23] have been the most commonly used.

In recent, it was reported that high performance activated carbons can be prepared from KOH-activation of pre-carbonized cellulosic biomasses [24, 25]. Because of pre-carbonization stage to the activation, this is called two-stage preparation method of activated carbons. However, such high performance activated carbons could not be obtained from the one-stage preparation methods, although rice straw itself has well-developed in-born porous structure [25-27].

So, the goal of the present study is thus aiming at elucidating the reason why high performance activated carbons could not be obtained from the one-stage preparation method, by studying the role of KOH during heat-treatment of virgin rice straw as a cellulosic biomass precursor.

2. Experimental

2.1. Materials

Rice straw as the precursor material was chopped and sieved to the size of about 3 cm in length and used after oven-drying at 110°C for 3 hrs. Table 1 shows the proximate and ultimate analyses of the rice straw.

2.2. Thermal analysis

Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out for the virgin rice straw and KOH-treated rice straw samples using a TG/DTA 220 (Seiko instrument inc., Japan). The heating rate was adjusted to 10 °C/min under nitrogen atmosphere.

Table 1. The proximate and ultimate analysis of precursor (unit: wt%)

	C	H	O	N	Volatile	Fixed carbon	Ash
Rice straw	39.8	5.5	54	0.9	68	17.8	14.8

2.3. Structure analysis

Changes of chemical structure induced by chemical and thermal treatments were monitored with a KBr pelleted sample on an FTIR spectrometer (Perkin-Elmer spectrometer spectrum 2000, USA) with the scan number of 32 and the resolution of 4 cm^{-1} . The obtained spectrum was analyzed by using MIDAC GRAMS/386 for MS windows by Galactic Industries Co. by mathematical curve-fitting, followed by curve deconvolution into component peaks. The variation in the absorption peak intensity of characteristic functional groups was recorded as a function of heat-treatment temperature.

Surface element analysis was conducted on an XPS in order to evaluate the distribution of surface elements and surface functional groups on the chemically activated carbon samples. X-ray photoelectron spectroscopy (XPS, Kratos, UK) with Mg KX-ray source (1253.6 eV photons) was used to obtain C, O, and Si core-level spectra of precursors and activated carbons. Samples were carefully mounted on a spectrometer probe tip by means of double-sided adhesive tape. The pressure of the sample chamber was maintained at 10^{-8} Torr or lower during measurement. All binding energies were referred to the carbon 1s peak. Atomic concentrations were estimated from the XPS element peak area after applying an atomic sensitivity factor [28].

3. Results and Discussion

3.1. The effect of KOH impregnation on the chemical structural change of rice straw

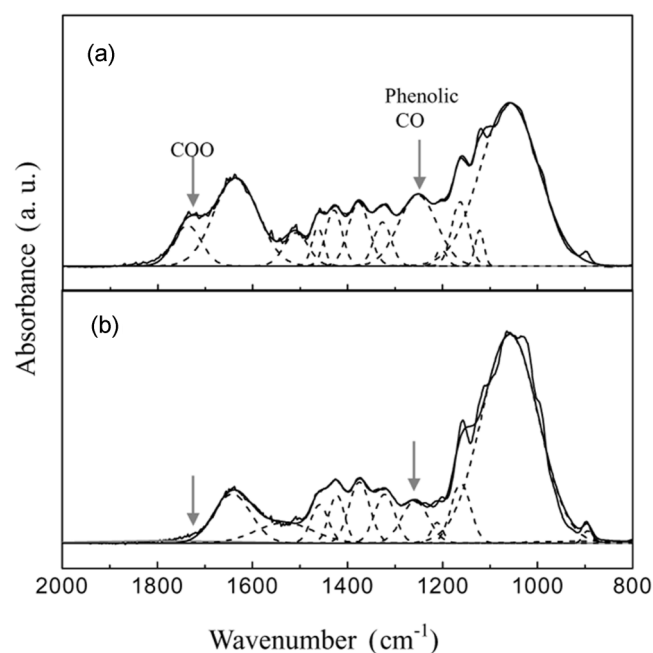


Fig. 1. FTIR spectra of (a) rice straw and (b) KOH-treated rice straw.

Table 2. Absorption bands in the FTIR spectra of rice straws and their assignment

Region (cm^{-1})	Assigned to
3100-3600	O-H (stretching)
2800-3000	C-H (stretching)
1735	O=C-O (stretching)
1640	C=O (stretching)
1540	C=C (aromatic ring stretching)
1410	CH_2 (bending)
1310-1360	C-C and C-O (skeletal vibrations)
1360	C-H (bending)
1200	C-O (stretching in pyranose ring)
1170	C-O (antisymmetric bridge stretching)
1110	C-OH (skeletal vibrations)
1080	C-O-C (pyranose ring skeletal vibrations)
1030	C-O (C-6 skeletal vibrations)
990	C-O (secondary alcohols skeletal vibrations)

The FTIR spectrum of rice straw, Figure 1, shows several absorption bands that can be assigned to individual structural units of rice straw as listed in Table 2.

It can be clearly seen from Figure 1 that the peak intensities of ester band at 1735 cm^{-1} and phenolic ether band at 1250 cm^{-1} decreased considerably after KOH treatment. This

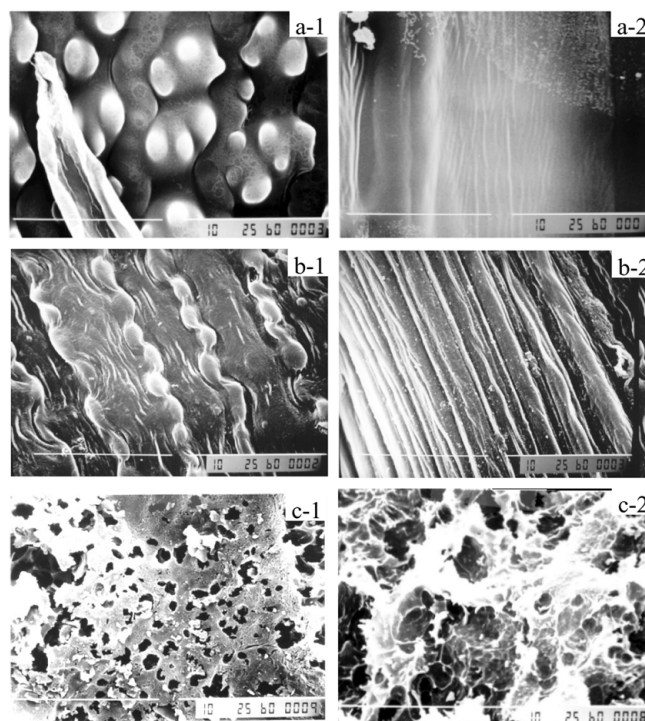


Fig. 2. SEM micrographs of the (1) outer and (2) inner parts of (a) the virgin rice straw, (b) KOH-treated rice straw, and (c) its activated carbon obtained from the one-stage process [Adopted from reference 25 by courtesy of Elsevier].

observation indicates that the lignin that consists of many ester and ether bonds in crosslinked structure [28] is damaged by KOH impregnation. Indeed, from the comparison of the outer and inner parts of virgin rice straw with the equivalent parts of KOH-treated rice straws shown in Figure 2, it is clear that the surface morphology of rice straw deformed considerably by KOH impregnation due possibly to the extraction of lignin components that help to sustain the morphology of rice straws.

3.2. The effect of KOH on the chemical structure change during heat treatment of rice straw

Figure 3 shows the FTIR spectra of heat-treated rice straws. The spectrum of the sample heat-treated at 300°C is very similar to that of cellulose. However, on heat-treatment at the higher temperatures, the development of aromatic structures can be recognized with the evidences such as the decreased intensity of the band at 3600-3100 cm^{-1} for O-H stretching absorption as well as the band at 1740 cm^{-1} for ester carbonyl group. The aromatic C=C and C=O stretching bands at 1520 and 1640 cm^{-1} respectively became more pronounced with increasing pre-carbonized rice straw. The greater extent of dehydration and aromatization could be observable from the sample heat-treated at 700°C (see Figure 3(d)). The characteristic bands appearing in the 1500-1000 cm^{-1} region may be attributed to the aromatic C=C skeletal vibration (at 1450 cm^{-1}) and C-H deformation modes in alkenes. Further loss of oxygen from the heat-treated rice straw is reflected in the change in the peak-intensity ratio of

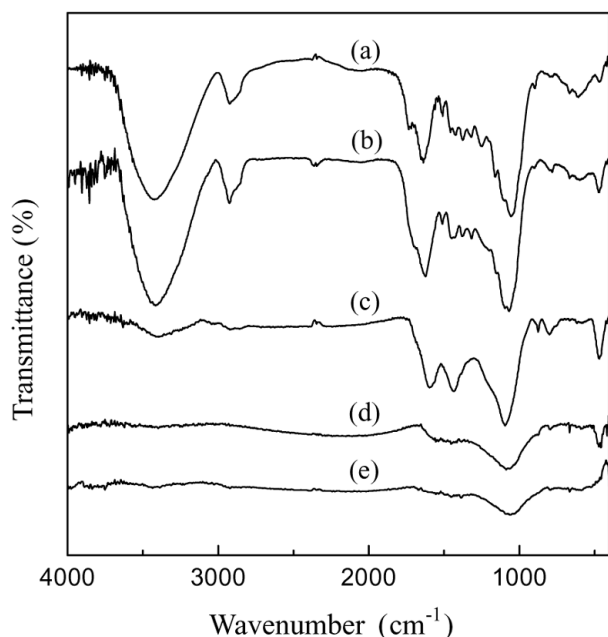


Fig. 3. FTIR spectra of heat-treated rice straws as a function of heat-treatment temperature of (a) 110, (b) 300, (c) 500, (d) 700, and 900°C.

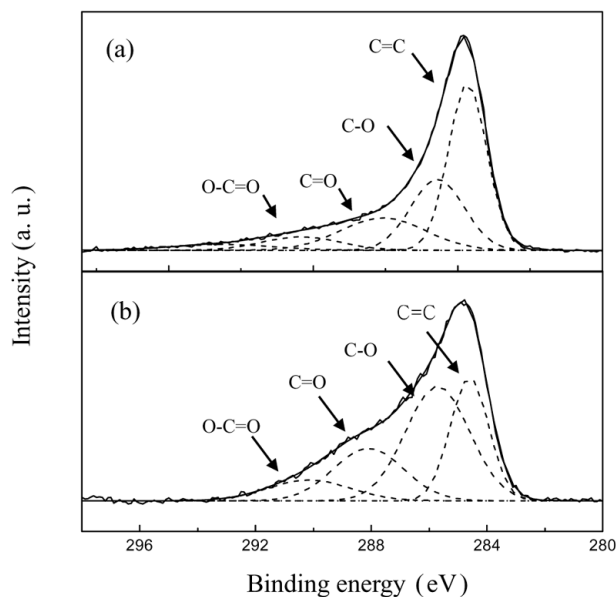


Fig. 4. XPS spectra of C_{1s} narrow scan of (a) the rice straw heat-treated at 700°C and (b) one-stage KOH-activated carbon at 800°C.

C=O band to C=C stretching band. It is interesting to note that, on further heat treatment over 700°C, most of the pyranose structures of cellulose still survives as evidenced by the characteristic peaks of C-O stretching at 1200 cm^{-1} and C-O-C skeletal vibrations at 1080 cm^{-1} .

Figure 4 shows XPS narrow scan spectra of C_{1s} region at 285 eV for the rice straw heat-treated at 700°C and the one stage KOH-activated carbons at 800°C. It is evident that the oxygen content in the activated carbon is much higher than that in the heat-treated rice straw. Particularly, it is noteworthy that carbonyl (C=O) group still remains on the carbon surface in spite of high activation temperature of 800°C. This observation suggests that KOH may contribute to creating the oxygen atom containing functional groups onto the carbon layers during thermal degradation. This means that carbon consumption by means of CO and CO_2 evolution from carbon structure may be facilitated by the presence of this oxygen containing functional groups at high activation temperature. After washing process, the atomic concentration of potassium could not be determined due to the absence of K_{2p} peak on the surface of the KOH-activated carbons. This result indicates that the KOH was completely removed by washing after the activation process, so it did not influence on the observed spectrum as discussed above.

3.3. The effect of KOH impregnation on thermal degradation behavior of rice straw

Figure 5 shows the thermal degradation behavior of the virgin rice straw. The thermogram consists of four stages, i.e. the stage 1 below 270°C, the stage 2 ranging from 270 to 340°C where a rapid degradation occurs, the stage 3 in the

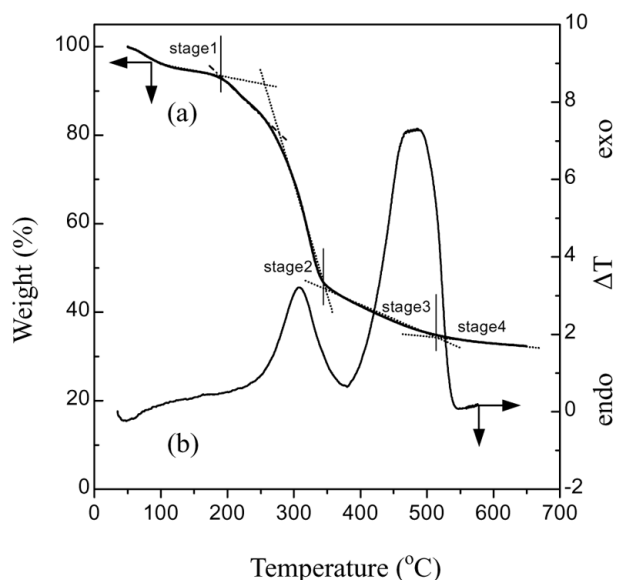


Fig. 5. (a) TGA and (b) DTA thermograms of rice straw.

range from 340 to 510°C, and the stage 4 above 510°C. Generally, it has been known for cellulose (in abb. Cell-OH) that the heat-treatment at lower temperature results in the depolymerization of the cellulose molecule, accompanied by the evolution of H₂O, CO₂, CO, and charred residue. The charred residue undergoes at the higher temperature further reactions including the formation of 1,6-anhydro-β-D-glucopyranose (levoglucosan) [29, 30]. As compared with such a generally known thermal degradation behavior of cellulose, a distinctively different thermal degradation behavior of rice straw can be recognized between the stage 1 and the stage 2. That is, during thermal degradation of rice straw, initiation temperature of rapid degradation in the stage 2 became the lower and subsequently the main degradation occurred through two steps. This result may be correlated with the fact that the branched structure of hemi-cellulose in rice straw has lower crystallinity than α-cellulose. That is, hemi-cellulose part degrades first at the lower temperature, followed by the degradation of α-cellulose of high crystallinity [31-33]. However, DTA thermogram did not clearly show this stepwise degradation, so it needs further work on this particular issue.

Figure 6 illustrates the thermograms of KOH-impregnated rice straws. It is interesting to note that the rapid degradation region from 270 to 340°C gradually disappears to be a gentle linear slope and the degradation onset temperature is lowered with increasing KOH contents. These phenomena may result from the retarding role of KOH in the thermal degradation of rice straws. That is, at the impregnation stage, KOH may substitute the hydrogen atoms in hydroxyl groups, particularly hydrogen atoms on C6 and C2 hydroxyl groups of anhydroglucose unit, as well as some dissolution of lignin component. The substituted potassiums on C6 position may interfere and

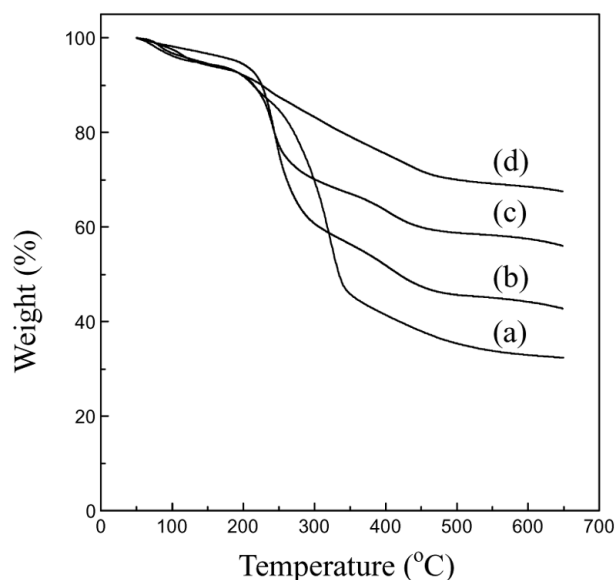


Fig. 6. TGA thermograms of (a) virgin rice straw and KOH-impregnated rice straws with the impregnation ratios (KOH: precursor) of (b) K51 (0.5:1), (c) K11 (1:1), and (d) K21 (2:1).

consequently retard the depolymerization of cellulose molecules by the hydrolysis reaction of glycosidic ether bond, which otherwise easily occur by the attack of C6 hydroxyl groups

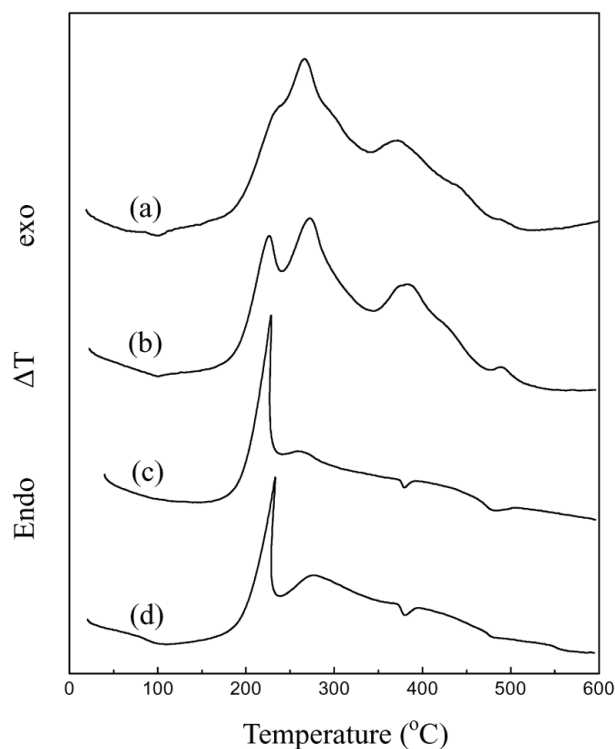


Fig. 7. DTA thermograms of KOH-impregnated rice straws with the impregnation ratios (KOH: precursor) of (a) K5 (0.5:1), (b) K11 (1:1), (c) K151 (1.5:1) and (d) K21 (2:1).

during heat-treatment. However, intermolecular condensation reaction occur at lower heat treatment temperature due to catalytic action of KOH. By this way, the degradation of KOH-impregnated rice straws occurs gradually rather than abruptly and thus relatively high char yield may be able to result from. However, it should be mentioned that the residue fractions observable from Figure 6 is not pure the carbon because it consists of carbons and potassium compound. Indeed, after washing out the potassium compounds from the thermal degradation residue, the char yield of KOH-impregnated rice straw was slightly higher than that of the virgin rice straw, but did not linearly increase with increasing KOH amounts.

Figure 7 shows the DTA thermograms of KOH-impregnated rice straws. With increasing the impregnation ratio, it can be clearly seen that the two exo-thermal peaks appearing at around 300°C and 480°C, respectively, disappears and a new exothermal peak is emerging at around 220°C. These data show again the facilitated condensation reaction and the retardation of thermal degradation of rice straw. The endothermal peak at around 380°C is due to the melting of KOH.

From all the abovementioned, it may be possible to draw a tentative conclusion that KOH promotes the dehydration reaction at the initial decomposition stage and retards the rapid degradation reaction by interfering depolymerization reaction of cellulose molecules at the later stage of thermal degradation of rice straw.

4. Conclusion

At the impregnation stage, KOH extracts to some extent the lignin component from rice straw and reacts with hydroxyl groups. On heat-treatment, the impregnated KOH facilitates intermolecular condensation reaction on one hand but retards the thermal degradation of cellulose molecules on the other hand. The oxygen-containing surface functional groups survived the high temperature activation or newly created by oxidation of KOH may facilitate the bulk, not controlled, consumption of carbon atoms so that the effective porosities may not be able to be developed by the one-stage activation process.

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