A comparison of chemical treatment methods for the preparation of rice husk cellulosic fibers

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Abstract— *NaOH, H_2O_2 and $NaOH/H_2O_2$ treatment methods were investigated to eliminate the lignin and hemicellulose distributed in the lignocellulosic matrix of rice husk. In order to prevent the decomposition of H_2O_2 at higher temperatures, a low temperature treatment for 4 hours has been performed. A composition analysis indicated that $NaOH/H_2O_2$ may achieve the highest concentration of α-cellulose, but had the lowest overall solid recovery rate. Both FTIR and TGA results confirmed that only the H_2O_2 treated rice husk contained hemicellulose residue, which could be found at the absorption peak 1740 cm^{-1}. The TGA analysis demonstrated the $NaOH/H_2O_2$ modified rice husks presented the most uniform structure. The SEM gave a clear picture of the raw rice husks and modified rice husks.*

Keywords— *cellulose, delignification, H_2O_2, kinetics, NaOH.*

I. INTRODUCTION

Due to its properties of weightless, inexpensive, tractable, renewable, biodegradable and biocompatible, cellulose has attracted the attention of many researchers in recent years. As one of the most abundant natural polymers, cellulosic materials are easily accessible, especially from agricultural wastes, like rice husks [1,2]. Globally, up to 120 million tons of rice husks are produced annually. Although some are used as animal feed or burned for energy generation, huge quantities of rice husk are still burnt or dumped as a waste [3-4].

Previous studies demonstrated that rice husks contains cellulose (25 to 35%), hemicellulose (18 to 21%), lignin(26 to 31%), silica (15 to 17%), solubles (2 to 5%), and moisture ca (7.5%) [4]. In the rice husks cell wall, cellulose exists in a complex lignocellulosic matrix, surrounded by hemicellulose and lignin [5]. Linking together by both intermolecular and intramolecular hydrogen bonds, the cellulose polymers present a microfibrils structure in the nature [6]. The crystalline structure is formed by combined hydrogen bond energy that makes it insoluble and nonundegradable. In association with cellulose, hemicellulose is mainly made up of arabinose, galactose, glucose, mannose and xylose. Different from cellulose, hemicellulose presents a branched and amorphous form and tends to be hydrolyzed by chemical solvents. Consisting of coniferyl alcohol, sinapyl alcohol and coumaryl alcohol, lignin is a large three-dimensional polymer, which stiffens and coheres the cell wall fibers together [7].

In order to selectively separate cellulose from the lignocellulosic matrix, alkaline and peroxide treatments were applied to the rice husks. As one of the most wildly used alkali treated agents, sodium hydroxide (NaOH) can perform a saponification effect on the intermolecular ester bonds linked between xylan hemicellulose and lignin. This may decrease the degree of polymerization and crystallization and hence break the crosslinks exiting in the lignin structure [8]. Using the hydrogen peroxide treatment (H_2O_2), the H_2O_2 can decompose into hydroxyl radicals (OH) and superoxide anions (O^{2-}) under heat, promote lignin degradation. Since H_2O_2 treatment is costly, lower H_2O_2 concentrations in alkaline hydrogen peroxide (AHP) treatment could be selected and adjusted to overcome the economic drawbacks. After AHP treatment, the three-dimensional structure of the lignicellulosic matrix become more open and fragile and the cellulosic crystallinity remain the same [9].

In the present work, rice husks were pretreated by NaOH, H_2O_2 and NaOH combined with H_2O_2. High Performance Liquid Chromatography (HPLC) and Fourier Transform Infrared (FT-IR) analysis were undertaken as the basis to investigate the reaction. Thermogravimetric analysis (TGA) was carried out to study the thermal behavior of modified rice husks.

II.   MATERIAL AND METHOD

2.1   Reagents and material preparation

Sodium hydroxide (NaOH) pellets (Catalog No.: AC20606), and H_2O_2 (50wt% solution, Catalog No.: H341-500) were obtained from Fisher-scientific (Waltham, MA). The rice husks used for the present study were obtained from Hunan province in China. The rice husks were first washed with DI water at 50°C for 2h and dried at 60°C in an oven for 24h. The dry rice husks were extracted with toluene-ethanol (2:1, v/v) in a Soxhlet for 6 hours due to the presence of fatty acids, free alcohols and other extractives present. The dewaxed rice husks were then treated with water at 50°C for 2h. The rice husks were maintained at 60°C in an oven for at least 24 hours for further use.

2.2   Sodium hydroxide (NaOH) and hydrogen peroxide (H_2O_2) treatment

NaOH or H_2O_2 at concentrations of 2, 4, 6, and 8% (w/v) was used to pretreat 1 g rice husks samples at a solid loading of 2% (w/v). Treatments were performed at 40°C, 60°C, and 80°C with continuous stirring. Sodium hydroxide (NaOH) at concentrations of 2, 4, 6, and 8% (w/v) in 5% hydrogen peroxide (H_2O_2) solution was also used to treat 1 g rice husks samples at a solid loading of 2% (w/v). Treatments were performed by four different step-changes: 40°C for the first 4h and 60°C for the next 20h; 40°C for the first 4h and 80°C for the next 20h; 60°C for the first 4h and 80°C for the next 20h. The last one is heated at 80°C for 24h without any change. The collected solids were washed with 500 mL of hot deionized water 5 times and soaked for 24 hours. Then the modified rice husks were transferred into the oven at 60°C for 24 hours. The treatments were performed in triplicate and the residue solids were used for determining the concentration of lignin, holocellulose and carbohydrate.

2.3   Analysis methods

The lignin concentration is composed of acid soluble lignin and acid insoluble lignin, which may be calculated according to the National Renewable Energy Laboratory (NREL) analytical procedure [10,11]. All the analysis were conducted in duplicate. The holocellulose concentrations (combination of hemicellulose and cellulose) were measured by gravimetric methods [12]. The composition of carbohydrate was determined by using a high performance liquid chromatography system (HPLC) equipped with Accuflow Series Ⅲ Pump, degasser (ERC 3215 ALPHA, ERC Inc.), RI detertor (Shodex RI-71; Tokyo, Japan) and Bio-Rad Aminex HPX-87P column, according to the standard National Renewable Energy Laboratory (NREL) methods [13].

2.4   Fourier Transform Infrared Spectroscopy(FTIR) and Thermogravimetric Analysis(TGA)

The modified rice husk samples were analyzed by ATR-FTIR (Vertex 70 Hyperion 1000 (Bruker)) at the Materials Characterization and Preparation Facility(MCPF), Hong Kong University of Science and Technology. The tests were conducted with the use of 128 scans, $4cm^{-1}$ resolution, and an interval of $1 \ cm^{-1}$. The thermogravimetric experiments were conducted by applying a Thermo-gravimetric analyzer (Model Q5000, Thermal Analysis instruments) also at MCPF. Nitrogen gas was used as carrier gas. Experiments were carried out using a thermobalance at a linear heating rate of 10 °C /min, with the temperature range from 30 to 750°C, at a steady nitrogen flow of 100 mL/min.

III.   RESULTS AND DISCUSSION

3.1   Characterization of rice husk

According to a previous study, the chemical composition of rice husks is cellulose (25 to 35%), hemicellulose(18 to 20%), lignin(26 to 31%), silica(15 to 17%), solubles (2 to 5%), and moisture ca. 7.5%. Factors affecting the concentration of different components varied among harvesting methods, growing area and season, and testing procedures. The composition of the rice husks in this study is shown in Table 1.

TABLE 1
THE COMPOSITION OF RAW RICE HUSKS

Component		Percentage (%)
(a) Solid composition	**Holocellulose**	49.72
	α-cellulose	31.13
	Acid-insoluble lignin	24.89
	Acid-soluble lignin	3.36
	Extractives	5.01
	Ash	16.50
(b) Carbohydrate composition	**Glucan**	32.61
	Xylan	17.25
	Galactan	1.28
	Araban	1.52

Based on the analysis procedure of Han and Rowell (1997), the holocellulose concentration was 49.72% of the dry biomass. By comparing the concentration of holocellulose and carbohydrate, the difference in percentage could be explained by the sugar degradation caused by the hydrolysis effect of 72% sulfuric acid during the total sugar analysis experiments [14]. The α-cellulose content of 31.13% was nearly in the middle of the 25.89% to 35.50% range that has been reported for other lignocellulosic materials in rice husks [15]. The 28.25% lignin concentration, the total amount of acid soluble lignin and acid insoluble lignin, is also in the middle range comparing with the previously reported values. Although acid insoluble parts always considered as lignin, other possible parts like rice grain also resist the acid treatment and effect the actually lignin content. Because the protein portion of the rice grain would condense and become insoluble when treated by a high concentration sulfuric acid. However, by comparing with the lignin percentage, rice grain only comprise a tiny part of the totally acid insoluble material [16].

3.2   Sodium hydroxide (NaOH) treatment

The effects of NaOH treatment on the delignification of rice husks are shown in Table 2. The lignin, after NaOH treatment, varied from 14.71% (24 h, 40°C) to 6.5% (24 h, 80°C). Concentration had a significant effect on delignification for treatments at 40°C for 24h and 60°C for 24h. Increasing the temperature from 40°C to 80°C sharply increased the delignification results. The lignin concentration was analyzed based on acid soluble and acid insoluble lignin. As one of the major portions of the rice husk cell wall, the lignin concentration stands for the major indicator of the delignification effectiveness of alkaline treatment. By performing experiments in tirplicate, similar results were achieved, which confirmed the validity of the experimental data and minimised the potential of experimental error. In addition, when the temperature rose from 40°C to 60°C and 60°C to 80°C, the delignification results from 2% NaOH always had a better performance than that from the 8% NaOH in the lower temperature stage. A reasonable explanation for this would be that the 20°C temperature variation had a significant effect on rice husk lignin degradation results.

Contrary to the lignin result, the holocellulose concentration, which stands for cellulose and hemicellulose concentration, varied from 71.66% (24h, 40°C) to 84.7% (24 h, 80°C). The changes in the NaOH concentration lead to a continuous increase in the holocellulose contents. The NaOH concentration had a more obvious effect on the holocellullose concentration at a relatively lower temperature (40°C) than the higher ones, which implied the NaOH concentration effect was less significant when temperature rose. The solids from holocellulose analysis were used for α-cellulose analysis. The α-cellulose, which makes up the largest portion of cellulose, was considered as the most important indicator for evaluating the effectiveness of different treatments for the further oil sorption studies. The amount of α-cellulose after NaOH treatment ranged from 58.26% (24 h, 40°C) for 2% NaOH to 81.40% (24 h, 80°C) for 8% NaOH, with changes in concentration causing the most continuous increase in the α-cellulose contents. In addition, when the temperature rose from 40°C to 60°C and 60°C to 80°C, the increase of α-cellulose concentration did not appear in the same trend like the lignin concentration trend. A reasonable explanation for this would be that the lignin and hemicellulose are more unstable a the cellulose when treated with alkaline reagents. Thus when the α-cellulose concentration increases quickly, the rise in the lignin concentration is not as fast.

Based on HPLC analysis, xylan constituted between 13.40% (2%, 40°C, 24h) and 3.30% (8%, 80°C, 24h) of the modified solids. The percentage of xylan during NaOH treatment decreased with increasing concentration and still remained in the modified rice husks after NaOH treatment. At lower temperatures the NaOH concentration had no obvious effect. However, after a rising the temperature to 40°C in this study, the reduction of xylan dramatically increased. A possible explanation to this phenomenon would be that the high temperature was a good support for the xylan hydrolysis.

TABLE 2
PERCENTAGE OF LIGNIN FOR SODIUM HYDROXIDE TREATMENT

Concentration (%) Temperature°C	Lignin %	Holocellulose %	α-cellulose %	Xylan%	Solids Recovered %
2% NaOH, 40°C	14.71±2.07	71.66±1.41	58.26±2.31	13.40±1.75	68.16±1.54
4% NaOH, 40°C	13.39±1.35	74.40±1.18	61.45±2.59	12.95±0.96	64.94±1.21
6% NaOH, 40°C	11.94±1.52	74.64±1.74	62.64±1.42	12.00±1.02	61.31±2.06
8% NaOH, 40°C	10.87±1.23	77.79±1.21	67.20±2.11	10.59±0.45	56.29±1.77
2% NaOH, 60°C	11.12±1.61	77.39±1.45	67.72±2.29	9.67±0.67	60.52±1.49
4% NaOH, 60°C	10.64±1.04	78.15±1.76	69.39±1.81	8.76±0.81	57.01±3.37
6% NaOH, 60°C	9.45±0.75	79.97±1.62	71.98±1.77	7.99±1.32	53.98±1.18
8% NaOH, 60°C	8.84±0.95	81.00±1.29	74.87±1.02	6.13±0.27	49.24±2.40
2% NaOH, 80°C	8.92±0.36	80.55±2.75	75.52±1.33	5.03±0.39	50.47±1.73
4% NaOH, 80°C	7.43±0.72	83.23±2.98	78.29±1.46	4.94±0.64	47.86±1.65
6% NaOH, 80°C	6.71±1.51	84.37±2.22	80.10±2.27	4.27±0.25	45.92±1.92
8%NaOH, 80°C	6.50±0.37	84.7±1.83	81.40±1.94	3.30±0.41	42.37±1.41

3.3   Hydrogen peroxide treatment

Hydrogen peroxide treatment utilized oxidative delignification to detach and solubilize the lignin and loosen the lignocellulosic matrix. The extent by which lignin degradation occurred in this study was not as high as expected. The lignin after hydrogen peroxide pretreatment varied from 27.32% (24 h, 40°C) to 20.98% (24 h, 80°C). A summary of these results, as well as those for the amount of holocellulose in the hydrogen peroxide treatment, is presented in Table 3. Temperature and concentration had a continuous effect on the percent lignin reduction during hydrogen peroxide pretreatment. Hydrogen peroxide concentration had a significant effect on delignification for the treatment at 8% H_2O_2 for 24h. Increasing the temperature from 40°C to 60°C also increased delignification for 24h at 2%, 4%, 6%, 8% H_2O_2.

By analyzing acid soluble and acid insoluble lignin, when the temperature went from 40°C to 60 °C, the delignification results had a better performance than these from the 60°C to 80 °C NaOH treatment. A reasonable explanation is that when the hydrogen peroxide is exposed to heat, it undergoes the following decomposition reaction $2H_2O_2 ==> 2H_2O + O_2$ where the hydrogen peroxide decomposes to water. However, with the rising delignification results, it is possible that although hydrogen peroxide decomposition may happen, the higher concentration and reaction time of hydrogen peroxide can still have a slight rising trend in the delignification treatment.

The amount of holocellulose after H_2O_2 treatment ranged from 53.44% (24 h, 8% H_2O_2, 60°C) to 50.18% (24h, 2% H_2O_2, 40°C). When the temperature went from 60°C to 80 °C, the holocellulose percent production showed a little decrease, which was different from the lignin reduction percent when the highest temperature presented an increase. A reasonable explanation is the hydrogen peroxide decomposition at higher temperature may affected the holocellulose concentration, the other components of rice husks like silica, may not be affected strongly by hydrogen peroxide. Comparing with the NaOH treatment, in the same situation (concentration, time and temperature) the delignification effect and cellulose production percentage of hydrogen peroxide treatment is not as high as that of the sodium hydroxide treatment. In other words, without any other condition changes, sodium hydroxide treatment has the priority for delignification.

The amount of α-cellulose after H_2O_2 treatment ranged from 32.12% (24 h, 40°C) for 2% H_2O_2 to 37.02% (24 h, 80°C) for 8% H_2O_2, with changes in temperature causing a continuous increase in the α-cellulose content. However, when the temperature increased from 40°C to 60 °C, the α-cellulose percent production percent showed no significant rise, which was different from the lignin percent reduction when the temperature rise presented a sharp increase. A reasonable explanation for this would be that the effect belongs to the other components of rice husks like silica, which may not be affected strongly by hydrogen peroxide. The remaining percentage of xylan ranged from 18.06% (2%, 40°C, 24h) and 15.10% (8%, 80°C, 24h) of the modified rice husk. The major effect of temperature and concentration were mild for hemicellulose reduction during hydrogen peroxide pretreatment. Also the total recovered solids were higher than that of NaOH treatment.

TABLE 3
PERCENTAGE OF LIGNIN FOR HYDROGEN PEROXIDE TREATMENT

Concentration (%) Temperature°C	Lignin %	α-cellulose %	Holocellulose %	Xylan%	Solids Recovered %
2% H_2O_2, 40°C	27.32±1.31	32.12±1.92	50.18±2.22	18.06±1.07	92.27±1.01
4% H_2O_2, 40°C	26.94±2.29	33.20±0.86	51.15±1.46	17.95±1.54	90.52±1.25
6% H_2O_2, 40°C	26.51±1.48	34.66±2.11	52.05±1.52	17.43±0.68	89.46±0.57
8% H_2O_2, 40°C	25.77±1.63	34.75±1.06	51.92±1.37	17.17±0.92	88.35±1.33
2% H_2O_2, 60°C	23.92±1.73	34.29±1.63	51.78±1.98	17.49±1.11	88.61±1.96
4% H_2O_2, 60°C	23.13±1.91	35.60±1.77	52.62±1.49	17.02±0.71	87.11±1.28
6% H_2O_2, 60°C	22.77±1.88	36.42±1.22	53.32±2.03	16.90±0.32	85.85±1.68
8% H_2O_2, 60°C	22.17±1.89	36.63±1.34	53.44±1.92	16.81±0.95	83.70±1.64
2% H_2O_2, 80°C	22.09±1.03	35.70±1.56	51.91±1.25	16.21±0.23	83.00±1.03
4% H_2O_2, 80°C	21.92±0.96	36.31±1.81	52.08±3.08	15.77±0.46	81.43±1.85
6% H_2O_2, 80°C	21.49±1.21	36.63±2.75	52.31±1.62	15.68±0.81	79.14±2.43
8% H_2O_2, 80°C	20.98±1.47	37.02±1.64	52.12±2.35	15.10±0.47	78.09±1.96

3.4 Sodium hydroxide/ hydrogen peroxide (NaOH/H_2O_2) pretreatment

Sodium hydroxide pretreatment supplemented by 5% H_2O_2 caused a significant lignin degradation varying from 84.27% (24 h, 40°C) to 92.21% (24 h, 80°C). A summary of these results is presented in Table 4, which presented the amount of lignin and holocellulose concentration after the NaOH/H_2O_2 pretreatment. Temperature, concentration and time had significant effects on the percent lignin reduction during sodium hydroxide pretreatment. The amount of lignin after NaOH pretreatment ranged from 6.54% (24 h, 40°C-60°C) for 2% NaOH/5% H_2O_2 to 3.27% (24 h, 80°C) for 8% NaOH/5% H_2O_2, with changes in concentration causing the most significant decrease in the lignin contents compared with the previous two treatment methods. When H_2O_2 was supplemented to the NaOH pretreatment, the extent of delignification increased. A reasonable explanation for this would be that H_2O_2 promotes delignification by its oxidative action [17]. When there is an increase of temperature, the effectiveness of H_2O_2 decreases because of its unstable nature especially at high temperature. Because of the unstable property of H_2O_2, different temperature strategies were considered in order to maximize the efficiency of H_2O_2 and delignification in sodium hydroxide pretreatment with H_2O_2. Among the temperature policies attempted, a step-change of temperature has proven to be effective [18].

The amount of holocellulose after NaOH/H_2O_2 treatment ranged from 83.46% (24 h, 40°C-60°C) for 2% NaOH/5% H_2O_2 to 94.32% (24 h, 80°C) for 8% NaOH/5% H_2O_2, with change in temperature causing a continuous increasing trend. In addition, comparing with the step-change temperature (60°C to 80°C) with 80°C, such a change did not cause too much difference on the increasing trend of holocellulose concentration. A reasonable explanation for this would be that although high temperature might cause a certain degree of H_2O_2 decomposition, the temperature might not be high enough to cause a total decomposition of H_2O_2, making the NaOH/H_2O_2 treatment produce a better yield of holocellulose. Meanwhile, the amount of α-cellulose after NaOH/H_2O_2 pretreatment ranged from 74.42% (24 h, 40°C-60°C) for 2% NaOH/5% H_2O_2 to 88.71% (24 h,

80°C) for 8% NaOH/5% H_2O_2, with changes in temperature causing a continuous increase in the α-cellulose content. Also, like holocellulose, the concentration of α-cellulose was not affected too much by the decomposition of holocellulose. Another possibility, since holocellulose contains both cellulose and hemicellulose, is that the H_2O_2 concentration might not have too much effect on hemicellulose degradation as discussed before. However, the total results were still enhanced in the NaOH/H_2O_2 system [19]. The xylan concentration varied between 9.04% (2%, 40°C, 24h) and 5.52% (8%, 80°C, 24h) after modified by NaOH/H_2O_2. The temperature step-change in xylan degradation did have a slight effect to eliminate more xylan, compared with the no step change at 80°C. Although according to the previous results, the hydrolysis effect of H_2O_2 on xylan was limited; in the NaOH/H_2O_2 system the hydrolysis effect of xylan was enhanced.

TABLE 4
COMPOSITION OF SODIUM HYDROXIDE/ HYDROGEN PEROXIDE PRETREATED RICE HUSKS

Concentration (%) Temperature °C	Lignin %	α-cellulose %	Holocellulose %	Xylan%	Solids Recovered %
2% NaOH + 5% H_2O_2, 40°C(4h)-60°C(20h)	6.54±1.21	74.42±1.99	83.46±2.32	9.04±0.46	56.23±1.46
4% NaOH + 5% H_2O_2, 40°C(4h)-60°C(20h)	5.97±0.36	75.66±2.05	84.53±2.05	8.87±0.52	53.84±1.35
6% NaOH + 5% H_2O_2, 40°C(4h)-60°C(20h)	5.62±0.79	76.99±1.03	85.38±2.26	8.39±0.97	50.07±1.59
8% NaOH + 5% H_2O_2, 40°C(4h)-60°C(20h)	4.88±0.98	78.91±1.29	86.62±3.71	7.71±0.31	49.97±3.47
2% NaOH + 5% H_2O_2, 40°C(4h)-80°C(20h)	5.03±1.03	78.41±1.73	86.97±1.09	8.56±0.12	50.02±1.92
4% NaOH + 5% H_2O_2, 40°C(4h)-80°C(20h)	4.71±0.65	80.52±1.47	87.79±1.96	7.27±0.64	47.11±2.18
6% NaOH + 5% H_2O_2, 40°C(4h)-80°C(20h)	4.42±0.67	81.72±2.23	88.58±2.58	6.86±0.25	45.83±1.42
8% NaOH + 5% H_2O_2, 40°C(4h)-80°C(20h)	3.94±0.32	83.22±1.59	89.56±2.94	6.34±0.18	42.68±1.76
2% NaOH + 5% H_2O_2, 60°C(4h)-80°C(20h)	4.49±0.77	82.46±1.76	89.51±1.72	7.05±0.71	43.91±1.81
4% NaOH + 5% H_2O_2, 60°C(4h)-80°C(20h)	4.23±0.54	83.70±2.07	90.27±3.37	6.57±0.22	41.72±2.24
6% NaOH + 5% H_2O_2, 60°C(4h)-80°C(20h)	3.71±0.49	85.52±3.11	91.61±3.44	6.09±0.69	39.98±1.82
8% NaOH + 5% H_2O_2, 60°C(4h)-80°C(20h)	3.50±0.82	86.02±2.17	92.00±2.17	5.98±0.33	37.52±1.53
2% NaOH + 5% H_2O_2, 80°C(24h)	4.38±0.21	85.17±1.94	91.62±3.36	6.45±0.46	38.74±1.80
4% NaOH + 5% H_2O_2, 80°C(24h)	3.86±0.33	86.47±2.58	92.64±2.56	6.17±0.52	37.12±1.39
6% NaOH + 5% H_2O_2, 80°C(24h)	3.41±0.22	87.75±1.12	93.59±2.54	5.84±0.21	35.91±2.44
8% NaOH + 5% H_2O_2, 80°C(24h)	3.27±0.27	88.71±2.37	94.23±3.15	5.52±0.67	34.07±1.07

In all the treatment methods in Table 4, considerable amounts of lignin were dissolved. The residue lignin concentrations were dependent upon the types of chemicals and conditions. In NaOH treatment, better delignification performance was achieved than that with H_2O_2 pretreatment. Although H_2O_2 was not very effective on lignin degradation, the addition of H_2O_2

in NaOH treatment was effective for delignification, and also caused sugar degradation especially at high temperature. Meanwhile high temperature was considered as a drawback for the hydrolysis of H_2O_2, according to the experimental results. By increasing the temperature, the delignification effect in both H_2O_2 and $NaOH/H_2O_2$ pretreatments was enhanced. However, the total solid recovered after $H_2O_2/NaOH$ was extremely low when compared with the other methods, and hence affected the productivity.

3.5   Scanning electron microscope (SEM) analysis

SEM technology was used to study the morphology of both raw rice husk and modified rice husk, in order to give a visualized insight. SEM micrographs of outer and inner surfaces of raw rice husk are shown Fig.1.
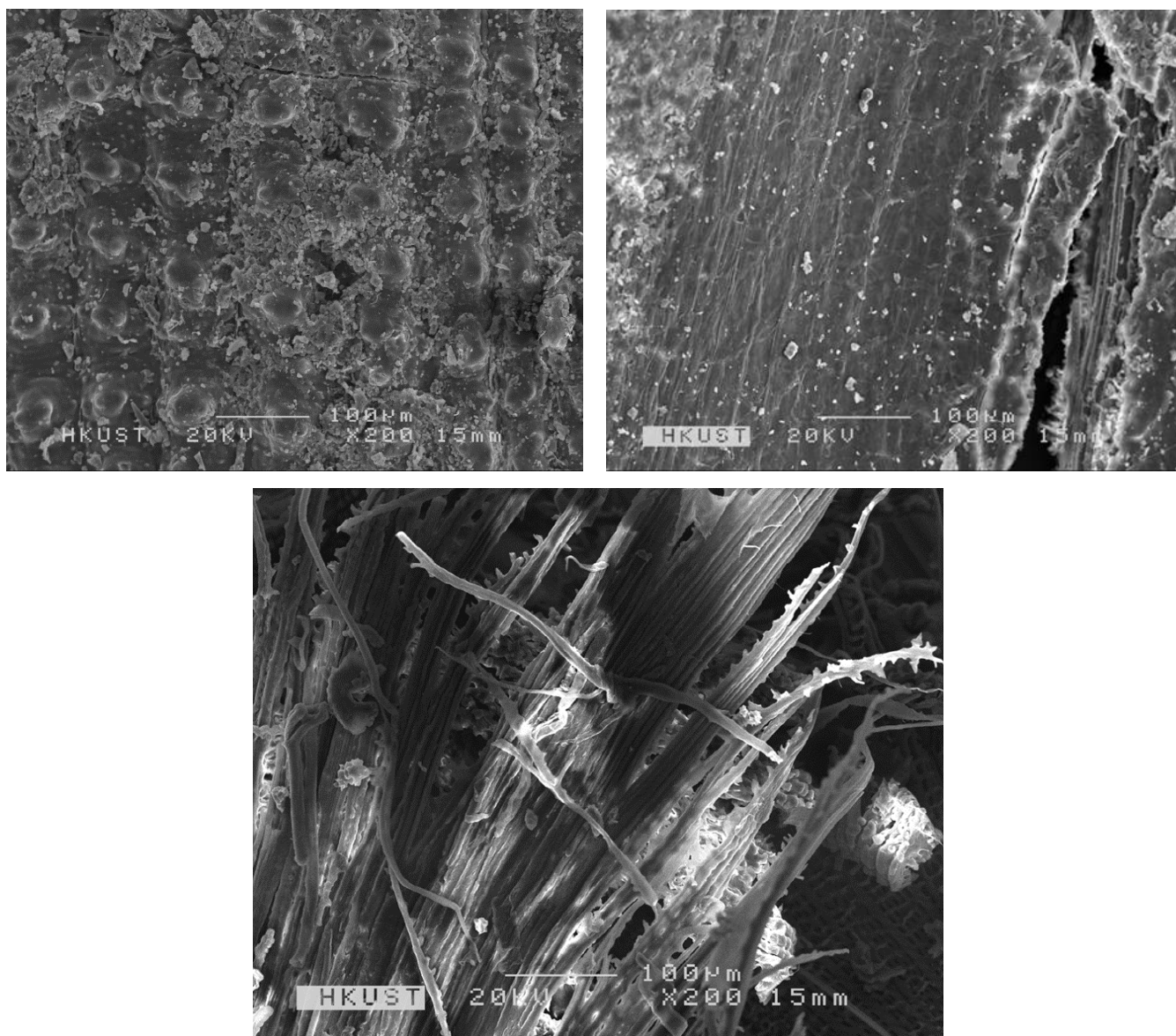

FIGURE 1. SEM MICROGRAPHS OF RAW RICE HUSK OUTER (A) AND INNER (B) SURFACES AND RICE HUSK
TREATED BY $8\%NaOH/5\%H_2O_2$ AT 80°C (c).

Comparing with the smooth inter surface of raw rice husk in Fig. 1(b), the outer epidermis was highly asperous and presented a linear ridged conformation with bright dome-like structures, due to a more concentrated distribution of silica. However, a previous study [20] applying field-emission SEM (FE-SEM) and energy dispersive X-ray micro-analysis (EDXA) technology proved that silica also appeared in other parts of rice husk with a relatively low concentration. Such silica throughout structure enhanced the strength of the rice husk epidermis [21].

Considering the effect of cellulosic concentration, the micrographs of 8%NaOH/5%H$_2$O$_2$ at 80°C treated rice husks was observed by SEM and illustrate the original structure of rice husks were almost destroyed and the inorganic fraction (mainly silica) present as the conical protrusions on the raw rice husks was removed(Fig. 1(c)). The removal of the outer surface and the disappearance of the inner surface also implied the elimination of theorganic part. Meanwhile, after preferential degradation of the cementing lignin and hemicellulose among the lignocellulosic matrix, the light color of the sample seemed to show that the resultant modified rice husks could mostly be cellulose. This was due to the lignin concentration of raw rice husks always presenting a really dark color.

The SEM analysis proved that the rice husk morphology was significatnly changed in both inner and outer surface after being treated in alkaline conditions, which confirmed the elimination of inorganic components (like silica), organic components (like hemicellulose and lignin) and the decrease in cellulosic crystallization. The resultant rice husk presented a bright color and a more uniform fiber distribution.

3.6 Fourier transform infrared (FTIR) spectra of modified rice husk

The FTIR spectra comparison among raw rice husks, NaOH treated rice husks, H$_2$O$_2$ treated rice husks and NaOH/H$_2$O$_2$ treated rice husks were compared in Fig. 2. A broad band, ranged from 3800 to 3040 cm^{-1} and centered around 3350 cm^{-1}, was associated with the –OH stretching from the hydrogen bonds of cellulose [22-25]. The FTIR spectra of raw rice husks, NaOH treated rice husks, H$_2$O$_2$ treated rice husks and NaOH/H$_2$O$_2$ treated rice husks presented a similar absorption peak. However, the intensity of those four spectra showed an increasing trend and the broad region became centered and sharper, which implied that the treatment methods did not disrupt the crystallinity of cellulose, but even enhanced such a structure. Meanwhile, the absorption band around 2900 cm^{-1} was related to the symmetric methyl and methylene stretching bonds [26]. The CH$_2$ scissoring motion located at 1414 cm^{-1} was related to the cellulose. The C-H bending at 1362 cm^{-1} indicated both cellulose and hemicellulose [27-29]. The cellulose and hemicellulose related bonds also ranged from 1200 to 1000 cm^{-1}. The peak around 1126 cm^{-1} was assigned to the C-O-C ring skeletal vibration. The C=O stretching was located at 1029 cm^{-1} [30]. After delignification, the intensity of the peaks was enhanced dealing to the increase of the cellulosic concentration. For the hemicellulose, the peak located at 1740 cm^{-1} was associated with the C=O stretching of acetyl groups from the raw rice husk, and also considered as the linkage of hemicellulose and lignin. According to the experimental results, both NaOH and NaOH/H$_2$O$_2$ treatments were effective in the elimination of hemicellulose and the decrease of xylan, which was connected with the disappearance of the 1740 cm^{-1} peak in their FTIR spectra.
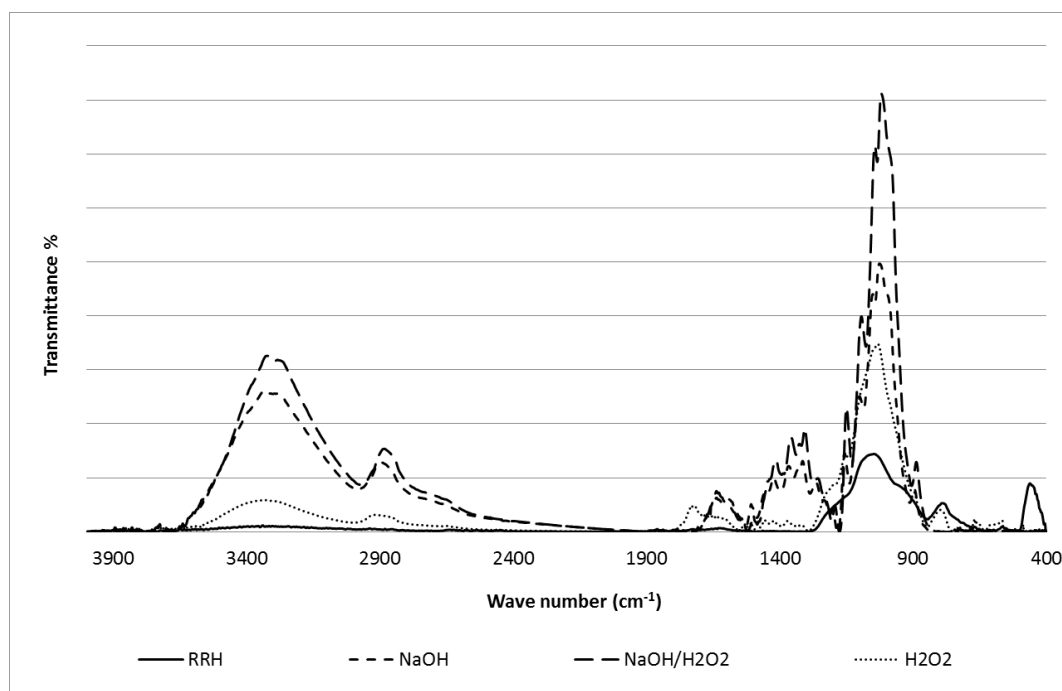

FIGURE 2. FTIR SPECTRA OF RAW RICE HUSK AND MODIFIED RICE HUSKS SAMPLES PRETREATED WITH 8%H$_2$O$_2$, 8%NaOH AND 8%NaOH+5%H$_2$O$_2$ AT 80°C.

The lignin associated groups could be found at 1640, 1606, 1506, 1460, 1425, 1305 and 1240 cm^{-1} [31]. The C=O group at 1640 cm^{-1} was suggested to conjugated with the aromatic structure from aldehydes and ketones from the lignin. The C=C aromatic skeletal stretching was located at 1600 and 1506 cm^{-1}. The peaks at 1460 and 1425 cm^{-1} were associated to the CH$_3$ deformation with the methoxyl groups of lignin [32]. Also the C-O stretching in the syringyl ring of lignin could be found at 1305 and 1240 cm^{-1}. Although the intensities of some lignin peaks still could be found and even presented a higher trend, such a trap trend could be concluded to the hydrolysis of the lignin. Groups like C=O could generate after different treatments. When the lignin matrix was destroyed, the degradation of ester-associated bonds lead to the smaller lignin fragments.

3.7   Thermo-gravimetric analysis (TGA)

The presence or absence of cellulose, hemicellulose and lignin of both raw rice husk and modified rice husks were determined by thermogravimetric analysis (TG). The TG/DTG curves (in nitrogen atmospheres) of raw rice husk are shown in Fig. 3.

The TG curves presented several continuous decomposition steps related to the complex thermal decomposition of the lignocellulosic matrix. The heating program may cause different physical and chemical decomposition steps. At the very beginning, the absorbed moisture and primary volatile substances evaporate with increasing temperature and mostly volatalise before 130°C. The first very small peak of the DTG curve can be observed around 300°C, and was associated with the thermal decomposition of hemicellulose and glycosidic links of cellulose. Previous studies also proved such decomposition patterns by analysis raw rice husk and a variety of other plants [33]. By continuous heating, when the temperature went up to 360°C, a thermal decomposition peak of cellulose could be found in the DTG curve [34, 35]. The different decomposition temperatures were due to the different structures between hemicellulose and amorphous cellulose and crystalline cellulose. With the crystallization structure, cellulose was more resistant to the heating process and became more difficulty to be degraded. The broad range from 200°C to 500°C and centered around 350°C indicated the thermal decomposition of lignin. This wide range is superimposed by the peaks of hemicellulose and cellulose coordinated with the complex structure of lignin. The residue found after heating consisted of carbonaceous products and silica, which occupied 44% of the total weight of the raw rice husk sample. Such high percentage residue may due to the high silica concentration and probably the incomplete lignin decomposition [36]. After the H$_2$O$_2$ pretreatment, the thermal decomposition temperature of cellulose as decreased by 10°C according to the DTG curve, since parts of the cementing materials were removed. As verified by the FTIR peaks, the residue color was still dark, and was associated to the existence of lignin.
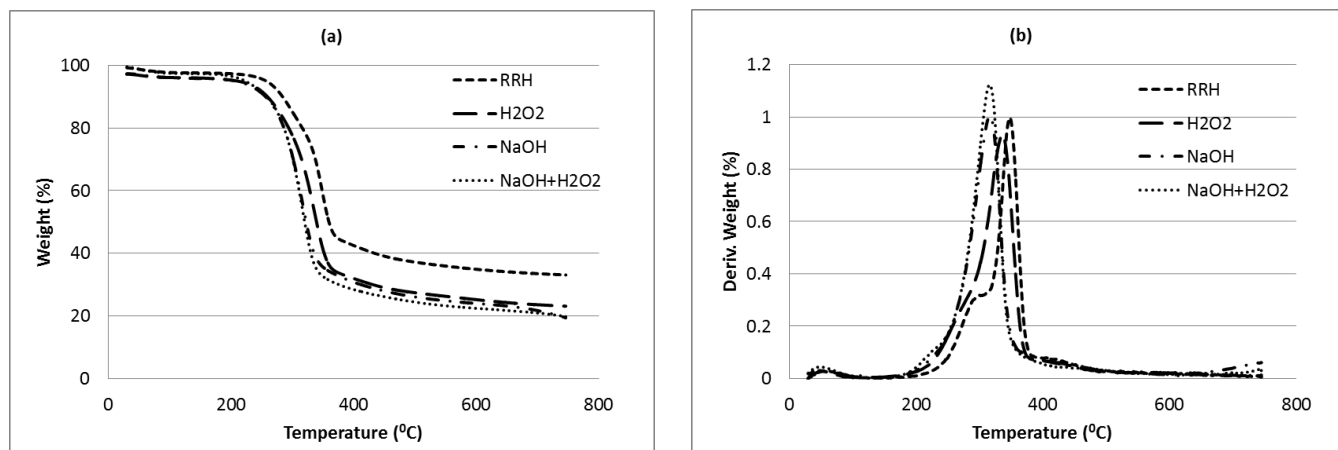

FIGURE 3. TG(a) AND DTG(b) CURVES OF RAW RICE HUSK, 8% H$_2$O$_2$ AT 80°C PRETREATED RICE HUSK, 8% NaOH AT 80 °C PRETREATED RICE HUSK AND 8%NaOH/5%H$_2$O$_2$ at 80 °C PRETREATED RICE HUSK IN NITROGEN.

The NaOH sample in Fig. 3(b) presented only one shoulder a with very smooth shape, which indicating the majority decomposition of hemicellulose was achieved. Following the first step of volatile substances evaporation between 60 and 135°C, the second decomposition of volatile material like hemicellulose started at 250 °C. The DTG curve became centralized around 340°C and its shape became sharper after NaOH treatment, which implied a more uniformed concentration, an increase of crystalized cellulosic percentage and a correspondingly lower lignin concentration. For the NaOH/H$_2$O$_2$ treatment, the single peak around 340°C became sharper than that of the NaOH treatment, which implied the

components like hemicellulose were almost gone. In the TGA analysis of raw rice husks, the hemicellulose decomposition temperature around 340°C could also be the potential decomposition temperature for the evaporation of volatile substances or the aliphatic chain and carbon bond of the lignin aromatic ring. After NaOH and NaOH/H_2O_2 treatment, the wax, natural fats, hemicellulose as well as lignin from raw rice husks were removed with the heating process. Comparing the cellulose and lignin degradation in the arrange from 350°C and 380°C with the raw rice husk, the largest weight loss after NaOH and NaOH/H_2O_2 treatment shifted to a lower range from 230 to 350°C, according to the decomposition of cementing components, such as lignin, hemicellulose and wax [37]. Such a phenomenon could also be found when comparing the H_2O_2 treated samples with raw rice husks.

IV.   CONCLUSION

The rice husks treated by NaOH/H_2O_2 were a superior on eliminating hemicellulose and lignin, with a correspondingly higher α-cellulose concentration. However, with higher α-cellulose, the total solid recovery percentage showed a reverse trend. The highest recovery rate was achieved by H_2O_2 methods, followed by NaOH and NaOH/H_2O_2 treatments. According to the FTIR and TGA results, H_2O_2 treatment was considered to be less effective. Hence, from the aspect of both increasing the cellulosic concentration and total solid recovery rate, the NaOH treatment assisted by a lower percentage of H_2O_2 in a mild temperature were suggested.

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