Analysis on the performance of hot water extraction and alkaline extraction for sodium hydroxide-assisted steam exploded empty fruit bunch at pilot scale

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Abstract. Empty fruit bunches (EFB) contribute the most to the biomass waste produced from palm oil industries. Biomass waste is made up of cellulose, hemicellulose, and lignin. By having high cellulose content, it has great potential for cellulose production. However, the cellulose extraction process has yet to be optimized. Therefore, the study on the operating conditions in extracting cellulose from EFB takes place by understanding the sodium hydroxide (NaOH) soaking process prior to steam explosion pre-treatment. The effects of retention time on the hot water extraction (HWE) treatment and NaOH concentration on the alkaline extraction (AE) treatment in term of the amount of dissolved sugar were observed. The chemical properties of original fibre and treated fibre were analysed by Fourier Transform Infrared (FTIR) Spectroscopy and the surface morphology were observed using scanning electron microscopy (SEM). In this study, it is found that the best condition for alkaline extraction was at 10% alkaline concentration and the FTIR spectroscopy shows that there a no changes on the chemical structure of the fibre. SEM also shows the changes on the surface morphology of the fibre. Showing that the sodium hydroxide assisted steam explosion pre-treatment does greatly influence the further process.

1. Introduction
The EFB constitutes about 20% to 22% of the weight of fresh fruit bunches and contains 30.5% dry matter, 2.5% oil and 67% water. Due to the abundance of EFB waste produced from the oil palm mill [1–3], the approach towards making an added value product from EFB by chemical modification is very promising. Typically, EFB comprises of cellulose about 24–65%, hemicellulose about 21–34% and finally lignin about 14–31% [4]. With the high amount of cellulose content, there is a possibility of using cellulose from EFB as fibre-reinforced composite in automotive industries. In the recent decades, many researchers from all around the globe have focused their study in the application using cellulose as replacement to the traditional reinforcing fibres in fibre-reinforced composite [5–10]. The increasing numbers of studies in this field were mainly due to the characteristic of the natural fibres in having low density, high strength, low cost and biodegradable. However, in order to make the natural fibres compatible with the polymer matrix, chemical treatments are needed in modifying the fibre surface [11].

Cellulose is a simple linear macromolecule polymer and it is embedded in a matrix of lignin and hemicelluloses [12]. Together, they form tightly packed cellular structures that form fibre bundles, and are the base for most biomass tissues. With their natural packed structure, it has the ability to bear high mechanical loads, and to resist chemical and enzymatic degradation through microorganisms. This
common feature of plant fibres is often termed as biomass recalcitrance, and is a major technical obstacle for most bio-refinery processes. Thus, the implementation of steam explosion and alkaline extraction treatment technology are essential in overcoming the recalcitrance of biomass structure. [11–14].

Steam explosion pre-treatment is a physic-chemical process. A highly pressurized saturated steam is used to heat up the biomass fibres where the process ends with an instantaneous release of pressure that causes the biomass fibres to rupture. The high temperature during this process catalyses the release of acetic acid from the cleavage of acetyl group and triggers the auto hydrolysis effect. This eventually results in the hydrolysis of hemicellulose and depolymerisation of lignin [15]. These make the biomass fibres more accessible for subsequent treatment. Steam explosion assisted with acid catalyst prior to the treatment has proven to increase the efficiency of the pre-treatment [16,17], but using acid will cause drawback such as corrosion to the equipment and extensive processing downstream effluents that will lead to high water consumption [18]. Thus alternative alkaline based catalyst has gather the attention of some researchers because of the proven capabilities to increase the removal of hemicellulose [17,19]. Alkaline extraction or mercerization is the most popular chemical treatment for the extraction of cellulose from biomass fibres. It alters the physical and chemical structure of the fibres; and removes the lignin and hemicellulose [20]. The dissolved hemicellulose is in sugar forms [21,22]. The major reaction that facilitates the formation of oligomers of sugars began with the depolymerisation and the dissolution of hemicellulose. The sugar will further be degraded to form monosaccharides and sugar-decomposition product [22,23].

In this study, the soaking of EFB fibres using sodium hydroxide (NaOH) was implemented prior to the steam explosion pre-treatment. The steam explosion pre-treatment was followed by the hot water and the alkaline extraction treatment for the removal of lignin and hemicellulose structure. The aim of this study was to analyse the effectiveness of sodium hydroxide-assisted steam explosion on the post treatment that were hot water and alkaline extraction. Throughout the process, the dissolved sugar content of the solutions were analysed and the changes in chemical structure fibres were observed by using FTIR analysis.

2. Experimental

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2.1. Material

The raw EFB (60% moisture content) was supplied by the LCSB Oil Palm Mill, owned by LKPP Corporation Sdn. Bhd that is located in Pahang, Malaysia. The chemical reagent used was Sigma Aldrich's 99% sodium hydroxide (NaOH) pallets that was provided by a local vendor.

2.2. Methods

2.2.1. Sample preparation. The EFB was dried under atmospheric condition for 7 days. Then, the dried EFB were manually chopped into smaller pieces and ground using SIMA grinder model FG 400×200 that comes with 200 mm mesh sieve.

2.2.2. Soaking of EFB. Ground EFB fibres were soaked with 3% (w/v) NaOH solution for 16 hours. Soaked EFB fibres were then dried at atmospheric condition until the moisture content reached approximately below 30%.

2.2.3. Steam explosion pre-treatment (SEP). SEP was carried out in a 700 L carbon steel reactor located at Cellulose Pilot Plant, Pahang, Malaysia. The sodium hydroxide-soaked EFB (SHIEFB) fibres were fed into the reactor, followed by the supply of saturated steam until the pressure reached 20 bar. After 20 bar was reached, the 10 minutes countdown started and when the countdown finished, the blowdown valve was opened to create the steam explosion reaction. The exploded EFB fibres were collected, washed using deionized (DI) water until the pH reached 7±0.5 (neutral) and dried overnight in an oven at 105°C.
2.2.4. Hot water extraction treatment (HWE). The exploded SHIEFB fibres undergo the hot water extraction treatment using 5% fibres consistency at 80°C and stirred for various retention times (15 min, 30 min, 45 min, 60 min and 90 min). Then, the treated fibres were washed using DI water and dried at 80°C overnight.

2.2.5. Alkaline extraction treatment (AE). Hot water treated fibres were then treated using different concentrations (5%, 10% and 20%) of NaOH solution using 0.05% fibres consistency at 80°C and stirred for 1 hour. The treated fibres were then washed using DI water until neutral (pH 7±0.5) pH was reached and dried in oven at 105°C overnight.

2.3. Characterization

2.3.1. Sugar content analysis. The sugar content of the produced solution was measured using a refractometer. Tiny drop of solution was dropped onto the flat and slant surface of the refractometer. The cap of the refractometer was then closed and the reading was taken by looking through the eyepiece of the refractometer.

2.3.2. Fourier Transform Infrared (FTIR) analysis. FTIR spectroscopy analysis was carried out using Thermo Scientific Nicolet iS5 FTIR equipment with resolution of 4 cm⁻¹, 32 scan per minute and transmittance technique. The range of wavenumber was set from 400 cm⁻¹ to 4000 cm⁻¹. The analyses were for all the treated fibres.

2.3.3. Scanning electron microscopy (SEM) analysis. The microstructure and surface morphology of the produced pulp was analysed using SEM analysis. The equipment used was a FEI Quanta 450 under the acceleration voltage between 1 to 15kV. The analysis was done by putting the sample on an aluminium stud then were observed using the SEM with difference magnification.
3. Results and discussion

3.1. Sugar content analysis

Based on figure 2, the dissolved sugar contents were increasing with the increase of HWE time. The trend of the graph started with a rapid increase of dissolved sugar content from 0 minute to 15 minutes, with the dissolved sugar measured to be 1% at 15 minutes. At 30 minutes, the dissolved sugar content gradually increased to 1.2% and 1.3% at 45 minutes. After that, a rapid increase of 0.5% occurred at 60 minutes, (1.8%). The highest dissolved sugar content was recorded to be 2.2%, at 90 minutes. The increasing numbers of dissolved sugar content were mainly caused by the organic acetic acid release during the HWE, which cause the removal of hemicellulose. This release of organic acid happened when the fibres were exposed to high temperature [24,25]. Hemicellulose in which included the polysaccharides contain many different sugar monomers [26]. Chang, (2014) also agreed that as the HWE time was increased, higher amount of released hemicellulose was observed [4].

Figure 3 displays the sugar content against varied NaOH concentrations. At 5% concentration, the sugar content recorded was 1.6%. Then, the dissolved sugar increased sharply to 2.2% when 10% NaOH concentration was used. At the highest concentration of NaOH (20%), the sugar content still increased but subtly at 2.3%. The subtle increase from 2.2% to 2.3% for 10% and 20% NaOH concentration respectively was because most hemicellulose been removed using 10% NaOH concentration, leaving only a small portion of hemicellulose structure within the fibres. The number of dissolved sugar increased due to the hydrolysed sugar, which was released into the alkaline hydrolysate during the AE [27]. Although AE was specified to remove lignin, it may affect the molecular structure of hemicellulose and cause the hydrolysis of hemicellulose [28]. Therefore, the increase of NaOH concentration influences the hemicellulose to be released.
3.2. Sugar content analysis

The absorption bands located near 1740 cm\(^{-1}\) are assigned to C=O stretching of acetyl or carboxylic acid in which referring to hemicellulose and lignin. On the other hand, the wavenumbers at 1610 cm\(^{-1}\), 1598 cm\(^{-1}\), 1510 cm\(^{-1}\), and 1465 cm\(^{-1}\) are referring to lignin in which all of it are assigned to C=C stretching of aromatic ring, C-C, C-C stretching of aromatic ring, and asymmetric bending in C-H\(_3\), respectively [28,29]. As seen in figure 4, the spectra satisfy the trends from spectra analysis of Nieves et al, (2011) in which the transmittance increases gradually in accordance to the parameters. Based on figure 5, the untreated SHIEFB has the highest absorbance which are 0.016,
0.031, 0.034, 0.026, and 0.032 for wavelength 1740 cm\(^{-1}\), 1610 cm\(^{-1}\), 1598 cm\(^{-1}\), 1510 cm\(^{-1}\), and 1465 cm\(^{-1}\) respectively. At 15 minutes, the absorbance started to decrease and after that, it gradually decreased with the lengthened time. At 90 minutes, the lowest absorbance was recorded for all five wavelengths. The wavelength 1740 cm\(^{-1}\) indicates hemicellulose. Therefore, as the time increased, hemicellulose content significantly decreased [28].

According to figure 6, the spectra satisfy the trends from spectra analysis of Nieves et al, (2011) in which the transmittance increases gradually in accordance to the parameters [28]. Based on figure 7, the untreated SHIEFB has the highest absorbances which are: 0.014, 0.024, 0.026, 0.023, and 0.029 for wavelength 1740 cm\(^{-1}\), 1610 cm\(^{-1}\), 1598 cm\(^{-1}\), 1510 cm\(^{-1}\), and 1465 cm\(^{-1}\) respectively. At 5\% NaOH concentration, the absorbance started to decrease and after that, it gradually decreased with the increasing concentration. At 10\% and 20\% NaOH concentration, the absorbance recorded did not follow the supposed pattern in which 20\% NaOH concentration should have lower absorbance for all five wavelengths. This shows that increasing the NaOH concentration above 10\% is not significant enough to get lower absorbance due to most hemicellulose and lignin structure are absent within the fibre. The wavelengths 1610 cm\(^{-1}\), 1598 cm\(^{-1}\), 1510 cm\(^{-1}\), and 1465 cm\(^{-1}\) indicates lignin content [28,30,31]. Therefore, as the NaOH concentration increased, lignin content reduced until 10\% NaOH concentration.

Based on Nieves et al, (2011), the absorbance for the un-soaked EFB at wavelength 1740 cm\(^{-1}\) is 0.121. By comparing the absorbance of all parameters in hot water treatment, none of the absorbance exceeded 0.121 in which the highest absorbance was at 15 minutes of treatment with 0.015 of absorbance. This demonstrates that most of the hemicellulose has been removed during the steam explosion process. Since all other wavelength besides 1740 cm\(^{-1}\) are assigned to lignin, one of them is taken account to be compared with data from previous study [30–32]. According to Nieves et al., (2011), the absorbance at wavelength 1610 cm\(^{-1}\) was 0.198. By comparing it to the data in figure 7, the absorbance for 5\%, 10\%, and 20\% are 0.023, 0.012, and 0.011 respectively. This indicates that the removal of lignin in figure 7 is more effective than the previous study. The concentration of sodium hydroxide used in the previous study was 8\% without performing SEP. The effectiveness of the lignin removal in this study s due to the soaking of EFB with sodium hydroxide in which most of the lignin is removed after SEP.

![Figure 4. Infrared spectra for HWE treatment](image-url)
Figure 5. Absorbance against time

Figure 6. Infrared spectra for AE treatment
3.3. Sugar content analysis

The SEM provided a clear image of the pulp produced as shown in Figure 8. The morphology of the produced pulp shows that the fibre has been defibrillated where the original fibre has separated into smaller fibrils. From Figure 8.A, it portrays that cleavages were formed between the fibrils. It can also be observed from Figure 8.B that silica bodies have been removed throughout the pulp production where it is proven by the crater that used to embody the silica bodies [33]. The fibre also shows smooth fibrils structure due to the impurities such as oil that covered the surface which has been removed [33–35]. The formation of cleavage and removal of embedded silica bodies from the fibres were due to the severe treatments throughout the process of pulp production. Thus, increasing the porosity and the surface area of the fibre [33]. The formation of cleavage between the fibres is an advantage because many studies have proven that cleavage can increase the surface roughness of the fibre that leads to a better mechanical interlocking that consequently improves the adhesion ability of the fibre [34,36].

Figure 8. Surface morphology of pulp
4. Conclusion
Soaking of empty fruit bunch with 3% of sodium hydroxide has been proved to increase the effectiveness of hemicellulose and lignin removal in EFB fibres. The HWE treatment time illustrated the highest amount of hemicellulose removed at 90 minutes achieving the highest sugar content of 2.2%. The NaOH concentration in AE treatment shown at 10% concentration was the most preferable condition for the removal of hemicellulose achieving 2.2% dissolved sugar content compared to 2.3% at 20% NaOH concentration. This will greatly reduce the chemical consumption and cost of alkaline reagent for the AE treatment. This result has proven that the steam exploded SHIEFB effectively assisted in the removal of lignin and hemicellulose HWE and AE treatment and it is possible to implement the sodium hydroxide-assisted steam explosion pre-treatment in the production of cellulose from EFB biomass.

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