Reusing Alkaline Solution in Lignocellulose Pretreatment to Save Consumable Chemicals without Losing Efficiency

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High production costs are biggest obstacles for the commercialization of the lignocellulosic bioethanol. For an attempt to reduce the chemical consumption of the alkaline pretreatment process, the waste solution with high basicity was investigated to be re-used. In respect to the pretreatment efficiency, a minimum addition of NaOH was calculated and the calculation philosophy was presented. The efficiency is defined as the change in the ratio of lignin/cellulose, which leads to cellulose-enriched material after pretreatment. Rubber wood saw dust was employed as the lignocellulose biomass feedstock. HPLC was used to analyze the chemical contents of the starting and pretreated material samples instead of the poor evaluation of the pretreatment efficiency based on only mass loss as that done in the previous study. The experimental results showed that with an alkaline solution of NaOH 2.0 wt% treating the woody material for 24 hours, the cellulose content increased from 41.2 % to 53.52 %, while reusing the wasted alkaline solution with a minimum addition of NaOH gives an almost-equal increase of 41.2% to 52.83 %. This method was shown to cut 30.3 % NaOH and 41.2 % fresh water consumption, implying an impressive saving of chemicals and fresh water while lignin removal efficiency of the process was well reserved.

1. Introduction

In the recent decades, the fossil fuel crisis and its resulted global warming urge the development of renewable energy and biofuels. In both literature and practice, any natural carbohydrate, such as starch, sugars, glycogen, cellulose, etc., can be a feedstock to be bio-converted to ethanol (Palonen, 2004). Among the materials, lignocellulosic biomass is the most abundant, cheapest, and thus an attractive choice for bioethanol production. In general, to convert lignocellulose to bioethanol, three major processes are vital: physical and chemical pre-treatment to liberate cellulose and hemicellulose; enzymatic hydrolysis of cellulose and hemicellulose to produce fermentable sugars (Bes et al., 1989); and fermentation of sugars to bioethanol by microorganisms (Talebnia and Taherzadeh, 2006).

Since lignocellulose has a very strong structure composed of hemicellulose surrounding cellulose fibrils, overall coated and glued with lignin, pretreatment is a vital step in the technology of converting biomass to bioethanol. A lignocellulosic biomass pretreatment method is defined as a process that takes in raw lignocellulosic biomass, and produces treated biomass suitable for hydrolysis and fermentation into bioethanol (Rahman and Amin, 2019). Pretreatment is to destruct the lignocellulose matrix, remove lignin and enhance the penetration of hydrolysis agents (Tran et al., 2019).

Among conventional pretreatment methods for lignocellulosic biomass, alkaline pretreatment is most preferred due to its simplicity and high efficiency (Saravanakumar and Kathiresan, 2014). Alkaline pretreatment can be carried out under mild conditions with less corrosiveness than that of acidic methods (Kim et al., 2016). Strong bases, such as sodium hydroxide can solubilize lignin by saponification and a part of hemicellulose by crosslinking cleaving reactions (Sjostrom, 1993).

Unfortunately, lignocellulosic bioethanol is currently still far from commercialization due to its high cost (Wang et al., 2012). The high costs of chemicals, enzymes (Koullas et al., 1992), and energy consumed (Ramos et al., 1993) make the production of lignocellulose-based bioethanol face many obstacles to be profitable (Sarkar

et al., 2012). Therefore, reducing the production cost of lignocellulosic bioethanol would be among the practical approaches for consideration.

In an attempt to cut the pretreatment cost of lignocellulose in term of NaOH and fresh water consumption, it was proposed that the waste alkaline solution after a pretreatment batch be re-used for the following batches with a minimum sufficient addition of consumables in respect to the pretreatment efficiency (Nguyen et al., 2018). The idea was illustrated in Figure 1.

Call C1 the initial concentration of the alkaline solution used in the first pretreatment batch of lignocellulose, which yields a pretreatment efficiency as ATE1. Pretreated solid biomass is then filtered and the remaining solution is collected from the mixture. Without any addition of NaOH and water, the remaining alkaline solution is as-is reused for the following batch to yield a certainly lower pretreatment efficiency of ATE2, which is equal to the pretreatment efficiency by a first-use solution with NaOH concentration of C2. It is expected that if an amount of NaOH and water added to solution C2 can make up solution C1, the same amount of NaOH and water added to the as-is-reuse solution C1 can restore its treatment efficiency of ATE1.
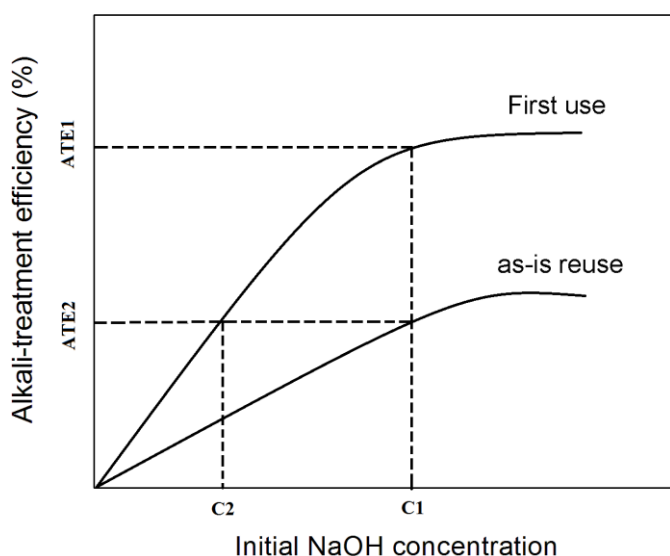

Figure 1: Illustration of the idea of reusing waste alkaline solution with addition of NaOH and water to restore the pretreatment efficiency toward lignocellulosic biomass.

In the previous study, reusing waste alkaline solution after alkali pretreatment of lignocellulosic biomass (steam-exploded rice straw) with minimum addition of NaOH was reported as a technique to significantly reduce the consumption of chemicals and water (Nguyen et al., 2018). However, the alkaline pretreatment efficiency in the previous study was evaluated by basing on the mass loss of the biomass, which was supposed only due to lignin removal when the lignin is dissolved in the solution. This must lead to large errors in calculation because the use of an alkali also cracks ester and glycosidic side chains, creating structural alteration of lignin, cellulose swelling, partial decrystallisation of cellulose, and partial solvation of hemicellulose (Cheng et al., 2010).

In this context, the experiments were carried out in an innovated approach, where pretreatment efficiency is defined as the cellulose enrichment degree. The green economy strategy is also demonstrated by using rubber wood saw dust as the lignocellulosic biomass. This feedstock is an abundant sub-product of rubber forestry in Vietnam, popularly just used as a cheap fuel for biomass boilers.

2. Materials and methods

2.1 Materials

Commercialized rubber wood saw dust with an average moisture content of 15 wt% was purchased from a saw mill in Nam Tan Uyen, Binh Duong province, Vietnam. The saw dust is mixed homogeneous, screened to be obtained with an average particle size of less than 0.1 mm, then dried at 80 °C in an oven for 24 hours prior being stored in a desiccator to avoid risk of fungi contamination. Before any experiment, the moisture content of the material is measured with a Sartorius infrared moisture analyser to determine the dry mass of the solid. The water content is counted into the water content of the mixture afterward.

Concentrated H_2SO_4 98 wt%; flaked NaOH 99,99 wt%, aqueous HCl 37 wt% are purchased from TCL company (Taiwan).

2.2 Alkaline pretreatment of lignocellulose material

As a typical procedure of alkaline pretreatment of lignocellulose, in a 250-ml round flask, 5 g rubber wood saw dust is mixed and soaked in alkaline solution. The flask is then shaken by a shaker at 150 rpm speed to enhance the mass transfer process in the heterogeneous mixture. Pretreatment experiments were carried out with NaOH solutions of different concentration, for different time, and with different solid/liquid ratios.

After pretreatment, the solid residue is filtered out while the remaining solution can be collected for further experiments. The residue is mixed with 50 mL distilled water then neutralized to pH 7 with diluted H_2SO_4 acid. After that, the pretreated material is filtered, washed again to remove remaining salts before being dried at 80 °C in an oven for 24 h for chemical analysis.

2.3 Chemical analysis

The lignocellulose samples were hydrolysed in a two-step acidic hydrolysis so that cellulose and hemicellulose can be fractionated into glucose and xylose, which can be quantified with HPLC (Shimadzu HPLC analyzer, 2014), employing a column coded SH101, and H_2SO_4 0.005 N solution as the mobile phase. Cellulose and lignin contents of samples were analysed according to the NREL Laboratory Analytical Procedure (George et al., 2012). A UV-Vis analyser model NiR V770 (Jasco, Japan) was used in the procedure.

2.4 Pretreatment efficiency

The pretreatment efficiency in this study is defined as the enrichment degree of cellulose over lignin content, regardless other components. The pretreatment is considered mainly as the process to remove ligin and expose cellulose out from the lignocellulose matrix. For the truth that lignocellulose is cheap, the cellulose loss through the pretreatment can be ignored as long as it is less than 10 wt% of the total cellulose fraction of the starting material. Herein, the pretreatment efficiency is defined as at Eq(1):

$$H(\%) = 100(\%) \times \left(1 - \frac{Y_2}{Y_1}\right) \tag{1}$$

where Y_1 and Y_2 are the mass ratio of lignin/cellulose of the starting and the pretreated material, which are analysed by HPLC.

2.5 Calculation of the sufficient minimum addition of NaOH and water to restore the pretreatment efficiency of the re-used alkaline solution

As mentioned above, the amounts of supplemental NaOH and water added to the re-used solution (to restore the pretreatment efficiency of the re-used alkaline solution) are calculated supposing that the re-used solution is equal to solution C2 in term of NaOH and water content.

If there is totally A (g) of the initial solution C1 used in the first batch, the re-used solution C1 without adding NaOH and water is equal to solution C2 with total amount of B (g) (B < A due to solution loss during the process).

For the initial solution, the initial amount of NaOH is calculated as Eq(2):

$$m_{initial-NaOH}(g) = A(g) \times C1(\%) \tag{2}$$

and the initial amount of water is calculated as Eq(3)

$$m_{initial-water}(g) = A(g) \times (100 - C1)(\%) \tag{3}$$

For the post-pretreatment solution, the amount of NaOH is supposed to be as equal to that at Eq(4):

$$m_{eq-NaOH}(g) = B(g) \times C2(\%) \tag{4}$$

and the amount of water is considered equal to be calculated as at Eq(5):

$$m_{eq-water}(g) = B(g) \times (100 - C2)(\%) \tag{5}$$

Hence, the amounts of NaOH and water adding to the post-pretreatment solution to make-up a new solution with pretreatment ability equal to that of the initial solution C1 are calculated as Eq(6) and Eq(7):

$$m_{added-NaOH}(g) = m_{initial-NaOH}(g) - m_{eq-NaOH}(g) \tag{6}$$

$$m_{added-water}(g) = m_{initial-water}(g) - m_{eq-water}(g) \tag{7}$$

The re-used solution with supplemental NaOH and water is used to pretreat the same amount of saw dust as that in the previous batch. The comparison is done through calculation in the next section.

3. Results and discussion

3.1 Starting material analysis

The chemical analysis for the starting material showed that the rubber saw dust was composed with 25 wt% as lignin and 41.2 wt% as cellulose, implying if all the cellulose content can be completely converted to bioethanol, 0.22 kg bioethanol can be obtained from 1 kg rubber saw dust.

Ideally considering, because the purchasing price of dry rubber saw dust obtained as the starting material from Binh Duong province (Vietnam) is 800 VND/kg, while the absolute ethanol price in the market is 6,000 VND/kg (ex-work, produced from cassava), the potential value of cellulose-based bioethanol could be produced from 1 kg saw dust is 1,320 VND. Obviously, there is still a long way to cut the production cost and bring the situation closer to feasible commercialization. Hemicellulose is also another ingredient of the material, which can be converted to bioethanol.

Anyway, in this context, it is focusing to the technique of recycling alkaline solution in pretreating the lignocellulosic biomass to contribute to the cost reduction. It is noteworthy to think of the alkaline solution containing more lignin after several cycles of pretreating lignocellulose, since lignin is also another valuable product. The high concentration of lignin in the alkaline solution can facilitate the lignin collection process afterward (Mosier, 2005).

3.2 Pretreatment time

As shown in Figure 2, the pretreatment efficiency is dependent on the pretreatment time. The longer time of pretreatment by soaking the material in NaOH solution, the higher pretreatment efficiency could be reached. The higher concentration of NaOH solution also gives the higher pretreatment efficiency. However, after 24 (h), all the inspected cases showed saturation, when the pretreatment efficiency remained near constants. This fact could be ascribed to the maximum penetration of the alkaline solution into the lignocellulose matrix, in which the mass transfer process could not promote more the reaction between lignin, hemicellulose and NaOH as discussed elsewhere (14). In addition, it can be also understood that there will always be remaining NaOH after the reaction, beside the formation of basic sodium compounds, such as R-O-Na and R-COONa. Utilization or reusing the alkaline solution after the pretreatment, therefore, are obviously positive as presented at the beginning of the study. In the following experiments, a pretreatment time of 24 (h) is chosen as the model time to inspect other factors of the alkaline pretreatment.
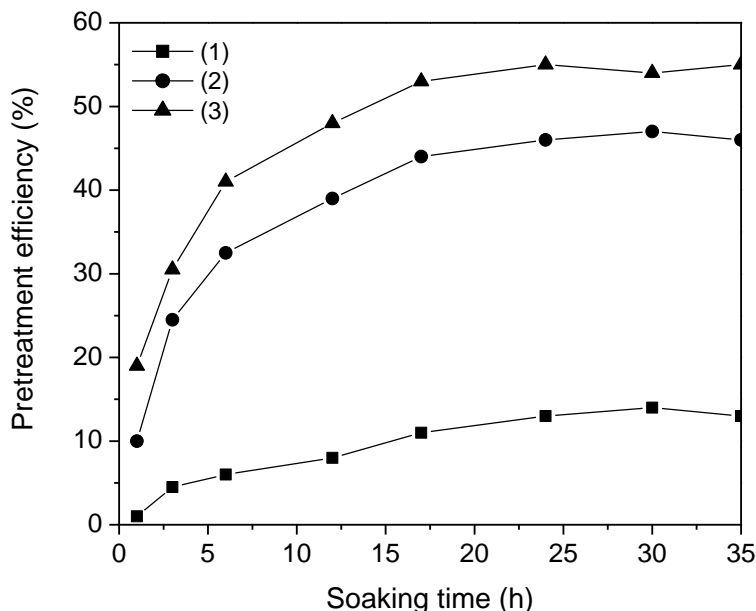

Figure 2: The dependence of pretreatment efficiency (%) on the pretreatment time (soaking time) of the material in NaOH solution of (1) 0.2 wt%, (2) 2.0 wt%, and (3) 4.0 wt%; solid/solution wt./wt. ratio of 1/10.

3.3 The effects of alkaline concentration and the reuse

There is no doubt that the increase in the alkaline solution concentration leads to the increase in pretreatment efficiency due to the increase in reaction rate. As confirmed by the results shown in Figure 3, the higher

alkaline concentration of the solution used to pretreat lignocellulose material, the higher pretreatment efficiency was reached.
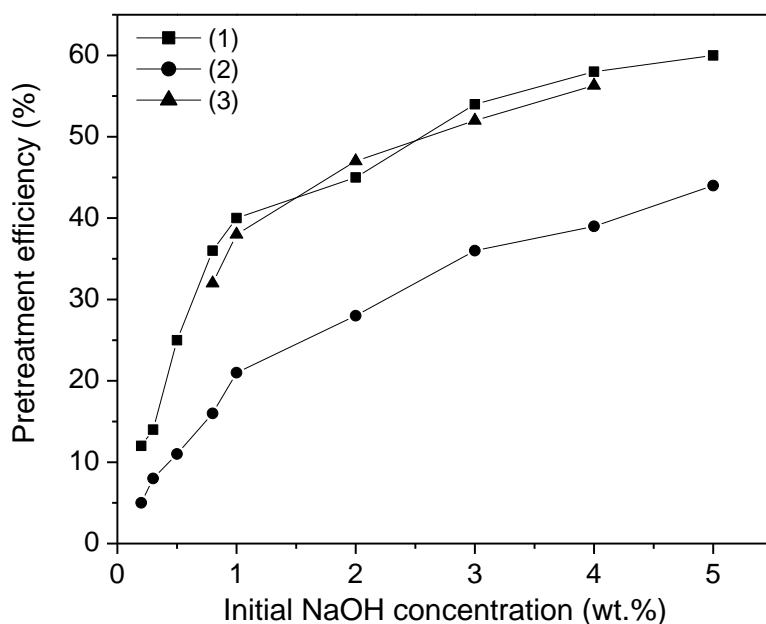

Figure 3: The pretreatment efficiency (%) for 24 hours with solid/solution wt./wt. ratio of 1/10 when using (1) fresh NaOH solution, (2) the as-is reused NaOH solution without adding neither extra NaOH nor H_2O, and (3) the reused NaOH solution with the addition of calculated amount of NaOH and H_2O to restore the original solution as described in the purpose of the study.

However, such increasing rate was sharp when the NaOH concentration was lower than 1.0 wt% and slowing down afterward. The alkaline pretreatment could destruct the cell wall of the lignocellulose structure by dissolving lignin and cleaving crosslinking between lignin with hemicellulose, as well as by swelling and decreasing the crystallinity degree of cellulose. Hereby, the cellulose fibrils are exposed. However, although the outer parts of the material particles were reacted in the pretreatment, below the outer cellulose layers are still the remaining lignocellulose structure, implying pretreatment efficiency could not be 100% and it is not a linear relationship between the reactant concentration and the pretreatment efficiency.

After the first use, the alkaline solution was collected and re-used to pretreat the next batch of saw dust. The results shown in Figure 3 showed the certainty of lower pretreatment efficiency of the reused solution (2) in comparison with the fresh alkaline solution (2). But interestingly, when adding NaOH and H_2O as supposing above, the pretreatment efficiency of the reused solution (3) could be almost as restored as the identical to that of the fresh solution.

Take NaOH solution of 2.0 wt% concentration as the model solution to pretreat rubber saw dust in this comparative study, a calculation based on experimental data showed that to treat 2 batches of saw dust, only 69.7 % NaOH and 58.8 % fresh water were used while pretreatment efficiency was remained almost unchanged of 46-47 %. In a similar study, Kim et al (2016) also reported a saving in NaOH consumption of 26.84 % compared with that of 30.3 % in this study.

4. Conclusion

The reuse of 2.0 wt% NaOH solution in lignocellulose pretreatment (at ambient temperature for 24 hours) with minimum addition of NaOH and fresh water as described in this context could reduce the NaOH and fresh water consumption down to 69.7 % and 58.8 %, while the pretreatment efficiency was unchanged of 46-47 %. This technique helps the pretreatment of lignocellulose in a more efficient and feasible way with lower chemical costs. In addition, the new definition of pretreatment efficiency in this context is useful to extend the study to different pretreatment strategies by a practical and more scientific evaluation method than that in the previous work.

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