

Second Stage Fractionation from Bagasse for Lignin Removal

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Abstract: Two-stage fractionation is a promising method to improve the efficiency of hemicellulose and lignin removal, leading to high purity of cellulose fraction. In this study, hemicellulose content was firstly removed by hydrothermal process using formic acid under optimal conditions. The subsequent step was aimed to separate lignin fraction from cellulose content via organosolv pretreatment using different organic solvents (methyl isobutyl ketone; MIBK and dimethyl sulfoxide; DMSO) with varying reaction parameters. The optimal two-stage fractionation contained in hydrothermal process with MIBK and water in ratio 80: 20 and 5% v/v formic acid at 180°C for 80 min, resulting in the highest lignin yield and cellulose recovery with 65.36% and 64.69% respectively. After bleaching process with 1% sodium chlorite (NaClO₂), it led to decrease in lignin content from 33.54 to 5.94% w/w reflected to increasing cellulose fraction from 46.60 to 91.73% w/w compared to the pretreated sample. Fourier-transform infrared spectroscopy (FTIR) revealed efficient removal of non-cellulosic components, resulting in exposed cellulose microfibrils with a reduced crystalline size as determined by X-ray diffraction (XRD). With potential on obtaining high purified cellulose, the work demonstrated potential of two-stage pretreatment from sugarcane bagasse using hydrothermal and organosolv process in presence of formic acid catalyst for further converting to value added cellulose products in biorefineries.

Keywords: Bagasse, fractionation, bleaching, hydrothermal.

1. Introduction

According to an agricultural based country in Thailand, the government has support utilization of crop residues and processing residue in order to mitigate global warming impact and drive to bio-based economy. Many researchers have been developing the effective utilization of low-cost agricultural and biomass to energy, fuel value added chemical and other materials. Biomass is an organic material as abundant carbon source that can be commonly converted to bioenergy (biodiesel, bioethanol and bio oil) as well as chemical product such as ammonia, methanol, acetic acid and succinic acid [1]. Biomass includes agricultural residues (rice husk, rice straw), industrial processing residues (bagasse, palm waste, and dried distillers grain), forestry and wood, municipal solid waste and animal wastes [1]. Sugarcane bagasse is one of promising economic crop in Thailand derived from sugar production processing for sugar industry. In 2017, Thailand is main sugar producer in the world which can produce 94.7 million-ton of sugar, leading to sugar production efficiency with 107.90 kg/ton of sugarcane [2].

The structure of lignocellulosic biomass mainly consists of three components as cellulose, hemicellulose, and lignin. Especially, cellulose fraction has been attractively interested for research study in order to apply using many applications such as fuels (bioethanol, biobutanol, and biohydrogen), composite materials (microcrystalline cellulose, nanocellulose, activated carbon), and cellulose derivatives (methylcellulose, carboxymethylcellulose; CMC, cellulose acetate) [3-4]. Cellulose is polysaccharide of D-glucose link with β -1,4 glycosidic bonds consisting of glucose more than 10,000 units, commonly cellulose has molecular formula (C₆H₁₀O₅)_n, that consist amount number of polar oxygen and hydrogen atoms, which are link with intermolecular and intramolecular of hydrogen bond [5]. Cellulose is rigid, more crystalline, not meltable, insoluble in common solvents, such as organic solvents, water and alkaline solutions and resistance to oxidizing agent but not resistance in acid [6]. While, hemicelluloses is a polysaccharide consist several sugars include hexose (glucose, galactose, mannose) and pentose (xylose and arabinose) that they normally convert to ethanol, xylitol, furfural, and so on. Among the biomass composition, lignin

is organic polymer of phenylpropane more than 10,000 units and it is major component in cell wall which encapsulated cellulose fiber and hemicellulose fiber together. The structure of lignin is very resistant to degradation that it used to produce for valuable chemicals and polymers. According to biomass separation, fractionation process is a promising method to fractionate the biomass components contained cellulose, hemicellulose and lignin by combination of pretreatment process such as hydrothermal process, organosolv process, dilute acid pretreatment and others [7]. It leads to conversion of each fraction to value added fuel and chemicals.

The purpose of this research is to isolate hemicellulose and lignin content from cellulose fraction in sugarcane bagasse based on using the pretreatment methods of hydrothermal and organosolv process, respectively. Firstly, hemicellulose fraction was removed by hydrothermal process with dilute acid under optimized condition. Secondly, lignin content was removed by organic solvent with dimethyl sulfoxide (DMSO) and methyl isobutyl ketone (MIBK) by varying the reaction parameters such as organic solvents type (DMSO and MIBK), organic solvent and water ratio, reaction temperature, and reaction time. Next, the solid pulps after pretreatment by hydrothermal and organosolv process were bleached with sodium chlorite (NaClO₂) under optimized condition. Later, cellulose enriched pulp after processing was characterized for their physicochemical characteristics using Fourier-transform infrared spectroscopy (FTIR) and X-ray powder diffraction (XRD). This work provides a platform for further study on value-added utilization of cellulose in integrated biorefineries.

2 Materials and methods

2.1 Raw materials

Sugarcane bagasse (SB) was obtained from Eastern Sugar and Industries Ltd, Srakaew, Thailand. It was physically processed using a cutting mill (Retsch ZM2000, Haan, Germany) and sieved to the size of <1 mm. The SB was subsequently extracted by acetone at 50°C until the solvent was clear of any color for removal of extractives e.g. starch, wax, syrup, organic acids, soluble protein, and other soluble components based on

TAPPI Standard T204 om-88 [8], followed by washing with hot water at 60°C for 1 h according Ajuong and Bresse (1998) [9]. This raw material was then dried at 60°C for overnight. Chemical composition of the raw materials was analyzed by NREL method based on dry weight basis [10]. The SB content contains 41.30 wt% cellulose, 24.77 wt% hemicelluloses, 24.10 wt% lignin, and 3.17 wt% ash. Analytical grade organic solvents and chemicals were purchased from major chemical suppliers i.e., Sigma-Aldrich, Merck, Labscan and Fluka.

2.2 Hydrothermal process in the first stage

The reaction contained 100 g of bagasse in 1,000 mL of water in presence of acid promoters as 5%v/v formic acid (HCOOH) 2 L of stainless steel reactor. Nitrogen gas was flowed into reactor for cleaned and adjusted the initial pressure at 20 bars. Reactor was heated by electric jacket with a thermocouple to measure temperature inside the reactor. It was done at 160°C for 40 min with stirred at 100 rpm for kept the system as homogeneous. After the reaction, the reaction will be immediately stopped in cooling on ice for 20 min. The solid fraction was separated by filter paper and washed with water and dried at 70°C in oven. The solid pulp after hydrothermal process was analyzed by National Renewable Energy Laboratory (NREL) method [10].

2.3 Organosolv process in the second stage

The reaction contained 10 g of pretreated sample from hydrothermal process in 100 mL of water and organic solvent (DMSO or MIBK) in different ratios with 5%v/v formic acid (HCOOH). This reaction was performed in a 600 mL of stainless steel reactor. Nitrogen gas was flowed into reactor for cleaned and adjusted the initial pressure at 20 bars. Reactor was heated by electric jacket with a thermocouple to measure temperature inside the reactor. It was done at 140-180°C for 20-80 min with stirred at 100 rpm for kept the system as homogeneous. After the reaction, the reaction will be immediately stopped in cooling on ice for 20 min. The solid fraction was separated by filter paper and washed with water and dried at 70°C in oven. The solid pulp after organosolv process was analyzed by National Renewable Energy Laboratory (NREL) method [10]. The lignin yield was calculated according to using Equation (1).

$$\text{lignin yield (\%)} = \frac{\text{Solid weight (g)}}{\text{Lignin in solid pulp before hydrothermal process (g)}} \times \text{Klason lignin (\%)} \quad (1)$$

2.4 Bleaching process

The bleaching process contained 5 g of pretreated samples from hydrothermal and organosolv process and 1% sodium chlorite (NaClO₂) into 250 mL breaker. The mixture was adjusted to pH = 5 using acetic acid before heated and stirred in water bath at 80°C for 1 h. After that, liquid phase was removed and added fresh 1% NaClO₂ into breaker. This step was repeatedly done by three times. Next, the mixture was cooled to room temperature and separated by filter paper and washed with water and dried at 70°C in oven. The solid pulp after bleaching process was analyzed by National Renewable Energy Laboratory (NREL) method [10].

2.5 Characterization

2.5.1 X-ray diffraction (XRD)

The crystallinity of samples was determined by X-ray diffraction (XRD) using an X'Pert PRO diffractometer (PANalytical, Almelo, The Netherlands). The samples were scanned at a speed of 0.5°/min in a range of 2θ=5-40° with a step size of 0.02° at 40 kV, 30 mA and radiation at Cu Kα (λ=1.5418 Å). The average size of crystallites was calculated from the Scherrer equation with the method based on the width of the diffraction patterns obtained from the highest intensity for the crystalline portion of biomass (I₀₀₂). The crystallinity index (CrI) and the crystallite

size (D_{hkl}) were calculated according to the following equation 2 and 3, respectively [11].

$$\text{CrI (\%)} = \left[\frac{I_{002} - I_{am}}{I_{002}} \right] \times 100 \quad (2)$$

where CrI is the crystallinity index of sample (%); I₀₀₂ is the highest intensity for the crystalline portion of biomass (i.e., cellulose) at 2θ = 22.03 and I_{am} is the peak for the amorphous portion (i.e., cellulose, hemicellulose, and lignin) at 2θ = 18.19.

$$D_{hkl} = \frac{K\lambda}{\beta \cos\theta} \quad (3)$$

where D_{hkl} is the average size of the crystallite (nm); K is the Scherrer constant (0.94); λ is X-ray wavelength (Cu, 0.15418 nm); β is the full-width at half-maximum of the crystalline portion (radian, π), and 2θ which is the corresponding Bragg angle.

2.5.2 Fourier-transform infrared spectroscopy (FTIR)

The native sugarcane bagasse and cellulose bleaching were analyzed by Fourier-transform infrared spectroscopy (FTIR) using a Spectrum one FTIR Spectrometer (Perkin Elmer). The samples were mixed to form thin film with KBr powder and characterized samples at the wavelength of 4000-400 cm⁻¹ with a resolution of 4 cm⁻¹.

3 Results and Discussion

3.1 Effect of organic solvents type

The effect of organic solvent types in organosolv process using DMSO and MIBK in presence and absence of acid promoter as a formic acid for removing lignin content was shown in Fig. 1. It was found that all organic solvents in presence of acid promoter gave the higher lignin yield compared to the condition without formic acid. It could be due to that addition of acid catalyst can increase the solubilization of lignin content into organic phase into the organic phases, resulting in enrichment of cellulose in the solid fraction. This result was consistency to the previous works [12]. Chutikan et al (2017) reported the organosolv fractionation of four lignocellulosic materials including bagasse, plum fiber, para rubber wood sawdust, and cassava fiber using a ternary solvent mixture (MIBK/ethanol/water). It was exposed that the use of acid promoter as H₂SO₄ led to increase in lignin removal efficiency from organosolv fractionation [12]. Comparison of solvent types in organosolv process, the use of DMSO gave the higher lignin yield (41.66%) than that of MIBK (16.13%). In term of cellulose component, it was found that the remaining cellulose content after two stage fractionations using MIBK was higher proportion (65.62%w/w) compared to using DMSO (59.19%w/w) in presence of formic acid. The higher lignin purity determined by Klason lignin method was also obtained from using MIBK compared to using DMSO, as shown in **Table 1**. Considering the maximal cellulose fraction, the organosolv fractionation using MIBK with formic acid is a good candidate for further study.

Table 1 Klason lignin and ash of solid phase after hydrothermal process incorporate with organic solvent (MIBK or DMSO) of solid pulp from first stage fractionation. The reaction contained 10% (w/v) solid pulp with/without formic acid as acid promoter 5%v/v and heated at 160°C for 40 min.

Solvent	Klason Lignin (%)	Ash (%w/w)
DMSO	78.36 ± 0.85	0.51 ± 0.28
MIBK	91.43 ± 0.07	0.25 ± 0.00
DMSO - FA	46.86 ± 0.59	16.31 ± 0.13
MIBK - FA	84.72 ± 1.02	0.23 ± 0.19

3.2 Effect of MIBK : water ratio

The effect of MIBK: water ratio as 100:0, 80:20, 50:50 and 20:80 for removing lignin content from lignocellulosic biomass was presented in Fig. 2. Increase in water ratio from 20% to 50% led to increasing of lignin yield in range of 42.80 to 55.93%. However, when increased in water ratio to 80% led to decreasing of lignin yield to 32.30%. It was found that the optimized condition achieved in 80:20 of MIBK and water ratio in presence of formic acid, resulting in cellulose composition with 67.88%w/w and lignin yield 55.93%. While, the little amount of water affected the solubilization of lignin because hydrothermal process assisting

to hydrolysis link between lignin and carbohydrates [13]. However, when increased excess amount of water and reduced amount of MIBK in the process. As a result, Solubilization of lignin in the process is reduced. Teng J. et al. (2016) reported the effect of MIBK dosage in organosolv lignin with MIBK/H₂O biphasic system. It showed that increase in MIBK dosage from 5 to 15 mL resulted in increasing the lignin product based on the pretreatment of bagasse at 5 mL of water at 180°C for 15 min in presence of 0.5 mmol [C₄H₈SO₃Hmim]-HSO₄ [14]. Thus, the optimized condition of MIBK: water ratio at 80:20 in presence of formic acid was subsequent to further study.

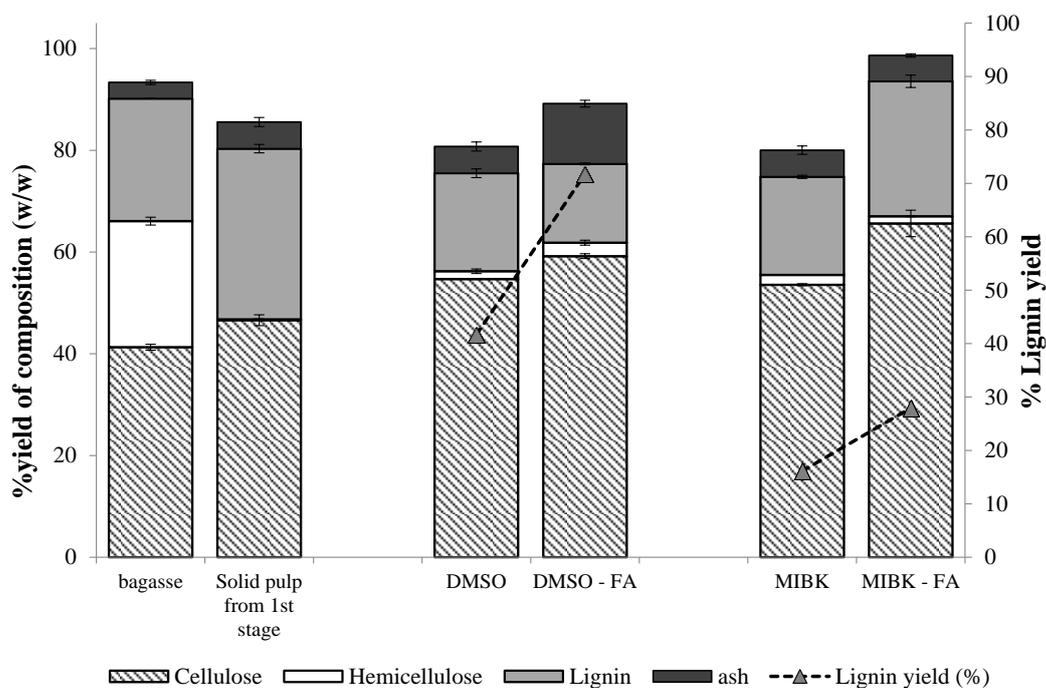


Figure 1 Chemical composition and lignin yield of cellulose pulp after hydrothermal process incorporate with organic solvent (MIBK or DMSO) of solid pulp from first stage fractionation. The reaction contained 10% (w/v) solid pulp with/without formic acid as acid promotor 5%v/v and heated at 160°C for 40 min.

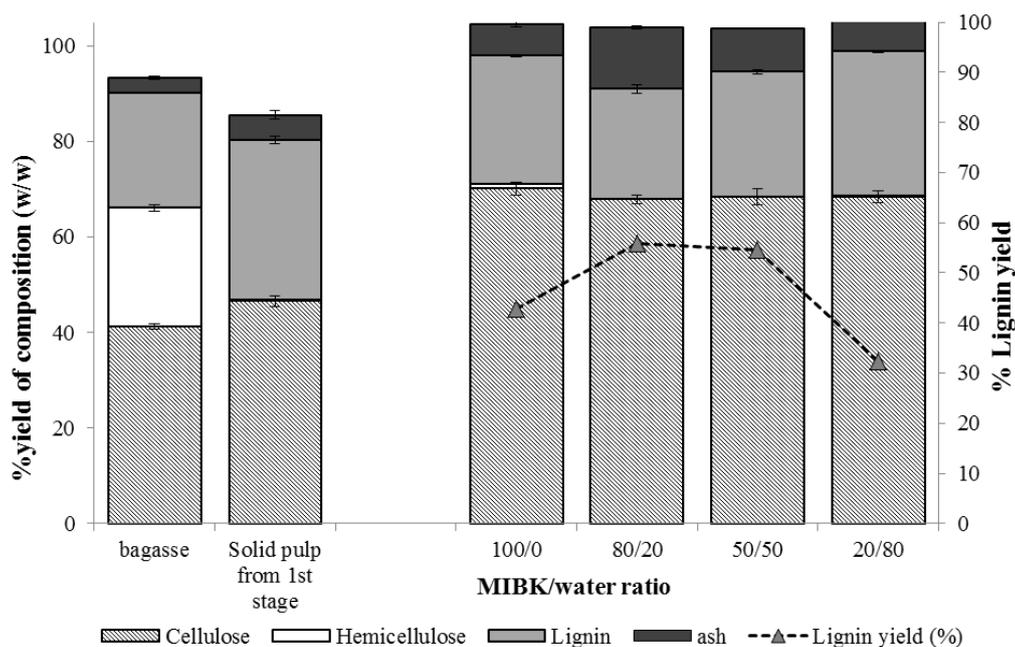


Figure 2 Chemical composition and lignin yield of cellulose pulp after hydrothermal process incorporate with different ratio of organic solvent (MIBK) and water of solid pulp from first stage fractionation. The reaction contained 10% (w/v) solid pulp with formic acid as acid promotor 5%v/v and heated at 160°C for 40 min.

3.3 Effect of temperature

The effect of temperature (140, 150, 160, 170 and 180°C) for lignin extraction using MIBK was observed from Fig. 3. Increase in reaction temperature from 140°C to 180°C led to increasing of lignin yield in range of 34.01% to 55.93% due to increment temperature led to solubilization of lignin content into organic phase into the organic phases, resulting in enrichment of cellulose in the solid fractions. In addition, the reaction temperature at 170°C and 180°C gave the higher cellulose fraction in solid pulp after organosolv fractionation compared to the mild temperature condition with cellulose composition in range of 67.88 to 72.48%w/w. This result is similar trend with another previous work. Teng et al (2016) reported the rising of lignin yield after increasing the reaction temperature from 160 to 200°C [14]. However, the harsh temperature over 180°C led to decrease in the cellulose fraction after fractionation process reported by Teng et al (2016) [14]. Therefore, the reaction temperature at 180°C based on 80:20 of MIBK and water ratio in 5% of HCOOH was selected to further study.

3.4 Effect of reaction time

Fig. 4 presented the effect of reaction time (20, 40, 60 and 80 min) for removing lignin content. Increase in reaction time from 20 to 80 min resulted in increasing of lignin yield from 50.05 to 65.36%. It could be due to the hydrolysis of amorphous cellulose and solubilization of lignin with MIBK incubated in longer time. However, the composition of cellulose was declined after 60 min which caused depolymerization of cellulose [14]. According to the result, the reaction time at 80 min contained 80:20 of MIBK and water ratio in 5% of HCOOH at 180°C gave the maximal lignin yield and high cellulose content with 65.36% and 64.69%w/w respectively. This condition was good candidate for next step in bleaching process due to efficiency of lignin removal and enhancement of cellulose fraction.

3.5 Effect of bleaching process

After the bleaching process with 1% NaClO₂, it was found that the composition of cellulose in solid pulp increased from 46.60 to 91.73 %w/w while the lignin content was decreased from 33.54 to 5.94% (Fig. 5). It could be due to the face that the lignin structure was degraded by chemical such as hydrogen peroxide (H₂O₂), ozone (O₃), sodium chlorite (NaClO₂) and other [15]. These affected with the structure of lignin at α-O-4 and β-O-4 linkage, leading to reducing the molecular weight (MW) of lignin [16]. The physical appearance of solid pulp enriched cellulose content was white color. Besides, the precipitated lignin after bleaching process was observed to the formation of kraft lignin with has molecular weight around 1,000-15,000 Da reported by Figueiredo, Lintinen et al. 2017 [17]. The kraft lignin can be converted to value added products such as adhesive, valinin, phenols, benzene, emulsifier, component for resin and thermoplastics for applying in many industries [17]. Later, the physical and chemical structure of bleached sample based on optimal condition was analyzed by several techniques such as XRD and FTIR.

3.6 X-ray diffraction (XRD)

The crystallinity index of native bagasse, solid pulp after fractionated with hydrothermal process at 160°C for 40 min incorporate with 5%v/v formic acid, and bleaching sample was 53.71, 61.51, and 75.92% respectively. It indicated that the two-stage fractionation process by using hydrothermal and organosolv pretreatment, and the bleaching process led to increase in the crystallinity index compared the native biomass. It could be due to removal of amorphous area derived from hemicellulose and lignin fraction after fractionation and bleaching process. In addition, the crystallinity size of bleaching sample, and solid pulp after two stage fractionation process was lower with 17.35 and 20.68, respectively compared to the native bagasse with 29.14. This was the same results with the other reports. Sá, Miranda et al. 2015 reported decrease in amorphous area of cellulose fiber and increase in crystallinity index after pretreating fiber arrowroot (*Maranta arundinacea*) with acid [18].

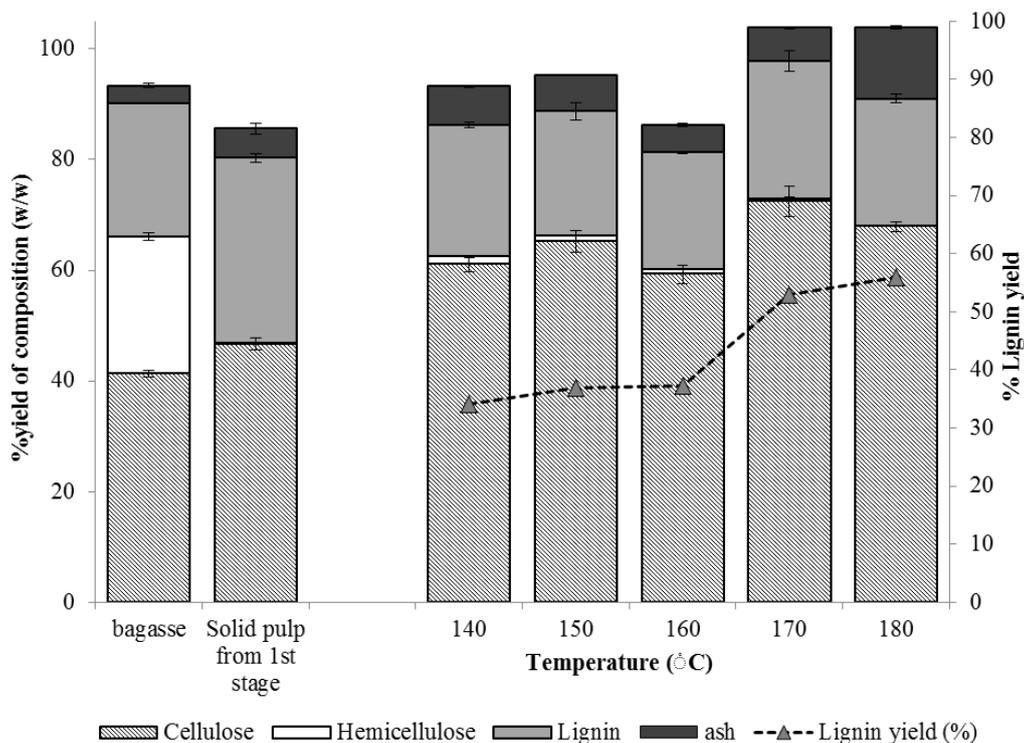


Figure 3 Chemical composition and lignin yield of cellulose pulp after hydrothermal process incorporate organosolv pretreatment with varying reaction temperature. The reaction contained 10% (w/v) solid pulp with formic acid as acid promotor 5%v/v and heated at 140-180 °C for 40 min.

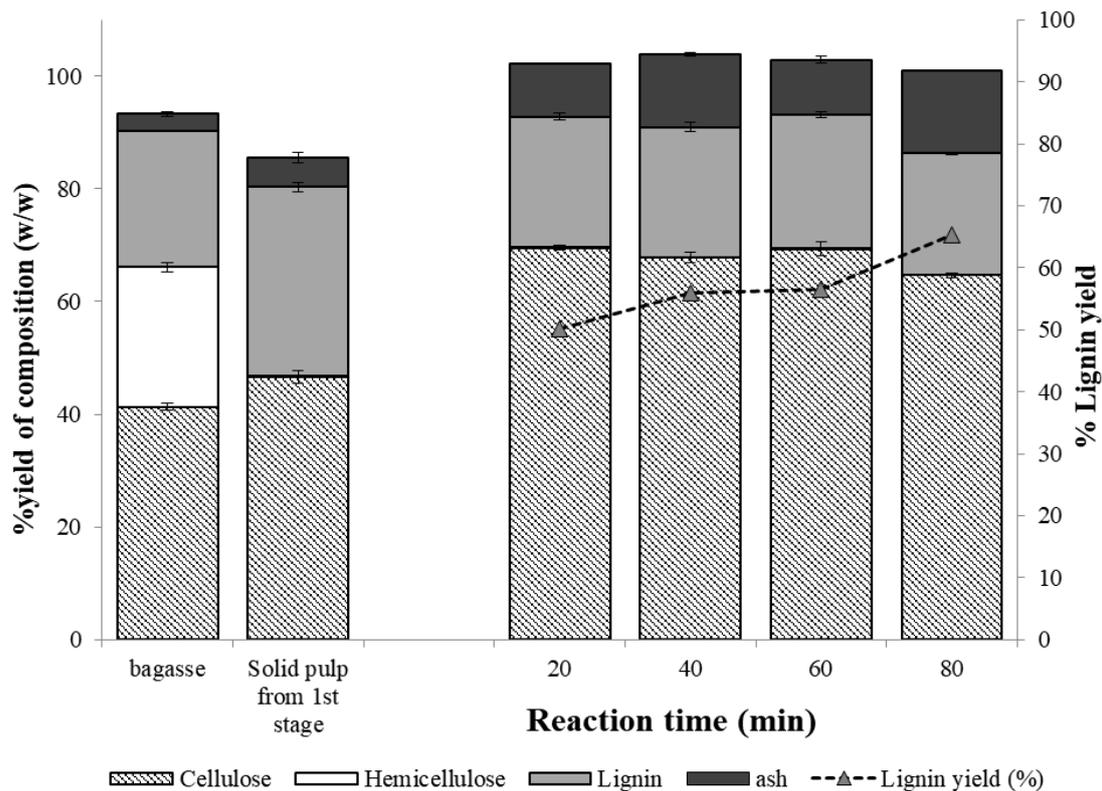


Figure 4 Chemical composition and lignin yield of cellulose pulp after hydrothermal process incorporate with ratio of organic solvent (MIBK) and water is 80:20 of solid pulp from first stage fractionation. The reaction contained 10% (w/v) solid pulp with formic acid as acid promotor 5%v/v and heated at 180 C for 20-80 min.



Figure 5 Chemical composition of cellulose pulp after bleaching process with 1% Sodium Chlorite of solid pulp from first stage fractionation.

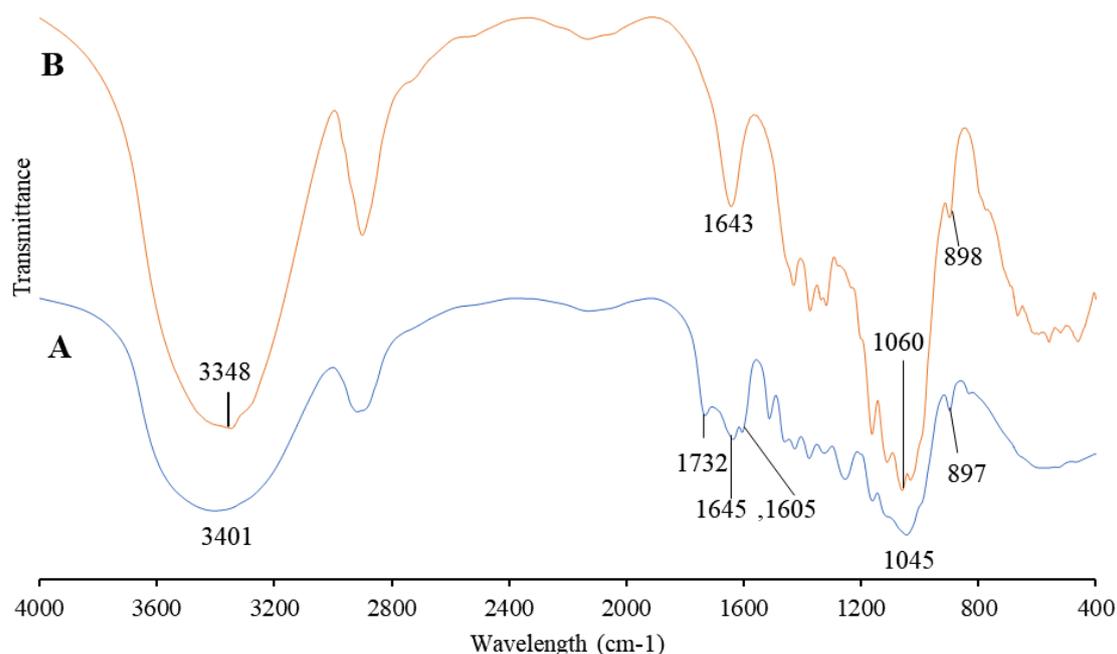


Figure 6 FTIR Spectra of (A) native bagasse, and (B) cellulose bleaching.

3.7 Fourier-transform infrared spectroscopy (FTIR)

The spectra of native bagasse and bleaching sample were shown in Fig. 6. The native bagasse and bleaching sample at wavelength in the range 3,300-3,400 cm^{-1} presented the hydroxyl group (-OH) in the three constituents of the fibers (cellulose, hemicellulose and lignin). At the range 750 to 900 cm^{-1} and 1,500 to 1,730 cm^{-1} in the native bagasse represented to the carbon-hydrogen bond (C-H) and aromatic skeletal vibration of lignin, respectively. These bands were not observed in bleaching cellulose after main removing lignin structure. In addition, the peak at 1,732 cm^{-1} in the native bagasse presented the C=O linkage of hemicellulose. After removing the hemicellulose content using 1st fractionation with hydrothermal process at 160°C for 40 min incorporate with 5%v/v formic acid, this band was disappeared in bleaching sample. The spectra of bleaching cellulose at 1,032 cm^{-1} to 1,163 cm^{-1} were observed in the cellulose fraction according to the previous works [18-19].

4. Conclusion

In this work, the pretreatment of sugarcane bagasse by method of hydrothermal, organosolv process with different organic acids (MIBK and DMSO), and bleaching process was studied for removal of hemicellulose and lignin content, leading to high separation to cellulose fraction. It was found that the optimization of lignin removal contained in hydrothermal process with water, MIBK at ratio 80: 20 and 5 %v/v formic acid at 180°C for 80 min showed the highest lignin yield and cellulose recovery with 65.36% and 64.69% respectively. The alternation of biomass structure after hydrothermal and organosolv process was estimated by XRD and FTIR analysis. Furthermore, the high purified cellulose after bleaching process was used for feedstock converted to high valuable products in industry further.

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