Production of High Concentration Hydrogen Gas from Sugarcane Bagasse and Sugarcane Leaf by Mechanochemical Treatment Followed with Gasification Method

Kanatip Kumproa[a] and Apinon Nuntiya*[b]

[a] Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai, 50200, Thailand.
[b] Department of Industrial Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, 50200, Thailand.

*Author for correspondence; e-mail: nuntiyaapinon@gmail.com

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ABSTRACT

The objectives of this work, including, produced high concentration hydrogen gas from sugarcane wastes by three-step process, studied the effect of ammonium hydroxide concentration on chemical treatment and studied the effects of milling time in mechanochemical treatment on hydrogen gas concentration in gaseous product and average particle size of milled mixture. The samples were characterized by UV-spectrophotometry, scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), thermogravimetry-mass spectroscopy (TG/MS) and particle size analysis. The gaseous products were analyzed by gas chromatography (GC). The results indicated that the highest lignin content from sugarcane bagasse and sugarcane leaves were 8.1 and 10.4 %w/w when applying of 10 %v/v of ammonium hydroxide. Scanning electron micrograph showed the sugarcane wastes consisted of cell wall and cellulose fibers. The cell wall and cellulose fibers were separated by removing lignin. Furthermore, the EDS analysis showed that the only cell wall of sugarcane wastes consisted of silicon. Hydrogen gas was emitted from the milled sample by heating at about 450-600°C with the low concentrations of methane, carbon monoxide and carbon dioxide. The highest concentration of hydrogen gas was 97 %mol, which was obtained from the milled mixture of sugarcane bagasse/Ni(OH)₂/Ca(OH)₂ with 120 min of milling time and the lowest concentrations of carbon dioxide below 0.3 %mol. According to, TG/MS and GC results showed that concentration of hydrogen gas increased with an increase in milling time in mechanochemical treatment. Due to the silicon in sugarcane wastes produced calcium silicate (CaSiO₃) and carbon dioxide, therefore; the concentration of carbon dioxide collected from sugarcane wastes are higher than from pure cellulose.

Keywords: hydrogen, mechanochemical, planetary ball mill, gasification, sugarcane bagasse, sugarcane leaf
1. INTRODUCTION

Recently, hydrogen which is a source power of fuel cell, has been considered as a novel fuel, due to an environmental problem of using fossil fuel. Due to the fact that biomass is a renewable and carbon neutral resource; therefore, hydrogen production from biomass has now become attractive research [1].

The intensive researches have been reported [1, 2] to produce hydrogen from biomass by using various methods, such as, gasification with pressure swing adsorption, supercritical, subcritical and hydrothermal method. However, these methods need high temperature, high pressure and several operation-step to obtain a high concentration hydrogen (90-99.9 %mol) [3]. William T. and Qiwu Z., et al [4-9] did the researches about hydrogen production by the method of gasification from polymer pellet and cellulose (analytical reagent grade) using preliminary mechanochemical treatment. They discovered that a solid state operation, which based on mechanochemical treatment particularly with catalyst and carbon dioxide capture agent followed with gasification method which offer the high-purity hydrogen.

Although cellulose is a major component in biomass, but biomass has variability of chemical composition, such as, silicon, calcium, magnesium, sodium, potassium nitrogen and sulfur. These elements are caused to reduce the purity of hydrogen gas; moreover, the unwanted by-products are occurred, which are extremely problem in gasifier and environment [10]. Previous researches reported [11-13] about chemical treatment of removing silicon and alkaline elements, which is on the cell wall of biomass, by using acid or base solution.

In this work, we propose a new pathway for hydrogen production with high concentration hydrogen from sugarcane bagasse and sugarcane leaves, which are the major agricultural biomass in Thailand and cause of environmental problem, in only three-step process. In the first step sugarcane wastes are treated for remove lignin and silicon by chemical treatment with ammonium hydroxide solution. The second step samples of sugarcane wastes/treated sugarcane wastes, nickel hydroxide (as a catalyst) and calcium hydroxide (as a carbon dioxide capture agent) are milled for trigger the mixtures and to obtain homogeneous mixtures by mechanochemical treatment and in the final step the milled samples are heated to produce hydrogen by gasification method. Furthermore, the effect of ammonium hydroxide concentration on chemical treatment, the effect of milling time on hydrogen production and the comparison between the concentration of gases from sugarcane wastes, treated sugarcane wastes and cellulose (analytical reagent grade) on hydrogen production are evaluated.

2. MATERIALS AND METHODS

2.1 Materials

Sugarcane bagasse and sugarcane leaves that are agricultural biomass from sugar extraction industry in Chiang Mai, Thailand were dried at 60°C for 1 h. Sugarcane wastes were milled by a grinder and sieve (45 mesh) to obtain the find particles. These samples were kept in the desiccator until it was used.

Ammonium hydroxide (NH4OH) from J.T. Baker was used as an extracted agent in chemical treatment and lignin (analytical reagent grade) from Aldrich chemistry was used as a standard reagent. Furthermore, nickel hydroxide (Ni(OH)₂) from Kanto chemical co., Inc. was used as a catalyst and calcium hydroxide (Ca(OH)₂) from Wako chemicals was used as a CO₂ capture agent in gasification method.
2.2 Methods

2.2.1 Chemical treatment

Milled sugarcane wastes were mixed with \( \text{NH}_4\text{OH} \) solution (8 %, 10 % and 12 % v/v) and shaken in a dual-action shakers (NB-101 MT, N-Biotex. Inc, Korea) at 200 rpm, room temperature for 24 h [11, 13]. The mixture was filtered out in order to separate solid fraction from the soluble fraction. The solid fractions were washed with deionized water to remove residual \( \text{NH}_4\text{OH} \) until pH was 7 and then dried in an oven (Binder, Edu System, Austria) at 70 °C for 24 h and kept it in desiccator until it used as starting material in mechanochemical treatment.

2.2.2 Mechanochemical treatment

Sugarcane wastes/treated sugarcane wastes, Ni(OH)\(_2\) and Ca(OH)\(_2\) were used as starting materials. The outstanding characteristics of cellulose (C\(_{6}\)H\(_{10}\)O\(_{5}\)) is to represent sugarcane wastes and chemical-treated sugarcane wastes for the use of chemical formula and reaction mechanism. According to the ideal reactions pathway that summarized in reaction (1), the samples were mixed at molar ratios of (1:0.5:6) for (C\(_{6}\)H\(_{10}\)O\(_{5}\);Ni(OH)\(_2\);Ca(OH)\(_2\)) and the 4.0 g mixture was milled by planetary ball mill (Pulverisette-7, Fritsch, Germany), which has two mill pots (45 cm\(^3\) inner volume each) made of ZrO\(_2\) with \(7 \times 15\) mm diameter of ZrO\(_2\) balls. Milling speed in this work was 700 rpm [4-9] and milling time was 0, 15, 30, 60 and 120 min.

\[
\text{C}_6\text{H}_{10}\text{O}_5 + 0.5\text{Ni(OH)}_2 + 6\text{Ca(OH)}_2 \rightarrow 11.5\text{H}_2 + 0.5\text{Ni} + 6\text{CaCO}_3
\] (1)

2.2.3 Gasification method

The sample of 2.0 g mixture, which was prepared by mechanochemical treatment, was put on a sample holder and placed in a glass tube. The glass tube connected to the source of argon gas and inserted in a furnace with discharge line for the product of gas collection [5-10]. The sample was heated in the furnace from room temperature to 600 °C for 60 min at heating rate of 20 °C/min. The products of gas were collected through the discharge line in an aluminum pack.

2.2.4 Characterization method

2.2.4.1 Ultimate analysis

The percentage of carbon, hydrogen, oxygen, sulfur and nitrogen in sugarcane wastes were determined by CHNS/O analyzer (PE 2400 series II, Perkin-Elmer, U.S.A.) for the ultimate analysis. Moreover, the heating value of sugarcane wastes were characterized by bomb calorimeter.

2.2.4.2 Lignin contents analysis

The lignin content in the soluble fraction was determined by UV spectrophotometer (HP 8453 UV-Vis, Hewlett Packard, Germany) at an absorbance of 260 nm [13].

2.2.4.3 Morphology analysis

The morphology of samples (before and after treated by chemical treatment) was observed by scanning electron microscope (SEM) (S4100, Hitachi and JSM-5910, JEOL Ltd., Japan). Furthermore, the percentage of element in the samples were characterized by Energy dispersive spectrometer (EDX) (JSM-5910, JEOL Ltd., Japan).

2.2.4.4 Thermogravimetric mass spectroscopy (TG/MS)

The optimum condition to obtain hydrogen was evaluated by TG/MS analysis using a thermobalance connected to a quadrupole mass spectrometer (Rigaku Thermo-Mass: Thermo plus TG-8120 with M-201QA). The measurements were carried out with helium gas at a flow rate of 300 ml/
min. About 2 mg of the milled samples were heated from 20 to 1000°C at a heating rate of 20°C/min.

2.2.4.5 Gas concentration analysis

The product gases were analyzed for component gas concentrations by Gas Chromatography (GC) using a Micro GC/QC system (Aglient Micro GC 3000A) with helium gas as carrier gas.

2.2.4.6 Mineralogical and functional analysis

The samples after milling and the milled samples after heating were characterized by X-ray diffractometer (XRD) (Rigaku, RINT-2200/PC) with a CuKα irradiation source (λ = 1.5405 Å) at 40 kV and 50 mA. Moreover, the heated samples were characterized by using Fourier transform infrared spectrometer (Digilab Excalibur Series, FTS-3000) with KBr as a diluent.

2.2.4.7 Particle size analysis

The average particle size of milled samples at different milling time (0, 15, 30, 60 and 120 min) were analyzed by particle size analyzer (Microtrac MT 3300 EX, Bel Japan Inc.).

3. RESULTS AND DISCUSSION

3.1 Ultimate Analysis of Sugarcane Wastes as Raw Materials

Table 1 shows the characteristics of sugarcane wastes. The optimum contents of nitrogen and sulfur are less than 0.5 %w/w. Nitrogen could react to form HCN and NH₃ or NOₓ in the combustion process. In addition, sulfur could also react to form H₂S and COS or SOₓ in combustion process. However, HCN, NH₃ or NOₓ, H₂S, COS or SOₓ formations could not affect or damage to the gasifier/reactor in the combustion process [10].

In this work, %N and %S of sugarcane bagasse and sugarcane leaves are both less than 0.5 %w/w. There are comparison between the heating value of sugarcane wastes in this work and lignite from U.S.A. (11176.62 kJ/kg), which was used as the raw material for gaseous production and electricity at present [10]. Furthermore, the optimum moisture content is less than 10 %w/w [10]. The moisture content of sugarcane bagasse and sugarcane leaves are both less than 10 %w/w. All of the characteristics indicate that both sugarcane bagasse and sugarcane leaves are acceptable as the good quality of raw materials for hydrogen production.

Table 1. characteristics of sugarcane bagasse and sugarcane leaves.

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Elemental analysis (%w/w)</th>
<th>Heating value (kJ/kg)</th>
<th>% Moisture content (%w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%C</td>
<td>%H</td>
<td>%O</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>42.19</td>
<td>6.30</td>
<td>50.97</td>
</tr>
<tr>
<td>Sugarcane leaves</td>
<td>42.84</td>
<td>6.63</td>
<td>49.85</td>
</tr>
</tbody>
</table>

3.2 Effect of NH₄OH Concentration on Chemical Treatment

The lignin contents in sugarcane bagasse and sugarcane leaves that treated by NH₄OH solution with different concentration (8, 10 and 12 %v/v) for 24 h are shown in Figure 1. The highest lignin content in the soluble fraction after chemical treatment from sugarcane bagasse and sugarcane leaves by using 10 %v/v of NH₄OH is 8.1 and 10.4 %w/w respectively. These results are similar to the results of Jose M.D., et al [11], indicate that NH₄OH could break the covalent bond between lignin and cellulose/hemicellulose [14].
is highly concentrated on cell wall of sugarcane wastes. Additionally, chemical treatment with NH₄OH could separate cell wall for reducing the amount of silicon.

Figure 1. Lignin contents of sugarcane bagasse and sugarcane leaves that are treated by using NH₄OH solution at different concentration (8, 10 and 12 %v/v) for 24 h of reaction time.

3.3 Morphological Studies of Untreated and Treated Samples

Figure 2(a) - (d) and Figure 3(a) - (d) show SEM images and EDS point analysis of untreated and treated sugarcane bagasse and sugarcane leaves with NH₄OH solution respectively. Figure 2(a) and Figure 3(a) show cell wall in “α” and “ω” areas, which consist of lignin, cover on cellulose fibers. Furthermore, Figure 2(b) and Figure 3(b) show cellulose fibers in “β” and “ε” areas are separated from cell wall by removing lignin with NH₄OH solution. These microfibril bundles have lengths of 400-600 μm and diameters of 30 - 50 μm. EDS point analysis of untreated sugarcane bagasse and untreated sugarcane leaves in “α” and “ω” areas are shown in Figure 2(c) and Figure 3(c), respectively. It appears high percentage of silicon. On the other hand, Figure 2(d) does not show any peak of silicon in “β” area of Figure 2(b) and Figure 3(d) shows low percentage of silicon in “ε” area of Figure 3(b). These results correspond to Haibo Z. and Byung D.P., et al’s results [12, 15]. It indicates that silicon

Figure 2. SEM images and EDS point analysis of sugarcane bagasse before and after chemical treatment; (a) untreated sugarcane bagasse, (b) treated sugarcane bagasse, (c) EDX point analysis of untreated sugarcane bagasse and (d) EDX point analysis of treated sugarcane bagasse.

Figure 3. SEM images and EDS point analysis of sugarcane leaves before and after chemical treatment; (a) untreated sugarcane leaves, (b) treated sugarcane leaves, (c) EDX point analysis of untreated sugarcane leaves and (d) EDX point analysis of treated sugarcane leaves.
3.4 TG/MS Analysis of Gas Composition

Figure 4 and 5 show the TG/MS spectra of the milled sugarcane bagasse/Ni(OH)$_2$/Ca(OH)$_2$ and sugarcane leaves/Ni(OH)$_2$/Ca(OH)$_2$ mixtures with 120 min of milling time at 700 rpm of speed milling. The Figure 4 and 5 clearly show production of H$_2$, H$_2$O, CH$_4$, CO and CO$_2$ as the main gaseous products. In TG curve, weight loss decreases at about 300°C. The MS spectrum is found at the peak of water at the same temperature. It indicates that a dehydration of Ni(OH)$_2$ occurs around this temperature. The reaction of dehydroxylation of Ni(OH)$_2$ as follow in reaction (2). Furthermore, TG curve shows large weight loss decrease at about 450 and 650°C, which are observed two endothermic peaks in DTA curves correspondingly. MS spectra shows the peak of H$_2$/CH$_4$ at about 450°C and the peaks of CO/CO$_2$ at about 650°C. It indicates that hydrogen and methane emit at about 450°C and carbon monoxide and carbon dioxide emit at about 650°C. The reactions of hydrogen, methane, carbon monoxide and carbon dioxide production are follow in reaction (1), (2), (3) (methanation), (4) (steam reforming) and (5) (water-gas shift reaction) respectively. The fact is that at the different temperature, hydrogen emission happens. Therefore, carbon monoxide and carbon dioxide are the key points to indicate the possibility of obtaining hydrogen with high purity.

\[
\text{Ni(OH)}_2 + \text{heat} \rightarrow \text{NiO} + \text{H}_2\text{O} \quad (5)
\]

\[
\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4 + \text{heat} \quad (6)
\]

\[
\text{CH}_4 + \text{H}_2\text{O} + \text{heat} \rightarrow \text{CO} + \text{H}_2 \quad (4)
\]

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (5)
\]
Figure 6(a) - (b) show the MS spectra of the sugarcane bagasse/Ni(OH)$_2$/Ca(OH)$_2$ and sugarcane leaves/Ni(OH)$_2$/Ca(OH)$_2$ samples milled for different milling time (0, 15, 30, 60 and 120 min) at 700 rpm of speed milling. It finds that a small peak of hydrogen emission occur from the sample without milling (0 min). The intensity of hydrogen peak and milling time increase rapidly indicates that mechanochemical treatment plays a significant role in hydrogen production from the mixture.

All of TG/MS results are similar to William T. and Qiwu Z., et al’s results [4-9]. It understands that the reactions in this work are similar to steam reforming reaction but our reactions occur with the milled samples for avoiding tar formation in gaseous products.

3.5 Characterization of The Mixtures

XRD patterns of sugarcane bagasse/Ni(OH)$_2$/Ca(OH)$_2$ and sugarcane leaves/Ni(OH)$_2$/Ca(OH)$_2$ mixture prepared by mechanochemical treatment for different milling time (0, 15, 30, 60 and 120 min) at 700 rpm of speed milling are shown in Figure 7(a) and Figure 7(b) respectively. The peaks of starting materials, including Ni(OH)$_2$ and Ca(OH)$_2$, still appear in the milled mixture, indicate that no solid state reaction occurs during mechanochemical treatment. However, the intensity of starting material peaks decrease with an increase in milling time. It indicates that the mixture becomes more amorphous state when milling time is increased.

Furthermore, it finds that the broad peak of amorphous silica in the mixtures indicate that sugarcane wastes are consist of amorphous silica as a trace element. These results in terms of milling time are similar to Qiwu Z, et al’s reports [7, 8].

Table 2 shows the average particle size of the milled sugarcane bagasse/Ni(OH)$_2$/Ca(OH)$_2$ and sugarcane leaves/Ni(OH)$_2$/Ca(OH)$_2$ mixtures prepared by mechanochemical treatment for different milling time (0, 15, 30, 60 and 120 min) at 700 rpm of speed milling. The results of particle size analysis show that the average particle size of the milled mixtures decrease with an increase in milling time. According to, the MS spectra and GC’s results in Figure 6, Table 3 and 4 respectively show that amount of H$_2$, concentration of total gases and concentration of H$_2$ increase when average particle size decreases. It indicates
that reactivity of reaction increase with the decrease in average particle size.

\[ \text{NiO} + \text{H}_2 \rightarrow \text{Ni} + \text{H}_2\text{O} \quad (8) \]

\[ \text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \quad (9) \]

\[ \text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + \text{CO}_2 \quad (10) \]

The peaks of Ni appear in heated samples, indicating that the reduction of NiO for producing Ni as a catalyst in hydrogen production, which are followed in reaction (6), are occur. Furthermore, the peaks of CaCO3 were found, indicate that the carbonation of Ca(OH)\(_2\) for reducing CO\(_2\) emission, which are followed in reaction (7), is occur. However, the peaks of NiO, which occur from the dehydroxylation of Ni(OH)\(_2\), and Ca(OH)\(_2\) still appear in heated samples. Interestingly the intensity of the peaks of CaCO3 decreases with an increase in milling time, because of a formation of CaSiO3 occur.

Figure 9(a) - (b) show XRD patterns of sugarcane bagasse/Ni(OH)\(_2\)/Ca(OH)\(_2\) and sugarcane leaves/Ni(OH)\(_2\)/Ca(OH)\(_2\) mixture prepared by mechanochemical treatment for 120 min at 700 rpm of speed milling and then heated at 600°C for 1 h. The peaks of CaSiO3, with low intensity, appear in heated samples, indicate that CaCO3 reacts with SiO2 in sugarcane wastes to produce CaSiO3 and emit CO2 [16]. The formation of CaSiO3 is followed in reaction (8). The results in terms of characterization of materials are different from Qiwu Z, et al’s researches [7, 8] because of starting materials in their research is cellulose (analytical reagent grade), which is only consist of carbon, hydrogen and oxygen.

XRD patterns of sugarcane bagasse/Ni(OH)\(_2\)/Ca(OH)\(_2\) and sugarcane leaves/Ni(OH)\(_2\)/Ca(OH)\(_2\) mixtures prepared by mechanochemical treatment for different milling time (0, 15, 30, 60 and 120 min) at 700 rpm of speed milling and then heated by gasification method at 600°C for 60 min under argon gas atmosphere are shown in Figure 8(a) and Figure 8(b) respectively. The peaks of Ni appear in heated samples,
Table 2. The average particle size of the milled sugarcane wastes/Ni(OH)$_2$/Ca(OH)$_2$ mixtures prepared by mechanochemical treatment for different milling time (0, 15, 30, 60 and 120 min) at 700 rpm.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Milling time (min)</th>
<th>Average particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SB/Ni(OH)$_2$/Ca(OH)$_2$</td>
<td>0</td>
<td>223.0</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>46.99</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>66.13</td>
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<tr>
<td></td>
<td>60</td>
<td>38.28</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>34.84</td>
</tr>
<tr>
<td>SL/Ni(OH)$_2$/Ca(OH)$_2$</td>
<td>0</td>
<td>163.6</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>39.72</td>
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<td></td>
<td>30</td>
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<tr>
<td></td>
<td>60</td>
<td>39.02</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>31.06</td>
</tr>
</tbody>
</table>

Table 3. Concentration of gases collected from sugarcane bagasse/Ni(OH)$_2$/Ca(OH)$_2$ and sugarcane bagasse (treated)/Ni(OH)$_2$/Ca(OH)$_2$ mixtures prepared mechanochemical treatment for different milling time (0, 15, 30, 60 and 120 min) at 700 rpm and then heated by gasification method at 600 °C for 60 min.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Milling time (min)</th>
<th>Total gas concentration (%mol)</th>
<th>Gas concentration (%mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H$_2$</td>
<td>CH$_4$</td>
</tr>
<tr>
<td>SB/Ni(OH)$_2$/Ca(OH)$_2$</td>
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<td>36.42</td>
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<td>95.95</td>
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<td>37.29</td>
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<td>0</td>
<td>34.31</td>
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<td>89.46</td>
</tr>
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<td></td>
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<td>93.16</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>39.03</td>
<td>97.10</td>
</tr>
</tbody>
</table>

Under argon gas atmosphere are shown in Figure 10. The peak at 3644 cm$^{-1}$, which is the stretching vibration of hydroxyl group in the hydroxide, was found in heated samples. It indicates that some hydroxide compound still remain in heated samples. The C-H stretch peaks at 2953, 2852 and 2511 cm$^{-1}$, C=C stretching vibration at 1798 cm$^{-1}$ and the peak at 714 cm$^{-1}$, which is represented to aromatic group, appears in heated samples. These wavelengths of organic compounds indicate the decomposition of sugarcane wastes at approximately 450 °C. Furthermore, the peaks at 1433 and 876 cm$^{-1}$ are observed. These wavelengths are represented to C-O stretch and C-O out of plane from CaCO$_3$. However, Si-O stretch peak is found at 1100 cm$^{-1}$. It indicates the occurrence of silicate compound in heated samples.
3.6 Analytical of Product Gas Concentration

Table 3 and 4 show gaseous concentrations collected from sugarcane bagasse/Ni(OH)$_2$/Ca(OH)$_2$, sugarcane bagasse (treated)/Ni(OH)$_2$/Ca(OH)$_2$, sugarcane leaves/Ni(OH)$_2$/Ca(OH)$_2$, and sugarcane leaves (treated)/Ni(OH)$_2$/Ca(OH)$_2$ mixtures prepared mechanochemical treatment for different milling time (0, 15, 30, 60 and 120 min) at 700 rpm and then heated by gasification method at 600 °C for 60 min.

<table>
<thead>
<tr>
<th>Milling time (min)</th>
<th>Total gas concentration (%mol)</th>
<th>Gas concentration (%mol)</th>
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<tbody>
<tr>
<td></td>
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<td>H$_2$</td>
</tr>
<tr>
<td>SL/Ni(OH)$_2$/Ca(OH)$_2$</td>
<td>0</td>
<td>24.88</td>
</tr>
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<td>15</td>
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<td>38.86</td>
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<td></td>
<td>120</td>
<td>43.30</td>
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</table>

Table 4. concentration of gases collected from sugarcane leaves/Ni(OH)$_2$/Ca(OH)$_2$ and sugarcane leaves (treated)/Ni(OH)$_2$/Ca(OH)$_2$ mixtures prepared mechanochemical treatment for different milling time (0, 15, 30, 60 and 120 min) at 700 rpm and then heated by gasification method at 600 °C for 60 min.

3.6 Analytical of Product Gas Concentration

Table 3 and 4 show gaseous concentrations collected from sugarcane bagasse/Ni(OH)$_2$/Ca(OH)$_2$, sugarcane bagasse (treated)/Ni(OH)$_2$/Ca(OH)$_2$, sugarcane leaves/Ni(OH)$_2$/Ca(OH)$_2$, and sugarcane leaves (treated)/Ni(OH)$_2$/Ca(OH)$_2$ mixtures prepared mechanochemical treatment for different milling time (0, 15, 30, 60 and 120 min) at 700 rpm of speed milling and then heated by gasification method at 600 °C for 60 min under argon gas atmosphere. The data shows the concentration of H$_2$ increases with an increase in milling time, indicating that mechanochemical treatment has influenced to hydrogen concentration in hydrogen production. However, the mixtures of H$_2$ concentration milled for 120 min, seem to decrease due to the formation of CaSiO$_3$ occurred to emit CO$_2$ [16]. H$_2$ concentration from treated sugarcane wastes mixtures is higher than H$_2$ concentration from untreated sugarcane wastes mixtures. In addition, CO$_2$ from treated sugarcane wastes mixtures is lower than CO$_2$ from untreated sugarcane wastes mixtures. The results reveal that the successful removal of lignin and silicon in chemical treatment. The highest concentration of H$_2$ is approximately 86-97 %mol. Thus, H$_2$ concentration in our work is in a range of high concentration H$_2$ (90-99.9 %mol) [3]. The lowest concentration of CO$_2$ is approximately 0.18 %mol.

Qiwu, et al’s researches [7, 8] produced the highest concentration of hydrogen gas is approximately 88-99.3 %mol. In addition, the lowest concentration of CO$_2$ is approximately 0.1 %mol. Furthermore, there are the comparisons of H$_2$ and CO$_2$ concentration with other works which are the researches of John and Nicholas [10] and Tomoaki et al [2]. John and Nicholas [10] produced H$_2$ (30-45 %mol) and CO$_2$ (15-25 %mol) by the gasification method and also circulating
Figure 8. X-ray diffraction patterns of mixtures prepared by mechanochemical treatment for different milling time (0, 15, 30, 60 and 120 min) at 700 rpm and heated by gasification method at 600°C for 60 min; (a) sugarcane bagasse/Ni(OH)₂/Ca(OH)₂ mixture and (b) sugarcane leaves/Ni(OH)₂/Ca(OH)₂ mixture.

Figure 9. X-ray diffraction patterns of mixtures prepared by mechanochemical treatment for 120 min at 700 rpm and heated by gasification method at 600°C for 60 min; (a) sugarcane bagasse/Ni(OH)₂/Ca(OH)₂ mixture and (b) sugarcane leaves/Ni(OH)₂/Ca(OH)₂ mixture.

fluid bed. Tomoaki et al [2] produced H₂ (0.4 %mol) and CO₂ (10 %mol) by the hydrothermal method.

4. CONCLUSIONS

The results in this work show that the high concentration hydrogen gas could be produced from sugarcane wastes in a three-step process. The first step sugarcane wastes are treated by chemical treatment with NH₄OH and the second step untreated sugarcane wastes/treated sugarcane wastes, Ni(OH)₂ and Ca(OH)₂ are prepared by mechanochemical treatment. Finally, the third step the milled samples are heated from room temperature to 600 °C by gasification method. The results are summarized as follow;

1. Chemical treatment using NH₄OH solution could separate cell wall, which consist of lignin and silicon, from microfibril bundles of cellulose fiber.
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