HYDROGEN PRODUCTION FROM STEAM PYROLYSIS-GASIFICATION OF SUGARCANE LEAVES WITH SORBENT-CATALYSTS

Teerayut Bunma, Prapan Kuchonthara

aDepartment of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
Center of Excellence on Petrochemical and Materials Technology, b7th Floor, Chulalongkorn University Research Building, Bangkok 10330, Thailand

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*Corresponding author
prapan.k@chula.ac.th

Graphical abstract

Abstract

In this work, the hydrogen production during biomass steam pyrolysis-gasification with a combined catalysts and sorbent. The biomass sample was originated from sugarcane leaves. The combined catalyst and sorbent (NiO-MgO-CaO/γ-Al2O3) was prepared by an excess-solution impregnation method and the property of fresh and used catalysts was characterized using XRD. The prepared sorbent-catalysts promoted both tar reforming and CO2 absorption. High hydrogen production was achieved due to the enhanced water-gas shift reaction by the latter. The pyrolysis-gasification experiments were conducted in a drop tube two-stage fixed bed reactor. The effect of operating parameters such as the amount of MgO (3, 5 and 10 wt.%) and CaO (3, 5 and 10 wt.%) on supported catalysts and the gasification temperatures (600, 700 and 800 °C) were investigated. It was found that the highest hydrogen yield of 23.2 mmol H2/gbiomass was attained using the Ni10Mg5Ca5 catalyst at the gasification temperature of 600 °C. However, the maximum of tar conversion was observed around 78 wt.% at gasification temperature up to 800 °C.

Keywords: Gasification, Hydrogen, Biomass, Catalyst and sorbent

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1.0 INTRODUCTION

Energy recovery from different types of waste biomass such as agricultural waste, food manufacture waste and forestry residues is gaining interest due to concern about the limited supply of fossil fuels and environmental impact from fossil fuel use. Sugarcane which is one of the lignocellulosic biomass occurs as a by-product of sugarcane manufacture and it is estimated that 180 million tons of sugarcane leaves is generated each year [1]. Such large tonnages of waste biomass have the potential to be used for a range of energy process with the added benefit of mitigating against climate change problems.

Hydrogen has the highest energy density in all fuels (122 kJ per kg about 2.75 times greater than other hydrocarbon fuels) [2]. At meantime, combustion of hydrogen does not give away any other emissions. Transformation of biomass into gases product is an important process to produce hydrogen [3-6]. Steam gasification of biomass is thought to be an efficient way to higher hydrogen yield [7, 8]. However, the tar formation leads to a decrease in the gas yield from gasification. Moreover, the hydrogen yield from biomass steam gasification is mostly low, therefore, addition of catalysts is interesting for development of hydrogen production.

Many types of catalysts have been investigated for biomass gasification including nickel (Ni), iron (Fe), rhodium (Rh), ruthenium (Ru), platinum (Pt), and palladium (Pd). Generally, Ni based catalysts have been commonly used with steam as for hydrogen production because of its high activity, stability and
relatively cheap price. Czernik and French [9] studied the gasification of polypropylene using C11-NK (commercial nickel catalyst), recovering 80% hydrogen of the theoretical potential of propylene. Bang et al. [10] investigated the Ni/Al2O3 catalyst on steam reforming of liquefied natural gas, resulting in 60% hydrogen production. Liu et al. [11] and Ruoppolo et al. [12] carried out the co-gasification of biomass/plastic mixtures using Ni loaded γ-Al2O3 and, Ni and Pd loaded Al-MCM-41(mesoporous aluminosilicates), respectively, which also promoted hydrogen production and tar reduction. Nevertheless, the metal on support catalysts is easily deactivation.

Herein, adding Mg in catalysts has been considered to moderate catalyst deactivation for biomass gasification. The Mg can promote the hydrogen production because it can increase the catalyst activity. Wu and Williams [13] investigated polypropylene gasification using Ni–Al and Ni–Mg–Al catalysts. They found that the introduction of Mg into the Ni–Al catalyst significantly decreased the coke forming on the surface of catalyst without deficit of hydrogen yield. The Ni–Mg–Al catalyst was also applied to the gasification of biomass components such as lignin, cellulose and xylan resulting in the highest gas yield of 73.0 wt.% from cellulose at 800 °C [14].

However, hydrogen concentration in the syngas from biomass steam gasification is controlled by thermodynamic equilibrium. In order to enhance hydrogen production, utilization of sorbent has been recommended [15]. CaO is known as a tar reforming catalyst and also one of the effective solid CO2 sorbents, inducing the carbonation reaction [16]. The reaction is in equilibrium expressed by:

\[ \text{CaO} + \text{CO}_2 = \text{CaCO}_3 + 178 \text{ kJ/kmol} \] (1)

In gasification, the water-gas shift reaction is an essential reaction that regulates CO and H2 compositions in the gas product. The reaction converts CO into CO2 by reacting with steam; concurrently H2 is given, as shown in Eq. (2).

\[ \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 + 41 \text{ kJ/mol} \] (2)

In general, decreasing of CO2 can shift the reaction equilibrium, leading to higher CO conversion. Consequently, the hydrogen yield become higher than the equilibrium value.

Wei et al. [17] conducted the effect of limestone, olivine and dolomite on biomass gasification at temperature range of 750-850 °C. They found that dolomite [CaO] showed better conduct in articles of catalytic activity on tar reduction and CO2 absorption. Zhang et al. [18] studied wet biomass for steam gasification with CaO/MgO sorbents. The result showed that CaO/MgO in the ratio of 1 (CaO:MgO=1:1) at 850 °C can increase the hydrogen yield by CO2 sorption to promote the water-gas shift reaction. Kamagai et al. studied the biomass gasification over Ni-Mg-Al-Ca catalysts. It was observed that Ca was the crucial parameter to develop the hydrogen production [19].

However, less consideration has been targeted on pyrolysis-gasification of biomass with catalyst and sorbent bed to produce hydrogen at high rapid heating rate. Moreover, it is needed to optimize the configuration of the catalyst for hydrogen production.

In this work, the NiO-MgO-CaO/γ-Al2O3 was prepared using an excess-solution impregnation method with different CaO and MgO contents. The prepared catalysts were characterized for physical and chemical properties. Experiments for hydrogen production from the pyrolysis-gasification of sugarcane leaves were tested in a drop tube two-stage fixed bed reactor. The gasification temperature was also investigated in this study.

### 2.0 EXPERIMENTAL

#### 2.1 Materials

Sugarcane leaves were squashed and sieved into the size of 0.25 mm and used as the biomass sample. Proximate analysis was performed. Elemental compositions, including carbon, hydrogen and nitrogen of the samples, were determined using a CHN 2000 elemental analyzer. The oxygen (O) element was computed by mass difference. The results are summarized in Table 1.

**Table 1** Proximate and elemental analysis of the sugarcane

<table>
<thead>
<tr>
<th>Proximate analysis (wt.%)</th>
<th>Moisture</th>
<th>Volatile</th>
<th>Fixed carbon</th>
<th>Ash</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>11.0</td>
<td>69.5</td>
<td>12.9</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Elemental analysis (wt.%)</th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Nitrogen</th>
<th>Oxygen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>51.8</td>
<td>9.3</td>
<td>0.9</td>
<td>38.0</td>
</tr>
</tbody>
</table>

a On wet basis
b Calculated by mass difference.

#### 2.2 Catalysts Preparation

NiO-MgO-CaO/γ-Al2O3 catalyst was prepared by the excess-solution impregnation using γ-Al2O3 as a support. Firstly, the γ-Al2O3 was mixed with water solution of calcium nitrate (Ca(NO3)2·6H2O). The mixture was evaporated at 70 °C, afterwards the sample was calcined in air at 950 °C for 3 hours. Then magnesium nitrate (Mg(NO3)2·6H2O) and nickel nitrate (Ni(NO3)2·6H2O) were added into catalyst at specific ratio and changed the calcination temperature to 750 and 500 °C, respectively. The corresponding names of the catalyst prepared under different conditions are listed in Table 2.
2.3 Pyrolysis-gasification Experiments

Pyrolysis-gasification of biomass was explored in a drop tube two-stage fixed bed reactor, as illustrated schematically in Figure 1. The pyrolysis was carried out in the first stage (pyrolysis zone) and the volatiles proceeded to the second stage reactor (gasification zone). The pyrolysis zone was maintained at 600 °C under constant Ar flow of 50 mL/min. The gasification zone was varied from 600 to 800 °C for investigation of CO2 sorbent. 0.12 g of sugarcane leaves was filled a drop tube and 1.5 g of catalysts was placed in the gasification zone. When constant temperature was achieved for both zone, the water was fed into the gasification zone via HPLC pump at the volumetric flow rate of 0.14 mL/min for maintain the concentration of steam to 60%. The volatile from pyrolysis zone was carried out by Ar flow into the gasification zone, where reaction with steam in the pyrolysis zone was carried out by Ar flow into the gasification zone. When constant temperature was achieved for both zone, the water was fed into the gasification zone via HPLC pump at the volumetric flow rate of 0.14 mL/min for maintain the concentration of steam to 60%. The volatile from pyrolysis zone was carried out by Ar flow into the gasification zone, where reaction with steam in the catalyst occurred. Tar and unreacted water were trapped by a cooler bottle containing i-propanal. The gases product was accumulated using gas bag and detected by gas chromatography. The amount of char and tar were defined as the solid residue in the reactor and the remaining tar in the trapped solution after evaporation.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Catalyst content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NiO</td>
</tr>
<tr>
<td>Ni10Mg3Ca3</td>
<td>10</td>
</tr>
<tr>
<td>Ni10Mg5Ca3</td>
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<td>Ni10Mg10Ca5</td>
<td>10</td>
</tr>
<tr>
<td>Ni10Mg10Ca10</td>
<td>10</td>
</tr>
</tbody>
</table>

Char yield and tar conversion were calculated by equations as follows:

Char yield = \( \frac{R(1-A)}{B} \times 100 \)  \( \text{(3)} \)

Where:
- \( R \) is the weight of solid residue in reactor (g)
- \( A \) is the fraction of ash content
- \( B \) is the weight of biomass sample (g)

Tar conversion = \( \frac{(To - T)}{To} \times 100 \)  \( \text{(4)} \)

Where:
- \( To \) is the weight of tar component in a controlled condition (without catalyst) (g)
- \( T \) is the weight of tar component in a condition with catalyst (g)

3.0 RESULTS AND DISCUSSION

3.1 Effect of Catalysts on Product Distribution for the Pyrolysis-Gasification Process

Catalysts can improve the reaction rate and also facilitate the tar conversion into valuable combustible gas via thermal cracking and hydrocracking or water gas shift reactions \([20]\). The decomposition products from pyrolysis-gasification experiments were classified into three groups: (1) gases, which did not condense in the cooling traps; (2) liquids, which were condensable in condensers including unreacted water and tar; and (3) char, which remained in the sample holder. The char yield and tar conversion was calculated by Eqs. (3) and (4), respectively.

3.1.1 Calcium Oxide (CaO) Content

The effect of increasing the CaO loading from 3 to 10 wt.% on product distribution is shown in Figure 2a. Char yield decreased with increasing the CaO content. The lowest of tar yield was observed in Ni10Mg5Ca10 catalyst around 18.9 wt.%. However, the results of gas yield can be divided into 2 stages. In the first stage, gas yield moved upward with rising the CaO capacity from 3 wt.% to 5 wt.%. The gas yield reached to maximum of 38.9 mmol/gbiomass in Ni10Mg5Ca5 catalyst. In the second stage, increasing the CaO content from 5 wt.% to 10 wt.% provided lower gas yield down to 28.0 mmol/gbiomass in Ni10Mg5Ca10 catalyst. The observed trends can be explained by the result of tar conversion. In the first stage, an increase in CaO from 3 to 5 wt.% increased the tar conversion up to 74.3 wt.%. It means that the CaO could take part in tar reduction. However, the tar conversion was found to dramatically drop with a further rise in CaO up to 10wt.%. It is attributable to the interaction between CaO and support (Al2O3), forming an inactive specie. This was discussed further using the XRD results.
3.2.2 Magnesium Oxide (MgO) Content

The effect of MgO loading on product distribution is shown in Figure 2b. As the MgO content increased from 3 to 10 wt%, gas yield increased from 26.6 to 42.9 mmol/gbiomass while char decreased from 22.5 to 18.9 wt%. For tar conversion, the addition of MgO leads to an increase in tar conversion up to 78.0 wt% with Ni10Mg10Ca5 catalyst. It would be due to the fact that the MgO can promote tar cracking in biomass gasification. The same trend was also found in the previous literature. Nakamura et al. [21] explored the role of MgO on steam gasification of biomass. They concluded that MgO can catalyze tar cracking and reforming of hydrocarbon as shown in Eqs. (5) and (6), respectively, leading to higher gas yield.

\[
\text{Tar} = \text{CH}_4 + \text{H}_2\text{O} + \text{C}_x\text{H}_y + \text{H}_2 \quad (5)
\]

\[
\text{C}_x\text{H}_m + n\text{H}_2\text{O} = n\text{CO} + (n+m/2)\text{H}_2 \quad (6)
\]

Therefore, it was concluded that the presence of MgO plays a catalytic role in tar reforming, giving lower tar and higher gas product.

3.2 Effect of Catalysts on Gas Composition for the Pyrolysis-Gasification Process

3.2.1 Calcium Oxide (CaO) Content

CaO is an alkali material that is extensively employed in gasification to promote tar conversion and increase gas yield. Furthermore, it has been reported that CaO can enhance the water-gas shift reaction through the carbonation reaction. The gas composition of gasification with CaO catalyst is shown in Figure 3. H₂ yield was dramatically increased from 2.5 mmol/gbiomass in the absence of catalyst to 12.0 mmol/gbiomass in the presence of Ni10Mg5Ca3. This is because the steam reforming was accelerated by CaO, MgO and NiO catalysts. The influence of CaO content on the hydrogen yield was investigated by comparing three different loading contents of CaO, namely Ni10Mg5Ca3, Ni10Mg5Ca5 and Ni10Mg5Ca10. H₂ yield was increased with increasing of CaO from 3 to 5 wt.% reaching a maximum of 16.8 mmol/gbiomass at Ni10Mg5Ca5 catalyst. The higher CaO content up to 10 wt.% provided the lower H₂ yield down to 10.4 mmol/gbiomass. CO yield exhibited a similar trend with H₂ yield. The maximum CO yield was 15.8 mmol/gbiomass with Na10Mg5Ca5 catalyst. However, the downward trend of CO₂ yield was observed with increasing CaO but the opposite trend was given when the CaO loading became higher than 5 wt.%.

The above finding, which the H₂ yield became higher, while the CO₂ yield dropped with the increase in the amount of CaO content. This indicated that the carbonation reaction, Eq. (2), could stimulate the water-gas shift reaction to produce more hydrogen. Zhang et al. [18] and Kumagai et al. [19] reported the same trend of H₂ yield and CO₂ yield. However, high content of CaO appeared to reduce H₂ yield. This could be due to the formation of inactive phases of Ca which was discussed later using the XRD result.
Figure 4 shows the XRD result of fresh and used catalysts for various CaO contents in biomass pyrolysis-gasification process. It can be seen that fresh catalysts all displayed Al2O3, NiO, MgO and CaO peaks. The fresh Ni10Mg5Ca10 gave the highest intensity of CaO peak, followed by Ni10Mg5Ca10 and Ni10Mg5Ca3. When CaO was loaded onto γ-Al2O3 supported, the mainly CaO phased was observed in Ni10Mg5Ca3 and Ni10Mg5Ca5, but Ni10Mg5Ca10 consisted of CaO and CaAl2O4. The result indicated that increasing CaO content from 5% to 10% provided the formation of CaAl2O4 phase. This was evidenced by the lower magnitude of CaO peak. It can be interpreted that CaAl2O4 had dispersed on the surface of the γ-Al2O3 support and reduced the active phase of CaO. For used catalysts, it can be seen that CaCO3 was observed in all used catalyst. Increasing the CaO content from 3% to 5% provided higher intensity of CaCO3 peak than the other. This result verified the CO2 adsorption by carbonation reaction of CaO. However, the intensity of CaCO3 decreased with increasing the CaO content from 5% to 10%. This indicated that the high CaO loading could induce the formation of CaAl2O4 phase, which is not preferable to promote the CO2 absorption.

![Figure 4: XRD pattern of catalyst before (Fresh) and after (Used) with different CaO content in pyrolysis-gasification](image)

Increasing the MgO contents provided higher H2 and CO yields. On the other hand, CO2 yield decreased and there was no significantly changed for CH4 yield. This is an evidence that MgO can promote both the reforming reaction and water-gas shift reaction, as mentioned above.

### 3.3 Effect of Gasification Temperature on Product Distribution and Gas Composition for the Pyrolysis-Gasification Process with Combined Catalysts and Sorbent

The influence of gasification temperature was explored by using the Ni10Mg10Ca5 catalyst. Figure 6 shows the product distribution with different gasification temperature. It was shown that gas yield raised at higher temperature, in a range of 600 to 800 °C. The maximum gas yield and tar conversion were 42.9 mmol/gbiomass and 78.1 wt.%, respectively, at 800 °C. This result confirmed the previous finding that high temperature significantly enhances the tar cracking reaction [22].

![Figure 6: Effect of gasification temperature on product distribution from pyrolysis-gasification. (NiO = 10 wt.%, MgO = 10 wt.%, CaO = 5 wt.%, Tpyrolysis = 600 °C, and concentration of steam = 60%)](image)

Figure 7 shows the influence of gasification temperature on the gas composition. It was observed that H2 decreased while the CO and CO2 yield gained with rising the gasification temperature. This result obeys the thermodynamic equilibrium of the water-gas shift and carbonation reactions which are both exothermic. At a low temperature, H2 production could be further enhanced by CO2 adsorption through the carbonation.

![Figure 7: Effect of gasification temperature on gas composition from pyrolysis-gasification. (NiO = 10 wt.%, CaO = 5 wt.%, Tpyrolysis = 600 °C, Tgasification = 800 °C, and concentration of steam = 60%)](image)

### 3.2.2 Magnesium Oxide (MgO) Content

Gas composition in relation to sample weight with different MgO contents is shown in Figure 5.
4.0 CONCLUSION

In this work, NiO-MgO-CaO/γ-Al₂O₃ catalysts with different CaO and MgO contents were synthesized to enhance hydrogen production from pyrolysis-gasification of sugarcane leaves through CO₂ absorption by CaO. The influences of Ca and Mg loading and gasification temperature on product yield and gas composition were studied. Several conclusions could be drawn as follows:

1. By increasing CaO content up to 5 wt.%, hydrogen yield was improved to 16.8 mmol/g生物质 at Ni10Mg5Ca5. The CaAl₂O₄ phase was formed at high CaO loading, i.e., 10 wt.%, lowering the activity of the catalyst.
2. The addition of MgO can promote the hydrogen production and tar conversion up to 19.2 mmol/g生物质 and 78 wt.%, respectively.
3. A decrease in gasification temperature in the presence of catalyst gave lower tar conversion down to 48.9 wt.%. However, the hydrogen was found to increase up to 23.3 mmol/g生物质.

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References
