Producing hydrogen-rich gas by fresh biomass co-pyrolysis with additive

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Abstract

Pyrolysis properties of fresh ficus lacor leaves with moisture content of 70wt. % was investigated in a TGA setup. The effects of different operating parameters on pyrolysis of biomass were studied in a fixed-bed reactor system. With addition of CaO, there showed an additional decrease in weight at temperature range of 382~490 °C, but 12wt. % weight was recovered in the first stage (40~220 °C). Fresh biomass pyrolysis was calculated to be first order reaction with activation energy about 29.8 kJ mol^{-1}. Activation energy was lowered to 20.4 kJ mol^{-1} by addition of CaO. With scope of temperature studied, higher temperature was found always favor hydrogen production during pyrolysis of fresh biomass. Carbonation and hydration of CaO enhanced water gas shift reaction (WGS) which led to hydrogen yield increasing. The highest hydrogen content (around 70vol. %) of hydrogen concentration and hydrogen yield (23.2 ml g^{-1}-biomass) were achieved when CaO/biomass mass ratio increased to 0.3. Pyrolysis of fresh biomass without pre-drying showed the potential of hydrogen production.

Keywords: Fresh biomass; Pyrolysis; CaO; NiO; Hydrogen

1. Introduction

Biomass plays an irreplaceable role in the energy world, for it is renewable and abundant. Thermochemical conversion is one of the most important conversion technologies of biomass. Through thermochemical treatment, biomass is decomposed to bio-oil, char, syngas and syngas mainly consists of H_2, CO, CO_2, and CH_4 (Nasir Uddin *et al.,* 2013). Hydrogen is thought to be the energy for future. It is being used in various transports, industrial, commercial and residential applications, where fossil fuels are currently used. High content of hydrogen can be produced by pyrolysis of biomass, and this technology is now attracting much attention (Ansari *et al.*, 2014; Liu *et al.*, 2014; Alvarez *et al.*, 2014).

However, traditional pyrolysis of biomass involves some problems: lower hydrogen, higher tar and residue char content. To overcome these disadvantages, catalytic pyrolysis was proposed. By using catalyst, condensable gas can reach the active sites of the catalyst, and the C-H bonds of the heavy hydrocarbons will be weaken which leads to cracking and reforming reactions happen in a more readily way. Hydrogen yield was promoted due to the enhanced shifting of H element from hydrocarbons to the target product. Several catalysts were reported to be effective in elimination of tar during pyrolysis of biomass (Bulushev and Ross, 2011). Jiang *et al.* (2012), conducted pyrolysis of biomass in molten alkali media. NiMo/Al$_2$O$_3$ catalyst was used during pyrolysis of biomass by Hao et.al (2010). ZnCl$_2$, K$_2$CO$_3$ and NaCO$_3$ were used as catalyst during pyrolysis of olive husk, and it was found that using about 17wt. % ZnCl$_2$ at about 752°C obtained largest hydrogen rich gas yield (Çağlar and Demirbaş, 2002). Corella *et al.* (2004) employed nickel-based monoliths for tar elimination in fuel gas produced by biomass gasification in a fluidized bed at a small pilot-plant scale. Recently, two different sorbents, CaO and CaO·MgO were evaluated and upgraded bio-oils were obtained in both cases (Veses *et al.*, 2014). It was also reported that addition of CaO could enhance the gaseous production and increased the production of hydrogen from pyrolysis of biomass (Kuan *et al.*, 2013), and Zhang *et al.* (2014) reported that CaO from different precursors had different impact on biomass pyrolysis.

By now, most of the studies on biomass thermochemical conversion used biomass with low moisture content. However, most of the available biomass are with high moisture and researches on conversion of biomass directly without pre-drying are still not enough. Also, some authors believe that H_2O would influence the sorbent performance on CO_2 capture which may further makes a non-ignorable effect on biomass pyrolysis (Zhang *et al.*, 2014). The aim of this paper is to study the pyrolysis properties of the biomass rich in water especially with additives. In this paper, pyrolysis of fresh ficus lacor leaves with moisture content as high as 70wt. % was investigated, and also the effect of additive (CaO and NiO) on pyrolysis was tested. Kinetic studies were conducted in a TGA setup. The influence of pyrolysis temperature, additive type, and additive loading on gas composition and hydrogen yield were studied in a bench scale fixed-bed reactor system.

2. Materials and Methods

2.1 Sample preparation

Ficus lacor is widely available in Southwest of China. The ficus lacor leaves were freshly collected, and sliced to the shape of square with side length of about 0.5 cm. Without drying, fresh leaf contains 70wt. % moisture. Based on air-dried basis, it owned volatiles content of 60.37wt. %, fixed carbon content of 13.2wt. % and ash content of 1.33wt. %. CaO and NiO were all analytical reagents with more than 99.9% purity (Sinopharm Chemical Reagent Beijing Co., Ltd.). A mixture of CaO and NiO (CaO/NiO) was prepared by physically mixing of both compounds at a mass ratio of one. Before pyrolysis experiments, all additives were totally calcined at 800 °C for 3h in muff furnace under N_2 flow, crushed and sieved to less than 60 mesh. Catalytic effects of CaO, NiO, CaO/NiO on pyrolysis of fresh biomass were investigated in the paper.

2.2 Experimental apparatus

Experiments were carried out in a TGA setup (STA409 PC, Germany) to study the pyrolysis characteristics of fresh biomass. 50 mg of biomass was used in each test and for the case with additive the amount of additive was 15 mg. Flow rate of carrying gas was 30 ml min^{-1} (N_2) and protecting gas was 20 ml min^{-1} (N_2). Temperature rose with a rate of 20 °C min^{-1} from room temperature to 800 °C during the test in TGA.

Pyrolysis of fresh biomass was also conducted in a fixed-bed system to investigate the syngas composition, as schematically showed in Fig. 1. The experimental apparatus consists of a gas supply unit, an electrical furnace, a vertical stainless steel reactor, an ice bath for water and tar elimination, a dryer for totally wiping off moisture and a gas bag for sampling syngas. The redundant syngas was ignited in air. The stainless steel reactor (120 cm in length, 30 mm I.D.) was placed in the electrical furnace vertically. A plastic tank filled with ice water was used as ice bath, and the first wash bottle was filled with deionized water and another one was filled with some acetone. After the syngas went through a drier, it was collected in a 1 l sample bag.

During the test in fixed-bed, 3 g biomass was used in each experiment and 10 ml min^{-1} of N_2 was used as carrying gas. Defined amount of additive was physically mixed with biomass sample before test, and then loaded into the vertical stainless steel reactor. The temperature in the reactor started from room temperature to desired pyrolysis temperature at a heating rate 15 ~19 °C min^{-1}. Syngas was collected when temperature reached 250 °C, and the total collection time was 20 min for each test. The product gas was analyzed in gas chromatograph (GC). The GC was equipped with a TCD detector, with 60 ml/min He (purity of 99.999%) as carrying gas. The temperature of gasify room, column and detector were 120 °C, 60 °C and 180 °C, respectively. 10 ml of the syngas was injected into the gasify room of the GC for each test by using syringe and external standard method was used to calculate the relative concentration of component gas. The

concentrations of CO, CO_2, CH_4, and H_2 were finally determined by TCD-GC.

The yield of hydrogen (ml $g^{-1}_{-biomass}$) was calculated using the following equation:

$$\text{Hydrogen yield} = \frac{V*t}{\Phi_N} * \frac{\Phi_H}{m} \tag{1}$$

Where V, t, Φ_H, Φ_N, m represents the flow rate of N_2, gas collection time, concentration of H_2, concentration of N_2 and weight of biomass, respectively.
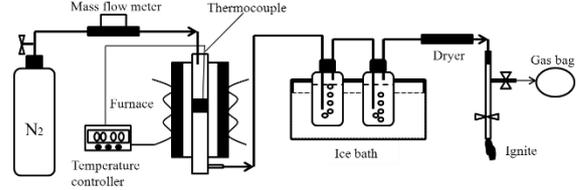

Figure 1. Schematic diagram of fixed-bed reactor system

2.3 Pyrolysis Kinetics

The non-isothermal kinetics equation for solid decomposition reaction can be written as follow:

$$\frac{da}{dt} = kf(a) \tag{2}$$

Where

$$a = \frac{m_0 - m_t}{m_0 - m_f} \tag{3}$$

In Eq. (3), m_0, m_t and m_f represent the initial, instantaneous and final weight of the sample, respectively. The rate constant *k* can be expressed by the *Arrhenius equation*:

$$k = A_0 \exp\left(\frac{-E}{RT}\right) \tag{4}$$

And here the mechanism function *f (a)* is used as follow:

$$f(a) = (1-a)^n \tag{5}$$

Plugging Eq. (4) and Eq. (5) into Eq. (2), we have:

$$\frac{da}{dt} = A_0 \exp\left(-\frac{E}{RT}\right)(1-a)^n \tag{6}$$

For, $\beta = dT/dt$ Eq. (6) can be re-written as:

$$\frac{da}{dt} = \frac{A_0}{\beta} \exp\left(-\frac{E}{RT}\right)(1-a)^n \tag{7}$$

Then, taking a natural logarithm (*ln*) on both sides of Eq. (7) gives:

$$\ln\frac{da}{dT} = \ln\frac{A_0}{\beta} - \frac{E}{RT} + n\ln(1-a) \tag{8}$$

The kinetic parameters, activation energy, pre-exponential factor, and the reaction order of biomass pyrolysis can be determined by linear fitting of the equation:

$$\frac{\Delta \ln\left(\frac{da}{dT}\right)}{\Delta \ln(1-a)} = n - \frac{E}{R}\frac{\Delta \frac{1}{T}}{\Delta \ln(1-a)} \tag{8}$$

3. Results and discussion

3.1 Pyrolysis characteristic of fresh biomass

The decomposition property of the fresh biomass was investigated and results were shown in Fig. 2. As can be seen in Fig. 2(a), largest weight loss of biomass was found in the temperature range of 40~220 °C, and the temperature for the highest decomposition rate was around 140 °C. In this temperature interval, weight loss is mainly from fast release of moisture. The second distinctly weight loss was located in the temperature range of 220~382 °C, and the peak decomposition rate was at temperature of 338 °C. Pyrolysis of hemicellulose, cellulose, and lignin was reported to occur in the following temperature ranges: 150~315, 315~400 and 250~900 °C, respectively (Nowakowski *et al.*, 2007). It indicates that cellulose and hemicellulose are mainly responsible to the second weight loss in temperature range of 220~382 °C. After that, weight loss curve went down slowly till the end and the DTG curve was leveled off. This period should be resulted from slow decomposition of lignin and gasification of char.
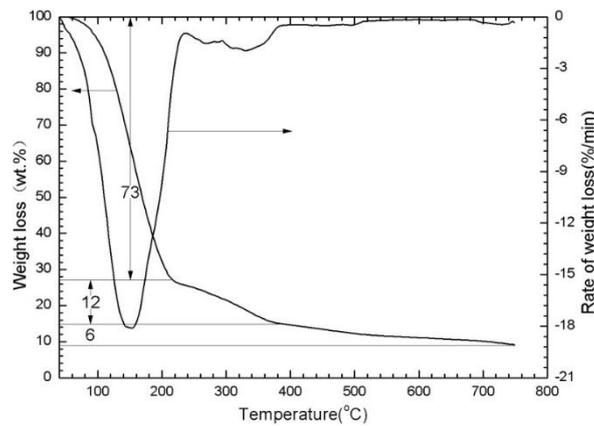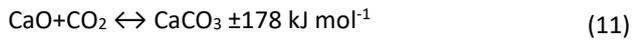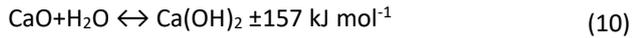

(a)
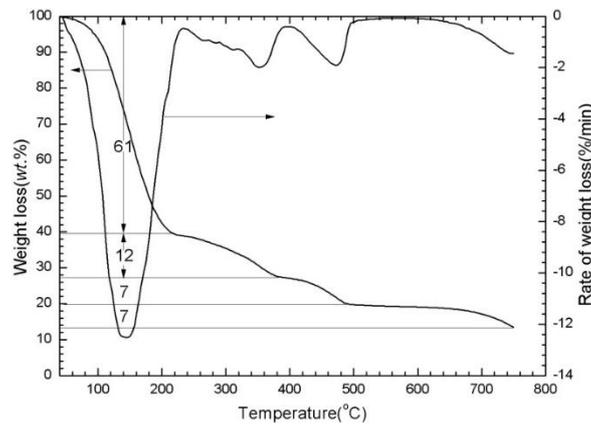
(b)

Figure 2. TG and DTG results of the fresh biomass. (a) Pure biomass; (b) With 30wt. % of CaO

From Fig. 2(b), with addition of CaO, the pyrolysis characteristic of fresh biomass was changed. Weight loss in the temperature range of 40~220 °C was much lower than that from pure biomass, almost decreased by 12*wt*. %. Suitable explanation for this observation can be consumption of moisture released from biomass by hydration of CaO (Eq. (10)) to form $Ca(OH)_2$. Weight loss in the temperature range of 220~382 °C (12*wt*. %) was similar with that of pure biomass. However, there showed an additional fast decrease stage in weight (7*wt*. %) at temperature range of 382~490 °C. That may indicate the happening of the reverse reaction of Eq. (10), for $Ca(OH)_2$ was easy to decompose at temperature higher than 400 °C. The highest decomposition rate was at temperature of 480 °C. The last fast decrease in weight after 700 °C should

be related to the beginning of $CaCO_3$ decomposition (the reverse reaction of Eq. (11)).

$$CaO+H_2O \leftrightarrow Ca(OH)_2 \pm 157 \text{ kJ mol}^{-1} \qquad (10)$$

$$CaO+CO_2 \leftrightarrow CaCO_3 \pm 178 \text{ kJ mol}^{-1} \qquad (11)$$

The kinetic calculations were carried out by using Eq. (9), based on the assumption that the A_0 was a constant in a given temperature range, and we had only done linear fitting to the main decomposition regions of the biomass (except the moisture release region). The calculation results were shown in Tab. 1. It can be seen that with addition of CaO the kinetic parameters were changed. The order of reaction (n) increased from 1.32 to 2.86 when additive was added. Apparent activation energy (*E*) decreased from 29.8 kJ mol^{-1} to 20.4 kJ mol^{-1} which represents a decrease almost by 31%. On the other hand, the reaction order in the temperature of 382~490 °C was 3.04 and with an activation energy of 40.9 kJ mol^{-1}.

Table 1. Kinetic parameters calculated from pyrolysis of fresh biomass with or without CaO

Sample	Temperature range(°C)	*n*	*E* (kJ mol^{-1})	-R^2
Biomass	220~382	1.32	29.8	0.99
Biomass/30	220~382	2.86	20.4	0.98
wt.%CaO	382~490	3.04	40.9	0.89

3.2 Activity test in fixed-bed reactor system

Temperature is the major factor that influences the hydrogen production from pyrolysis of biomass. Fig. 3 shows the dry gas composition and hydrogen yield at four pyrolysis temperatures without additive, from 500 to 800 °C with 100 °C interval. As can be seen that temperature influences pyrolysis mainly by hydrogen production. Hydrogen concentration and yield increased with increasing of temperature.
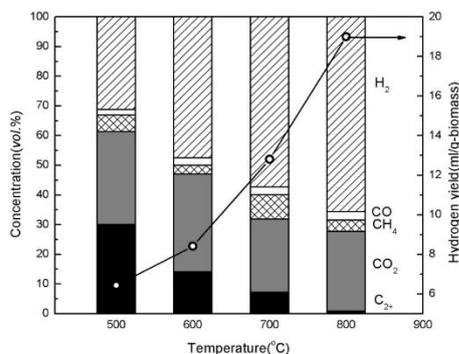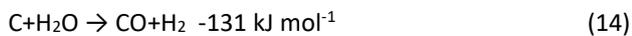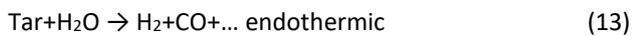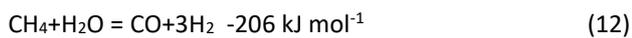
$$CH_4+H_2O = CO+3H_2 \quad -206 \text{ kJ mol}^{-1} \qquad (12)$$

$$Tar+H_2O \rightarrow H_2+CO+\dots \text{ endothermic} \qquad (13)$$

$$C+H_2O \rightarrow CO+H_2 \quad -131 \text{ kJ mol}^{-1} \qquad (14)$$


Figure 3. Gas composition and hydrogen yield at different pyrolysis temperatures.
Biomass weight was 3 g, additive/biomass (*wt*.) was 0, heating rate was 15~19 °C min^{-1}

At 800 °C, hydrogen yield was almost 2.8 times and hydrogen concentration was about 2 times more than that at 500 °C. CO content was slightly increased and CO_2 content was a little decreased with temperature increasing. It is clear that higher pyrolysis temperature benefited the hydrogen production. Methane steam reforming (Eq. (12)), tar elimination (Eq. (13)) and water gas reaction (Eq. (14)) are all endothermic reactions and can be enhanced by increasing of temperature, which may lead to production of more hydrogen.

There is a wide range of catalysts for pyrolysis and gasification of biomass, mainly consist of three categories including: mineral catalyst, alkali metal catalyst and transition metal catalyst (Sutton *et al.*, 2001). Ni-based catalyst is one of the catalysts that are widely used for its high activity on catalyst of methane steam reforming and elimination of tar. CaO is abundant and cheap, its usage in gasification and pyrolysis attracted intensive researches recently for the sorption enhanced hydrogen production (SEHP) (Han *et al.*, 2011). It was also reported that CaO had catalysis on tar reforming (Jordan and Akay, 2013).
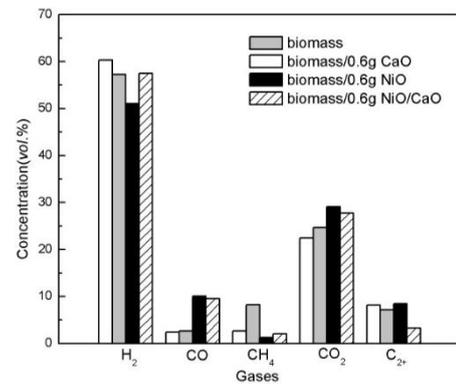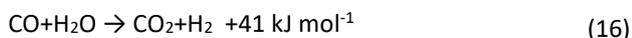

(a)
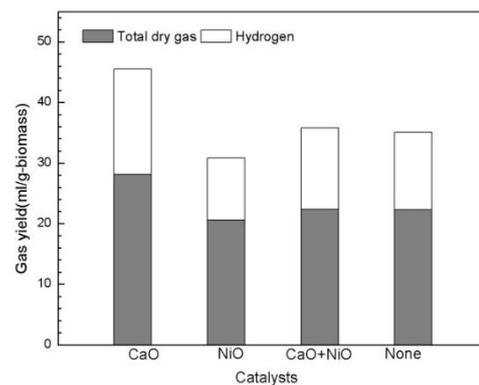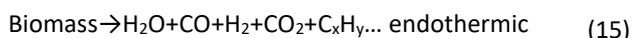

(b)

Figure 4. Effect of additive on biomass pyrolysis. (a) Gas composition; (b) Gas yield; Biomass weight was 3 g, heating rate was 15~19 °C min^{-1}, T=700 °C, additive/biomass was 20*wt*. %

Fig. 4 shows the effect of additive type on pyrolysis of fresh biomass. As can be seen that highest CO concentration (around 10*vol*. %) was obtained with the case of NiO

addition, followed by NiO/CaO. Meanwhile, CO concentration was lowered when biomass co-pyrolysis with CaO. Hydrogen concentration was highest (about 61vol. %) when CaO was added, and at the meantime NiO showed lower activity toward hydrogen production. Methane concentration was highest for pure biomass, around 9vol. %, and lowest for biomass with NiO (only about 2vol. %). Carbon dioxide content was slightly decreased because of CaO addition. Biomass with CaO/NiO showed a compromised gas composition between that of biomass with CaO and NiO only. Fig. 4(b) demonstrated the gas yield through pyrolysis of biomass with different additives. Pyrolysis of pure biomass got total dry gas of around 22 ml g^{-1}$_{-biomass}$. It was increased by 27% when biomass pyrolysis with CaO. Hydrogen yield was highest for the case of CaO addition, and lowest for that with NiO. The hydrogen yield decreased as the order following: [biomass+CaO]>[biomass+CaO/NiO]>pure biomass>[biomass+NiO].

CaO showed highest activity toward hydrogen production, and at the same time, with lowest CO_2 concentration. This result can be due to the enhanced WGS during pyrolysis of biomass with CaO (Guan $et\ al.$, 2007; Florin and Harris, 2008). The reactions take place during pyrolysis in presence of CaO can be written as following:

$$Biomass \rightarrow H_2O + CO + H_2 + CO_2 + C_xH_y \dots endothermic \quad (15)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \ + 41\ kJ\ mol^{-1} \quad (16)$$

$$CO_2 + CaO \rightarrow CaCO_3 \ -178\ kJ\ mol^{-1} \quad (17)$$

According to Le-chattier principle, a reaction would move forward if the partial pressure of the product is less than the partial pressure of reactant (Acharya $et\ al.$, 2010). In the reactor, CO_2 released during pyrolysis was captured by CaO according to reaction (17). This reaction led to decrease of CO_2 partial pressure, and resulted in promotion of reaction (16) to the forward direction.
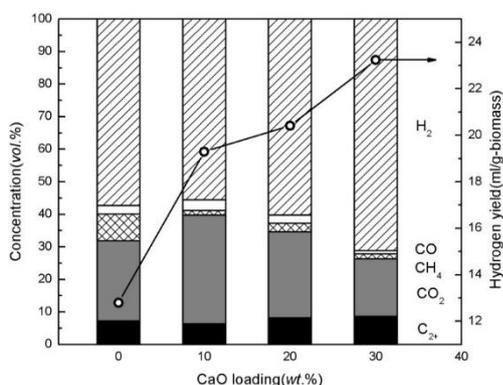

Figure 5 Effect of CaO loading on pyrolysis of fresh biomass.Biomass weight was 3 g, heating rate was 15~19 $^\circ$C min^{-1}, T=700 $^\circ$C

NiO could only play the role as catalyst during pyrolysis, its activity was decreased likely due to large content of moisture and lower temperature in the system. In the meantime, reduction of NiO during pyrolysis caused consumption of reducing gases, such as H_2 and CO. Thus, NiO alone showed no promotion on hydrogen production.

To study the effect of calcium oxide loading on gas composition and gas yield, experiments were done for CaO/biomass mass ratio of 0, 0.1, 0.2 and 0.3 and the results were shown in Fig. 5.

By increasing CaO/biomass from 0wt. % to 30wt. %, the volumetric composition of hydrogen was genarally increased. The highest hydrogen concentration was noted when CaO/biomass was 30wt. % with a value of about 70vol. %. The yield of hydrogen also increased with CaO loading, and it was nearly doubled (from 12.7 to 23.2 ml g^{-1}$_{-biomass}$) as CaO/biomass mass ratio rose from 0 to 0.3. When CaO/biomass was 10wt. %, it was interesting to observe that the percentage of carbon dioxide in dry gas was increased by almost 8vol. % compared with that of 0wt. % addition. Futher higher CaO loading, the CO_2 concentration gradually decreased. CaO appears to have catalytic behavior to break the tar and result in higher gas yield (Luo $et\ al.$, 2009). The suitable explaination could be that 10wt. % of CaO preferentially played a role of catalyst for the sharply reduction of methane concentration (from 10vol. % with CaO/biomass=0wt. % to 1.5vol. % with CaO/biomass=10wt. %). The higher hydrogen yield in CaO/biomass of 10wt. % should be resulted from the higher total dry gas yield, although percentage of hydrogen showed a slight decrease compared with that from pyrolysis of pure biomass. Higher CaO/biomass mass ratio could be helpful in production of hydrogen, not only because the enhanced WGS reaction but also the catalytic effect. On the other hand, the carbonation reaction (Eq. (3)) is exothermic and when it captures carbon dioxide it releases lots of heat at the same time which could benefit the process. The higher temperature results in an improvement in cracking of tar and converting of char (Jiang $et\ al.,$ 2012)

4.   Conclusions

Pyrolysis experiments of fresh biomass (moisture content was nearly 70wt. %) were conducted in a TGA setup and a fixed-bed reactor system. Activation energy of pyrolysis of fresh biomass was 29.8 kJ mol^{-1} and with a reaction order around 1. Addition of CaO lowered the weight loss in moisture release stage and led to form Ca(OH)$_2$. Activation energy of pyrolysis was lowered to 20.4 kJ mol^{-1} and resulted in an additional reduction in weight in temperature range of 382~490 °C when CaO was added. Higher temperature benefited biomass pyrolysis and produced more hydrogen. CaO showed better activity toward hydrogen production than NiO, but NiO showed higher catalysis on methane conversion. CaO/biomass of 30wt. % displayed the highest hydrogen yield. Hydrogen

concentration in dry gas from pyrolysis of fresh biomass displayed apparently high value which proved the possibility of hydrogen production directly from fresh biomass pyrolysis.

References

Ansari M.H., Jafarian S., Tavasoli A., Karimi A. and Rashidi M. (2014), Hydrogen rich gas production via nano-catalytic pyrolysis of bagasse in a dual bed reactor, *Journal of Natural Gas Science and Engineering*, **19**, 279-286.

Alvarez J., Kumagai S., Wu C.F., Yoshioka T., Bilbao J., Olazar M. and Williams T.P. (2014), Hydrogen production from biomass and plastic mixtures by pyrolysis-gasification, *International Journal of Hydrogen Energy*, **39**, 10883-10891.

Acharya B., Dutta A. and Basu P. (2010), An investigation into steam gasification of biomass for hydrogen enriched gas production in presence of CaO, *International journal of hydrogen energy*, **35**, 1582-1589.

Bulushev D.A. and Ross J.R.H. (2011), Catalysis for conversion of biomass to fuels via pyrolysis and gasification: A review, *Catalysis Today*, **171**, 1-13.

Çağlar A. and Demirbaş A. (2002), Hydrogen rich gas mixture from olive husk via pyrolysis, *Energy Conversion and Management*, **43**,109-117.

Corella J., Toledo J.M. and Padilla R. (2004), Catalytic hot gas cleaning with monoliths in biomass gasification in fluidized beds. 1. Their effectiveness for tar elimination, *Industrial & Engineering Chemistry Research*, **43**, 2433-2445.

Florin N.H. and Harris A.T.(2008), Enhanced hydrogen production from biomass with in situ carbon dioxide capture using calcium oxide sorbents, *Chemical Engineering Science*, **63**, 287-316.

Guan J., Wang Q., Li X., Luo Z. and Cen K.(2007), Thermodynamic analysis of a biomass anaerobic gasification process for hydrogen production with sufficient CaO, *Renewable Energy*, **32**, 2502-2515.

Han L., Wang Q.H., Yang Y.K., Yu C.J., Fang M.X. and Luo Z.Y. (2011), Hydrogen production via CaO sorption enhanced anaerobic gasification of sawdust in a bubbling fluidized bed, *International journal of hydrogen energy*, **36**, 4820-4829.

Hao Q.L., Wang C., Lu D.Q., Wang Y., Li D. and Li G. (2010), Production of hydrogen-rich gas from plant biomass by catalytic pyrolysis at low temperature, *International Journal of Hydrogen Energy*, **35**, 8884-8890.

Jiang H.T., Wu Y.R., Fan H. and Ji J.B. (2012), Hydrogen Production from Biomass Pyrolysis in Molten Alkali, *AASRI Procedia*, **3**, 217-223.

Jordan C.A. and Akay G. (2013), Effect of CaO on tar production and dew point depression during gasification of fuel cane bagasse in a novel downdraft gasifier, *Fuel Processing Technology*, **106**, 654-660.

Kuan W.H., Huang Y.F., Chang C.C. and Lo S.L. (2013), Catalytic pyrolysis of sugarcane bagasse by using microwave heating, *Bioresource Technology*, **146**, 324-329.

Liu S.M., Zhu J.L., Chen M.Q., Xin W.P., Yang Z.L. and Kong L.H. (2014), Hydrogen production via catalytic pyrolysis of biomass in a two-stage fixed bed reactor system, *International Journal of Hydrogen Energy*, **25**, 13128-13135.

Luo S.Y., Xiao B., Guo X.J., Hu Z.Q., Liu S.M. and He M.Y. (2009), Hydrogen-rich gas from catalytic steam gasification of biomass in a fixed bed reactor: influence of temperature and steam on gasification performance, Technical Communication, *International Journal of Hydrogen Energy*, **34**, 1260-1264.

Nasir Uddin M., Wan Daud W.M.A. and Abbas H.F. (2013), Potential hydrogen and non-condensable gases production from biomass pyrolysis: Insights into the process variables, *Renewable and Sustainable Energy Reviews*, **27**, 204-224.

Nowakowski D.J., Jones J.M., Brydson R.M.D. and Ross A.B. (2007), Potassium catalysis in the pyrolysis behavior of short rotation willow coppice, *Fuel*, **86**, 2389-2402.

Sutton D., Kelleher B. and Ross J.R.H. (2001), Review of literature on catalysts for biomass gasification, *Fuel Processing Technology*, **73**, 155-173.

Veses A., Aznar M., Martínez I., Martínez J.D., López J.M., Navarro M.V., Callén M.S., Murillo R. and García T. (2014), Catalytic pyrolysis of wood biomass in an auger reactor using calcium-based catalysts, *Bioresource Technology*, **162**, 250-258.

Zhang L., Zhang B., Yang Z.Q. and Yan Y.F. (2014), Pyrolysis Behavior of Biomass with Different Ca-based Additives, *RSC Adv*, **4**, 39145-39155.

Zhang L., Zhang B., Yang Z.Q. and Guo M.N. (2015), The Role of Water on the Performance of Calcium Oxide-Based Sorbents for Carbon Dioxide Capture: A Review, *Energy technology*, **1**, 10-19.