Lab-based Experimental Study and Simulation of Pyrolysis and Gasification of Biomass and Waste Plastics for H_2 Production

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Abstract

Energy security and environmental pollution are becoming important issues worldwide. Pyrolysis/gasification of biomass and plastics is an ideal method for H_2 production to solve these two problems. The aim of this paper is to develop a new dual-support catalyst Ni-CaO-C to improve H_2 production through experiments and to develop a model based two-stage fixed bed for pyrolysis/gasification. In experiment study section, different catalysts (Ni-Al$_2$O$_3$, Ni-CaO, Ni-C and Ni-Cao-C with different support ratio) were compared to test the performance of new Ni-CaO-C catalyst. Results indicates that only catalysts Ni-CaO-C have good performance to achieve high H_2 yield and composition simultaneously. The best H_2 production was achieved by catalyst Ni-CaO-C (Ni: 10wt%, CaO:C=5:5) with H_2 yield and composition 115.33 mmol/g and 86.74 mol%. In simulation study section, a two-stage bed reactor was developed and validated for pyrolysis/gasification of biomass and plastics using Aspen Plus®. Results show that the developed model can predict the products yield correctly compared to previous experimental data.

Keywords: Experiment; Simulation; Pyrolysis/gasification; Biomass; Plastics

1. Introduction

With development of human society, two concerns of energy security and environmental pollution occur and generally become severe problems worldwide (Jacobson, 2008). Energy security is caused by excessive exploration of unrenewable fossil fuels. Environmental pollution is caused by wastes generated after consuming considerable fossil fuels for power generation, manufacturing and transportation. Therefore, a renewable and clean energy source is required to solve these two problems. H_2 is a promising energy source to substitute traditional fossil fuels.

Pyrolysis/gasification of mixture of biomass and plastics for H_2 production is a good solution. Biomass is renewable and carbon-neutral resource (Wu et al., 2015). Plastics is discarded with huge quantity every year and it is hard to naturally decompose waste plastics. However, plastics can be totally decomposed during pyrolysis within seconds. The synergic effect between biomass and plastics has been demonstrated to promote process of pyrolysis/gasification. For example, plastics can increase the H/C ratio of feestocks mixture, which is effective to improve H_2 production and restrict char production (Alvarez et al., 2014).

The first motivation of this paper is to synthesise new catalyst to improve H_2 production. With development of co-pyrolysis/gasification technology, to develop

new catalyst with high catalytic activity is a new research hot topic (Kwon et al., 2018). Pyrolysis/gasification experiments without catalyst encounter problems of high tar yield and low H_2 yield in gaseous products. Introduction of catalyst can promote reforming and cracking reactions effectively to solve these two problems for higher H_2 production.

The second motivation of this paper is to carry out simulation study for pyrolysis/gasification of biomass and plastics. Obvious conveniences are provided when simulation results are obtained within seconds using software, which saves considerable time and resources to carry out experiments in reality (Olaleye et al., 2014).

The aim of this study is to develop a new dual-support catalyst Ni-CaO-C for pyrolysis/gasification of biomass and plastics and to evaluate the catalytic activity and CO_2 adsorption capability of the new catalyst. Furthermore, a model based two-stage fixed bed reactor is developed and validated using Aspen Plus® as preparation for further simulation study about pyrolysis/gasification.

2. Experimental study of new catalyst Ni-CaO-C for H2 production
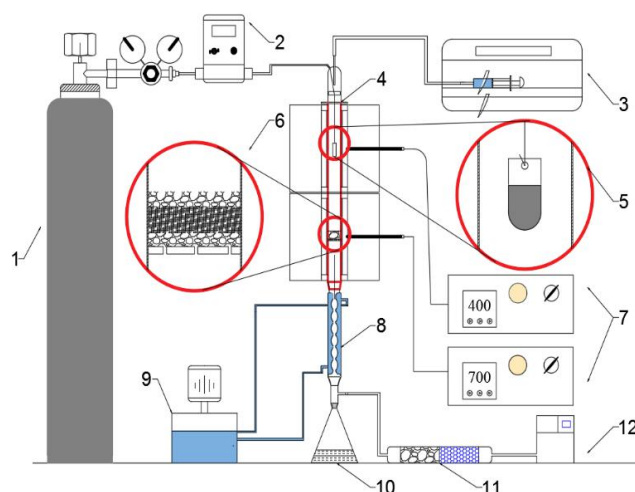
2.1 Materials and methods

Figure 1 Two-stage fixed bed pyrolysis/gasification system (Gao et al., 2018)(1. Nitrogen cylinder, 2. Mass flowmeter, 3. Microinjection pump, 4. Quartz reaction tube and heating furnaces (***Top: pyrolysis stage; Bottom: reforming stage***), 5. Quartz crucible, 6. Catalytic layer: quartz wool + catalyst, 7. Temperature controllers, 8. Condenser pipe, 9. Cooling water and water pump, 10. Conical flask, 11. Dryer, 12. Gas chromatography)

Pine sawdust and low density polyethylene (LDPE) were used as feedstock in this experiment. Rising pH method was used to synthesise new catalyst Ni-CaO-C in this study. The details of ultimate analysis and proximate analysis of feedstocks, other used chemicals and catalyst preparation procedures are shown in our previous paper (Chai et al., 2019). The experiments of pyrolysis/gasification of biomass and plastics were carried out in a two-stage fixed bed reactor (see Figure 1). Mixture of biomass and plastics is put in the top stage and catalyst is put in the bottom stage. Water is

used as gasification agent. Specific experiment procedures are summarised in our previous paper (Chai et al., 2019).

2.2 Influences of CaO:C and support type on catalyst performance

Table 1. List of experiment plan

Exp. Number	(1)	(2)	(3)	(4)	(5)
Ni load (wt%)	10%	10%	10%	10%	10%
CaO : C (weight ratio)	10:0	7:3	5:5	3:7	0:10

* In Exp. (6), Ni-Al$_2$O$_3$ catalyst was used. Ni load is still 10 wt% and Al$_2$O$_3$ is used as support, which is prepared using wet impregnation method. **For Exp. (1) ~ (6), operating conditions are listed here: feedstock ratio (Biomass:Plastic) 5:5; T of pyrolysis stage 700 ºC; T of reforming stage 600 ºC; water injection flowrate 5 mL/h.

The specific experiment plan is listed in Table 1 and the experiment results are shown in Figure 2. From Figure 2, when only CaO was used as catalyst support (i.e. CaO:C=10:0), the H$_2$ composition is 88.89 mol% and the H$_2$ yield is 33.20 mmol/g. Correspondingly, when only activated carbon was used as support (i.e. CaO:C=0:10), the H$_2$ composition is 69.84 mol% and the H$_2$ yield is 153.09 mmol/g. It can be concluded that CaO is effective to improve H$_2$ composition and activated carbon is effective to improve H$_2$ yield. To explain this phenomenon, following explanations are provided:
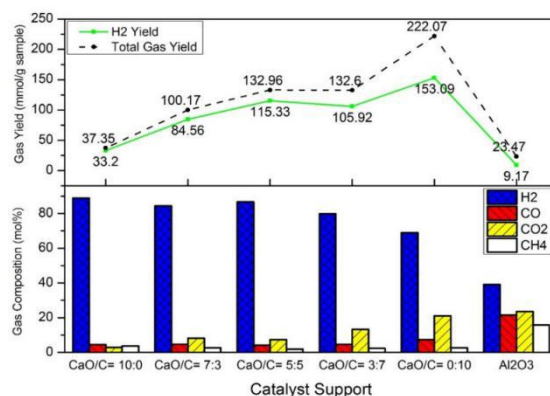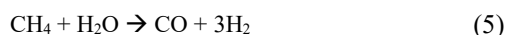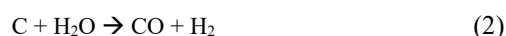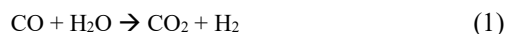

Figure 2 Gas compositions and yields when changing CaO:C ratios and support type

CaO has great CO$_2$ adsorption capability, which is key to influence H$_2$ composition from two aspects. Firstly, generated CO$_2$ can be adsorbed by CaO effectively. This can be reflected by the low CO$_2$ composition of using catalyst Ni-CaO (2.87 mol%) compared to the high CO$_2$ composition using catalyst Ni-C (21.09 mol%). Therefore, the H$_2$ composition is promoted to improve directly due to decreasing CO$_2$ composition. Secondly, according to thermodynamic, the decreasing CO$_2$ composition can result in chemical equilibrium of Water-gas-shift (WGS) reaction (*1*) moving toward generating more H$_2$, which increases H$_2$ composition furthermore.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (1)$$

$$C + H_2O \rightarrow CO + H_2 \qquad (2)$$

$$C + CO_2 \rightarrow 2CO \qquad (3)$$

$$C + 2H_2 \rightarrow CH_4 \qquad (4)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (5)$$

Activated carbon has great ability to influence gas yield due to its unique physical and chemical properties. Firstly, activated carbon is active to participate in series of reactions in reforming stage. Activated carbon directly joins in Water-Gas reaction (*2*) to generate H_2 to increase H_2 yield. Activated also joins in Boudouard reaction (*3*) and methanation reaction (*4*) to promote yields of CO and CH_4, which are reactants of WGS and Steam-methane-reforming (SMR) reaction (*5*). This helps to increase H_2 yield furthermore. Secondly, activated carbon has good pore structure as catalyst support with high specific area. Considerable inner space can be provided to load more active core, which improves gas yield. Thirdly, activated carbon itself has perfect reduction ability. It can reduce the active core from NiO into Ni during catalyst calcination. Ni has better catalytic activity than NiO in accelerating reactions, thus the total gas yield could be promoted effectively. This is consistent with the results in Figure 2, the total gas yield of using catalyst Ni-C is 222.07 mmol/g, which is nearly 7 times higher than that using catalyst Ni-CaO.

Therefore, a new idea is put forward to attach Ni on combination of CaO and activated carbon to realise high H_2 production with high yield and composition simultaneously. Three types of new Ni-CaO-C catalyst with different support ratios (CaO:C= 3:7, 5:5 and 7:3) were selected to test the performance. From Figure 2, the H_2 compositions for catalysts with support ratios of 3:7, 5:5 and 7:3 are 84.41 mol%, 86.74 mol% and 79.88 mol%. The H_2 yields for catalysts with support ratios of 3:7, 5:5 and 7:3 are 84.56 mmol/g, 115.33 mmol/g and 105.92 mmol/g. All the three Ni-CaO-C catalysts show relatively high H_2 composition and yield at the same time.
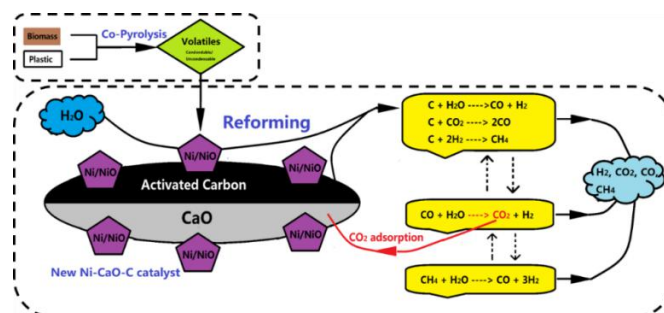

Figure 3 Synergic effect of catalyst Ni-CaO-C for pyrolysis/gasification of biomass and plastics (adapted from Kumagai et al., 2015)

Synergic effect of different components including active core Ni and two catalyst supports CaO and activated carbon results in good performance of Ni-CaO-C (Figure 3). After co-pyrolysis of biomass and plastics in top stage, volatiles are generated and transferred into the bottom stage to contact catalyst Ni-CaO-C. Ni and activated carbon function to improve the total gas yield (including H_2 yield). Although increasing H_2 yield can contribute to H_2 composition increase, the simultaneously

increasing of other gas yields may offset the improvement of H_2 composition. Therefore, CaO serves to remove CO_2 from product gas to promote H_2 composition and WGS reaction. That is how the three components of catalyst Ni-CaO-C synergise to improve the H_2 yield and composition.

Ni-Al_2O_3 is one of the mostly used traditional catalysts for pyrolysis/gasification experiments. In this study, pyrolysis/gasification of biomass and plastics under catalyst Ni-Al_2O_3 (Ni 10 wt%) was also performed to compare with new catalyst Ni-CaO-C. From Figure 2, the H_2 yield and composition using catalyst Ni-Al_2O_3 are only 9.17 mmol/g and 39.09 mol%. Alvarez et al (2014) carried out pyrolysis/gasification of polypropylene and pine sawdust under 800 °C reforming temperature using catalyst Ni-Al_2O_3. In their study, the H_2 yield and composition were 27.7 mmol/g and 52.10 mmol%. It can be concluded that new catalyst Ni-CaO-C has much better performance to promote H_2 yield and composition compared to catalyst Ni-Al_2O_3, demonstrating the advanced properties of dual supports CaO and activated carbon.

3. Simulation study of pyrolysis/gasification of biomass and plastics

3.1. Model development

The flowsheet of the developed model is shown in Figure 4. From Figure 4, it can be observed that the whole pyrolysis/gasification reactor is separated to be simulated in three parts, which are pyrolysis, reforming and gas separation respectively. The specific explanations of each part are summarised as following:

(i) In pyrolysis part, biomass and plastics are decomposed separately using two RYield reactor blocks (**BIOYIELD** and **PLAYIELD**). For both biomass and plastics, they are decomposed into different phases of products such as gas products (CO, CO_2, CH_4), water, tar (C_6H_6, C_7H_8, C_6H_6O and $C_{10}H_8$) and char by imputing specific product yields in RYield reactor block. The specific input yields can be obtained from measuring yields of various products in real experiments. A mixer (**MIX-1**) is used to combine the pyrolysis products of two feedstocks. Then, a separator block (**SEP-1**) is used to remove char in products and only the rest compositions including gases, water and tar are transferred to reforming part.

(ii) In reforming part, three CSTR reactor models are used simulate catalytic heterogeneous reactions (**REC-CATA**), normal heterogeneous reactions (**REC-HOM**) and oxidation reactions (**REC-OXD**). Series of reactions with known reaction kinetics are input to CSTR reactor models to predict product yields.

(iii) After reforming reactions, the products enter two separator blocks eventually. The first separator (**SEP-2**) is used to separate non-condensable products including syngas and considerable products. The second separator (**SEP-3**) is used to separate water and unreacted tar components.
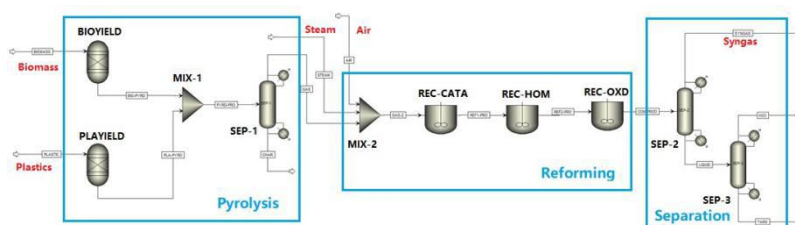

Figure 4 Flowsheet of pyrolysis/gasification of biomass and plastics
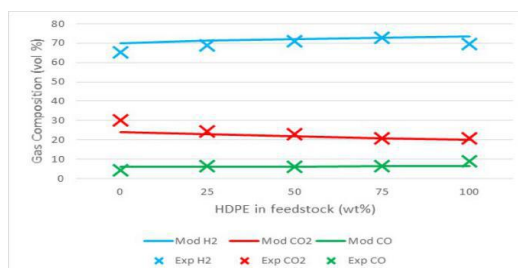
3.2. Model validation

Figure 5 Results of model validation

After model development, the gas compositions of products H_2, CO and CO_2 when changing feedstock ratios of biomass and plastics are compared with experimental results in the study of Arregi et al (2017) for validation. The results of model validation are shown in Figure 5. From Figure 5, it can be observed that the relative errors between results from developed model and experimental results are relatively small, which demonstrates the correctness of developed model to predict real process of pyrolysis/gasification of biomass and plastics.

4. Conclusion and future study

In this study, lab-based experimental study and simulation study were carried out to investigate H_2 production from pyrolysis/gasification of biomass and plastics. In experimental study section, new catalyst Ni-CaO-C was developed. Its catalytic activity and CO_2 adsorption capability were also tested by comparing with other catalysts with different support ratios or type. Results indicate that new catalyst Ni-CaO-C has perfect catalytic ability and CO_2 adsorption capacity. Compared to other catalysts Ni-CaO, Ni-C and Ni-Al_2O_3, catalyst Ni-CaO-C has the best performance to promote H_2 production with high H_2 composition and yield simultaneously. The best performance of catalyst Ni-CaO-C was achieved with H_2 yield and composition 115.33 mmol/g and 86.74 mol% when Ni load is 10 wt% and support ratio is CaO:C = 5:5. In simulation study section, a two-stage bed reactor was developed and validated for pyrolysis/gasification of biomass and plastics using Aspen Plus®. Results show that the developed model can predict the products yield correctly compared to previous experimental data.

In our future study, more detailed modelling and simulation studies will be carried out to simulate the process of pyrolysis/gasification of biomass and plastics depending on our experimental studies. One important research objective is to achieve simulating function of catalyst Ni-CaO-C accurately.

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