Applied Multifunctional Material by Pelletization for Hydrogen Production from By-product of Biodiesel Process

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Abstract

Biodiesel is renewable energy that has received much attention due to the depletion of fossil energy. Biodiesel can be produced from two processes: Fatty Acid Methyl Esters (FAME) and Bio-hydrogenated diesel (BHD). However, apart from biodiesel production, amount of by-products: glycerol (from FAME Process), methane and propane (from BHD process) are obtained. This research is therefore interested in converting these by-products to higher value by transforming into hydrogen or syngas via sorption-enhanced steam methane reforming, which can be used as a substrate in the BHD process. The main objective of the research is focused on developing multifunctional materials, sorbent/catalyst, in pellet form for the process. To pelletize the multifunctional materials; the effect of shape of multifunctional material and amount of binder were investigated. Properties of the synthesized multifunctional sorbent/catalyst material were characterized by X-ray diffraction (XRD), and scanning electron microscope (SEM). Performances of the system were analyzed in terms of %conversion of reactant, H_2 selectivity, H_2 yield. The results showed that multifunctional sorbent/catalyst containing NiO-CaO/Al_2O_3 could produce hydrogen with purity higher than 80% for spherical form.

Keywords: Multifunctional material, Hydrogen production, Steam methane reforming, Sorption-enhanced reaction

1. Introduction

Currently, renewable energy is one option that has received much attention for replacement of fossil energy. The Biodiesel is renewable energy which can be produced by biomass. It can be produced from main process, Fatty Acid Methyl Esters (FAME) or Bio-hydrogenated diesel (BHD). For the bio-hydrogenated diesel (BHD) process, H_2 is required for hydrodeoxygenation reaction and hydrodecarbonylation reaction. Methane is one of by-product in gas phase that can occur as by-product from BHD process. To improve process performance in term of energy requirement self-sufficient can be obtained by transform methane to hydrogen production to use in the BHD process (Donnis et al., 2009). With concerns of both process performances and environmental impact, sorption-enhanced steam methane reforming (SE-SMR) has been developed for the production of hydrogen. Combining catalyst and sorbent into one body call multifunctional material is a technique used for SE-SMR process. Ni-based catalyst is mostly used for steam methane reforming because it has high catalyst activity, and cheap when compare with noble metal-based catalysts such as platinum and ruthenium. CaO is used for CO_2 sorption due to high CO_2 sorption capacity (Arcotumapathy et al.,2014; Martavaltzi and Lemonidou, 2010; Martavaltzi et al.,2011; Xu et al., 2016). However, synthesized multifunctional material is mostly in powder, which can cause pressure drop effect during operation. To solve this problem, using catalyst in pelletized form can reduced drop within reactor. The main objective of the research is focused on developing multifunctional materials, sorbent/catalyst in pellet form for hydrogen production via sorption enhanced steam methane reforming. To pelletize the multifunctional materials; the effect of composition of multifunctional material was investigated.

2. Materials and Methods

2.1. Multifuntional material synthesis and characterized

NiO-CaO/Al_2O_3 was synthesized using sol-gel method followed by co-precipitation with using urea as metal dispersion medium. Firstly, $Al(NO_3)_3 \bullet 9H_2O$ and $Ca(NO_3)_2 \bullet 4H_2O$ was using as precursor and CaO/Al_2O_3 was synthesized by Zhao et al., 2016, of which amount of CaO and Al_2O_3 were varied: xCaO/yAl_2O_3 wt% ratio when x is 30,40,60,70wt%ofCaO. xCaO/yAl_2O_3 was calcined at 850^oC for 2 hr in air flow prepare for next step. After that, NiO was using as catalyst for steam reforming reaction by co-precipitation with urea and CaO/Al_2O_3 (Li et al., 2008) The Ni loading in the CaO/Al_2O_3 was maintained at 15 wt%. The NiO-CaO/Al_2O_3 were characterized by X-ray diffraction (XRD) to determine crystallinity and compositions, and Scanning Electron Microscope (SEM) to examine the morphology and characteristics of the samples.

2.2. Pelletization of multifuntional material

The NiO-CaO/Al_2O_3 samples were pelletized into 4 mm in diameter sphere shape. The ratio of powder to water are fixed 3g of NiO-CaO/Al_2O_3 to 4 ml of H_2O. The pellet was tested their thermal stability by exposure at for 850^oC 1 hr and mechanical was carried by test by Universal testing machine (QC-506M1-204, Comtech).

2.3. Hydrogen Production Test

Sorption-enhanced steam methane performance was carried out by using fixed-bed quartz reactor (i.d.11mm) in Fig. 1. The NiO-CaO/Al_2O_3 was fixed at 0.5 g in fixed-bed reactor. Prior to running experiment, NiO-CaO/Al_2O_3 was pretreated by Ar with flow rate of 40 ml/min at 850°C for 60 min followed H_2/Ar (50%v/v H_2) at 850°C for 60 min using total flow rate 40 ml/min were used for the reaction. SESMR conditions: steam to methane ratio of 3 at 650°C atmospheric pressure and total flow rate 40 ml/min. The dry gas outlets were analyzed by gas chromatography installed with thermal conductivity detector (TCD).

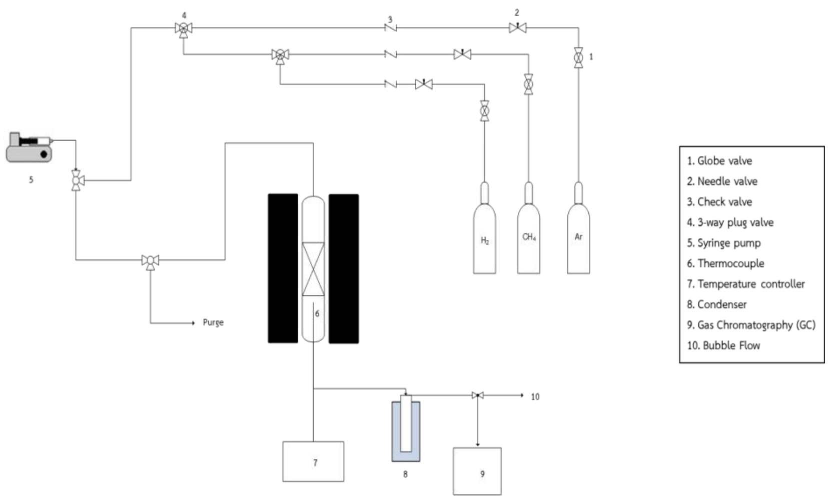

Fig.1 Flow diagram of experimental setup for Hydrogen production from SESMR.

3. Results and Discussions

3.1. Multifunctional material characterization

In Fig.2 shows XRD patterns of the synthetic multifunctional materials, NiO-CaO/Al_2O_3 containing different CaO/Al_2O_3 wt% ratios: (a) in powder and (b) spherical. In Fig.2(a) the results show XRD peaks corresponding to NiO, CaO, $Ca_{12}Al_{14}O_{33}$ $Ca(OH)_2$, and Al_2O_3. In Fig. 2(b) is shown XRD of pellet materials. The phase of multifunctional material in pellet was altered from their corresponding powder. This might be due to the effect of water content in pellet. The results spherical show XRD peaks include of NiO, CaO, $Ca_{12}Al_{14}O_{33}$, $Ca(OH)_2$, $Ca_3Al_2O_6(H_2O)_6$, and $NiAl_{10}O_{16}$/$5Al_2O_3$NiO. It is noted that 15wt%Ni-30CaO/70Al_2O_3 cannot form spherical pellet, this could be due to lower amount of CaO and hence less ability to form $Ca_{12}Al_{14}O_{33}$ that acts as a binder.

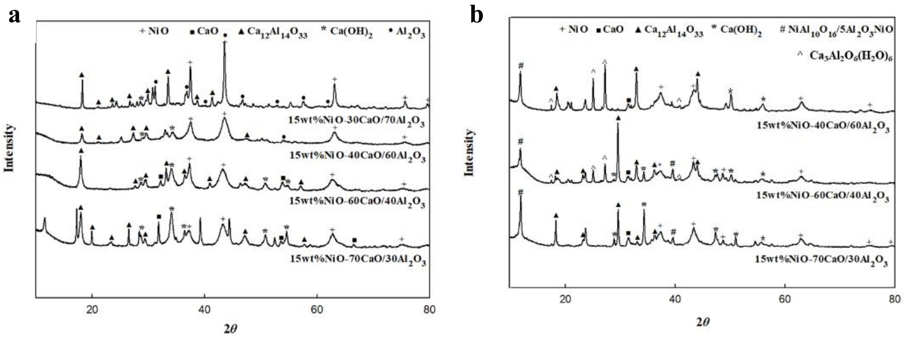

Fig.2 XRD patterns of fresh samples containing different CaO/Al_2O_3 weight ratios of 15wt%NiO-xCaO/yAl_2O_3 for: (a) powder and (b) spherical pellet.

In term of pellet crushing strength as depicted in Table 1, increasing of CaO/Al_2O_3 %wt ratio shows an enhancement of crushing strength of materials.

Table 1 Summary of crushing strength results various CaO/Al_2O_3 %wt ratio.

Sample	Shape	
	Powder	Sphere (N)
15wt%Ni-30CaO/70Al_2O_3	-	- [a]
15wt%Ni-40CaO/60Al_2O_3	-	14.9
15wt%Ni-60CaO/40Al_2O_3	-	80.6
15wt%Ni-70CaO/30Al_2O_3	-	76.1

[a] cannot be pelleted form.

The effect of CaO/Al_2O_3 weight ratio on the performance of SESMR process was demonstrated in Fig. 3. Methane conversion reaches about 90% for all samples investigated in this study. The 15wt%Ni-70CaO/30Al_2O_3 shows long pre-breakthrough to time at 90% of H_2 selectivity in powder form due to high CaO content. Spherical form shows similar result as observed with powder. However, pre-breakthrough period does not observe with 15wt%NiO-30CaO/70Al_2O_3, which is due to lower amount of CaO.

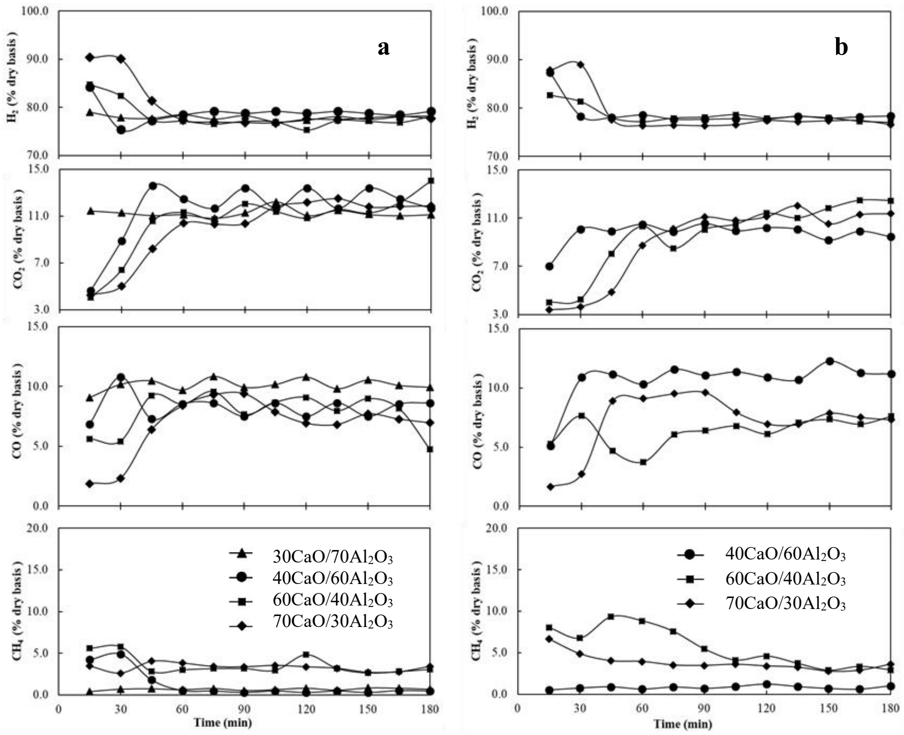

Fig.3 Product gas compositions (dry basis) of sorption-enhanced steam methane reforming (SESMR) of various CaO/Al_2O_3 ratio on 15wt%NiO-xCaO/yAl_2O_3 on shape : (a) powder and (b) sphere at conditions: S/C=3, 650^{o}C, 1 atm.

4. Conclusions

The multifunctional material, 15wt%Ni-70CaO/30Al_2O_3 provides the highest of 90% H_2 selectivity in powder form and spherical form. Our results demonstrate that multifunctional material can be applied for large scale application as the performance in pellet forms is similar to the powder form.

5. Acknowledgements

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