



Hydrogen rich gas production via nano-catalytic pyrolysis of bagasse in a dual bed reactor



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ABSTRACT

Pyrolysis of bagasse followed by nano-catalytic cracking of tar was carried out at atmospheric pressure using a dual bed micro reactor. The first bed was used for pyrolysis and the second bed was used for cracking of tar. Bimetallic 12%Ni6%Fe/ γ -Al₂O₃ nano catalysts were prepared using microemulsion technique with water-to-surfactant ratios of 1–5. The catalysts were characterized by ICP-AES, BET, XRD, H₂ chemisorption, TPR and TEM techniques and their activity and selectivity in bagasse pyrolysis were assessed. The physico-chemical properties and performance of the nano catalysts were compared with the catalyst prepared by impregnation method. The TEM images showed that small metal nanoparticles are dispersed on the surface of support in the range of 3–5 nm. Using microemulsion technique with water to surfactant ratio of 1 decreased the average metal particle sizes to 3.7 nm. The percentage reduction and percentage dispersion are almost doubled. A gas richer in hydrogen (15.3 mol.%) and carbon monoxide (45.7 mol.%) and poorer in carbon dioxide (31.6 mol.%) and hydrocarbons were produced through microemulsion synthesized nano-catalysts. The proposed catalyst prepared with microemulsion (water-to-surfactant ratios of 1) increased the gas yield from 0.397 to 0.758 (m³/kg) and decreased the tar yield from 0.445 to 0.237 (g/g of biomass) compared to noncatalytic process while the heating value of the product gas remained almost constant (10–11 MJ/m³).

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1. Introduction

Renewable energy sources are highly desirable in this era due to dwindling petroleum reserves and increasing environmental concerns (Huber et al., 2006). Several alternatives of renewable fuels, such as ethanol and biodiesel, are currently being exploited in order to promote a more sustainable development (Mas et al., 2008a, 2008b; Mariniño et al., 2001; Cortright et al., 2002). In this regard, the interest on the conversion of biomass to hydrogen has increased considerably during the last several years. Biomass is a potential energy resource (Tanksale et al., 2010; Wang et al., 2008) and there are several pathways to generate energy from it (e.g. physical, thermal, chemical and biological conversion). By the preceding methods, biomass could be converted to heat, electricity, solid fuels (coal), liquid fuels (bio-oil, methanol and ethanol) and gas fuels (hydrogen and syngas), respectively. Having no trace amount of nitrogen and ash, the biomass is considered as a clean

alternative source, which can be an excellent substitute for conventional fuels.

Pyrolysis and gasification are important to reform solid and liquid hydrocarbons to clean gaseous fuel which can be further processed to obtain clean and pure gaseous fuels or liquid fuels. Pyrolysis is thermal degradation process of organic compounds in the absence of oxygen or air to produce various gaseous components as well as tar and char residues (Ahmed and Gupta, 2009). Unlike gasification, pyrolysis is a process that occurs in the absence of oxygen and plays an important role on production of hydrogen-rich gas. Several previous studies have discussed the performance of biomass pyrolysis processes in presence and absence of catalysts (Kumar et al., 2009; Lv et al., 2004; Li et al., 2007). Furthermore, the ordinary pyrolysis results in significant amounts of char and tar during syngas production. Use of catalysts can affect further cracking of long chain hydrocarbons and reducing the amount of tar. Zeolite is mainly used as catalyst in catalytic pyrolysis of biomass. ZSM-5 is one of the most common zeolites in cracking of tar. Samolada et al. (2000) have used HZSM-5 zeolites as catalysts for pyrolysis of biomass and found that introduction of HZSM-5 to the reactor used for non-catalytic biomass pyrolysis led to decrease

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of the concentration of liquid products and increase of the quantity of gaseous products. This might be expected as the application of catalysts gives cracking, leading to a decrease of the molecular weight of the product molecules. Yorgun and Simsek (2008) have studied the effect of alumina addition to ZSM-5 on the pyrolysis of miscanthus grass. They showed that the content of aliphatic and aromatic hydrocarbons was increased as compared with non-catalytic pyrolysis; however, the oxygen content in the product was high.

There is a surplus bagasse in all over the world which has not been completely utilized in other industries such as paper, cattle feed, furfural and MDF, etc. Annually, more than six hundred thousand tons of bagasse is burned in Haft Tappe Industries Company in Iran, which creates serious environmental problems and wastes huge amount of energy. The ash content of bagasse is much lower than for other agricultural biomasses. Bagasse ash is relatively lower than other agricultural biomass. Theoretical calculations show that about 60–100 g of hydrogen can be produced by one kilogram of bagasse. The heating rates of the sample, pyrolysis temperature, catalyst type, catalysts' active metal size and distribution have important effects on the products evolved and their distribution during pyrolysis (Ahmed and Gupta, 2009).

Recent studies have represented structure-sensitivity of many catalysts. The size of nanoparticles is critical in determining catalytic properties, and understanding how size affects their catalytic properties remains a central goal in nano catalysis research. The dynamic surface restructuring of nanoparticles also depends on their size: smaller nanoparticles have higher surface energies and thus are more prone to surface reconstruction, which can lead to different catalytic dynamics for various nano particle sizes. Since the catalytic properties of nanoparticles depend on the size, nanoparticles with different sizes are expected to have a diverse catalytic activity and possibly different selectivity.

In this study to maximize bagasse pyrolysis efficiency, the effects of metal average particle size on the physico-chemical properties and performance of Ni–Fe/ γ -Al₂O₃ catalyst in a fixed bed reactor is investigated. The activity and products selectivity are also correlated with the properties of the catalysts. Ni–Fe/ γ -Al₂O₃ catalysts for catalytic pyrolysis of bagasse have been prepared by microemulsion technique. All the catalysts were characterized by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Brunauer–Emmett–Teller method (BET), X-ray diffraction (XRD), hydrogen absorption, temperature program reduction (TPR), and transmission electron microscopy (TEM). The main objective of the present work is preparing a nano catalyst that can optimize the hydrogen yield in pyrolysis of bagasse.

2. Materials and methods

2.1. Feed materials

The biomass particles used for the experiments were obtained as shavings, from Haft-Tappe Industries located at Haft-Tappe, Khuzestan province, Iran. The biomass was dried and grounded to a particle size ≤ 1 mm in diameter. The elemental composition of the whole biomass sample was analyzed using a CHNS analyzer.

2.2. Catalyst preparation

Condea Vista Catalox B γ -alumina (212.4 m²/g, impurities: Sodium oxide (Na₂O) < 0.05 (ppm); Silica (SiO₂) < 0.9 (ppm); Sulfate (SO₄) < 1.5 (ppm)) was used as support for preparation of the catalysts. Prior to catalyst preparation, the support was calcined at 400 °C for 4 h. After the calcination, it was crushed and sieved to particle sizes between 0.6 and 2.0 mm. Two different sets of

catalysts were prepared by co-impregnation and microemulsion methods. For all the catalysts the concentration of nickel and iron were adjusted at 12 wt.%, 6 wt.% respectively.

In co-impregnation method, catalyst was prepared by using the mixed aqueous solutions of Ni(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O. After the impregnation step, the catalysts were dried at 100 °C for 2 h and calcined at 450 °C under air flow for 3 h and slowly exposed to atmosphere during the cooling step. The catalyst prepared by this procedure was signified as CIW (see Table 3).

In second method, Ni–Fe nanoparticles were synthesized in a reverse microemulsion using a nonionic surfactant Triton X-100 (Chem-Lab), Hexane (C₆H₁₄, Chem-Lab) as the oil phase, and 1-butanol (C₄H₉OH, Merck) as the co-surfactant. The concentration of Ni–Fe was adjusted using aqueous solutions of Ni(NO₃)₂·H₂O (Merck) and Fe(NO₃)₃·9H₂O (Merck). The water-to-surfactant molar ratio (W/S) was adjusted at 5, 4, 3, 2 and 1. After vigorous stirring, a microemulsion was obtained (15 min). Sodium borohydrid was added in excess to improve nano particle formation in the core of the micelles by reducing the metal oxides. Then, the appropriate weight of support was added under stirring. During the 3 h of stirring, tetrahydrofuran (THF), an emulsion destabilizing agent, was added drop wise (0.3 ml/min). A fast addition could lead to fast particle agglomeration and uncontrolled particle deposition on the support. The mixture was left to mature and settle slowly overnight and then decanted. The solid sample was recovered by vacuum filtration using ashless filtration paper and washed several times with distilled water and ethanol. In order to remove the remaining traces of surfactant, the catalysts were dried at 100 °C for 2 h and calcined under air flow at 450 °C for 3 h and slowly exposed to atmosphere during the cooling step (Trepanier et al., 2009). The catalysts prepared by this procedure were signified as MC1, MC2, MC3, MC4 and MC5 for a W/S ratio of 5, 4, 3, 2 and 1 respectively (see Table 3).

2.3. Catalyst characterization

Temperature-programmed reduction (TPR) with H₂ was performed in a fixed-bed flow reactor. The TPR profile of each sample was recorded from room temperature to 1123 K under a flow 5.0% H₂/Ar, and the flow rate was 30 ml/min. The catalyst weight was 50 mg. The heating rate was 10 K/min and the temperature was maintained at 1123 K for 30 min after it reached 1123 K. The consumption of H₂ was monitored continuously with TCD gas chromatograph equipped with frozen acetone trap in order to remove H₂O from the effluent gas. The amount of H₂ consumption was estimated from the peaks area in the TPR profiles.

The size of the particles and morphology of the catalyst surface were also characterized by transmission electron microscopy (TEM). Sample specimens for TEM studies were prepared by ultrasonic dispersion of the catalysts in ethanol, and the suspensions were dropped onto a carbon-coated copper grid. TEM investigations were carried out using a Philips CM120 (100 kV) transmission electron microscope equipped with a NARON energy-dispersive spectrometer with a germanium detector.

Table 1
Design of experimental runs.

Run	Reaction Time (min)	Temperature (°C)	Second bed
1	30	850	–
2	30	850	Catalyst (CIW)
3	30	850	Catalyst (MC1)
4	30	850	Catalyst (MC2)
5	30	850	Catalyst (MC3)
6	30	850	Catalyst (MC4)
7	30	850	Catalyst (MC5)

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