

Steam Gasification of Palm Kernel Shell (PKS): Effect of Fe/BEA and Ni/BEA Catalysts and Steam to Biomass Ratio on Composition of Gaseous Products

M.F. Mohamad, Anita Ramli, S.E.E Misi, and S. Yusup

Abstract—This work presents the hydrogen production from steam gasification of palm kernel shell (PKS) at 700 °C in the presence of 5% Ni/BEA and 5% Fe/BEA as catalysts. The steam gasification was performed in two-staged reactors to evaluate the effect of calcinations temperature and the steam to biomass ratio on the product gas composition. The catalytic activity of Ni/BEA catalyst decreases with increasing calcinations temperatures from 500 to 700 °C. The highest H₂ concentration is produced by Fe/BEA (600) with more than 71 vol%. The catalytic activity of the catalysts tested is found to correspond to its physicochemical properties. The optimum range for steam to biomass ratio is found to be between 2 to 4. Excess steam content results in temperature drop in the gasifier which is undesirable for the gasification reactions.

Keywords—Hydrogen, Palm Kernel Shell, Steam gasification, Ni/BEA, Fe/BEA

I. INTRODUCTION

CONCERNS about the hiking prices of petroleum and the growing issues on emission of greenhouse gases have prompted the search for an alternative energy. Hydrogen is being promoted as the energy carrier for the future since it would provide pollution-free, carbon-free power and fuels for buildings, industry and transportation.

Hydrogen could be produced from renewable biomass resources via gasification technology. Biomass gasification converts carbonaceous material to gases such as H₂, CO, CO₂, CH₄ and light hydrocarbons. In most cases, trace amount of char, ash and tar are also produced during biomass gasification. The formation of tar that would be liquids under ambient conditions creates operational interruption as they might condense and lead to pipes blockages. Utilization of catalyst in biomass gasification would not only help in tar

abatement, but also has strong influence in promoting high content of product gases [1].

Various literatures reported on employment of different catalysts to eliminate tar and thus upgrade the product gas in biomass gasification. Alkali metals are found suitable as primary catalysts since they are active for H₂O and CO₂ gasification of carbon [2]. Dolomite and olivine are two natural resources that show high tar reforming activity, however, olivine is much stronger material and able to resist attrition in fluidized-bed reactors [3]. For metallic based catalysts, Nickel (Ni) and Rhodium (Rh) are claimed to be efficient catalysts for both steam and dry reforming of methane and hydrocarbons [4]. However, Rh is seen as unfeasible to be used due to its high cost. On top of being used as water gas shift (WGS) catalysts, metallic Iron (Fe) also shows significant performance in tar cracking [5]. The high activity of dolomite in tar reforming has thus been attributed to its Fe content.

In this paper, steam gasification of palm kernel shell (PKS) to hydrogen was performed in the presence of Zeolite β (BEA) supported Fe and Ni catalysts to investigate the effects of catalysts calcination temperature and steam to biomass (S/B) ratio on product gas distribution.

II. EXPERIMENTAL

A. Materials Preparation

Palm kernel shell (PKS) used as biomass feedstock was first dried at 110 °C for 4 h before they were crushed and sieved to 500 μm. The ultimate analyses of PKS is C 49.65 %, H 6.13 %, N 0.41 %, S 0.48 % and O 39.22 %.

Zeolite β (BEA) chosen as the support was first calcined at 500 °C for 16 h to remove any impurities. 5% Ni/BEA and 5% Fe/BEA catalysts were prepared using incipient wetness impregnation method where a required amount of FeCl₃·6H₂O or NiCl₂·6H₂O was first dissolved in sufficient amount of deionised water. Then the calcined BEA was added to the metal solution. The slurry formed was left for 4 h for impregnation at room temperature under stirring and later dried at 120 °C for 16 h. Finally, the dried sample was calcined at 500 to 700 °C for 16 h. The prepared catalysts are designated as A/BEA (X00) where A is the active metal used and X00 is the calcinations temperature used e.g. Fe/BEA (500) is Fe/BEA catalyst calcined at 500 °C.

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B. Characterization Techniques

The catalysts were characterized for their crystal structures using XRD Bruker D8 Advance diffractometer with Cu-K α as the radiation source. The reducibility of the catalysts was analyzed using a Thermo Electron TPDRO 1100 Analyser. The TPR analysis was performed using 5% H₂/N₂ at 20 cm³ min⁻¹ and heating rate of 10 °C min⁻¹ from room temperature to 900 °C. N₂ adsorption-desorption isotherm was performed using Micromeritics ASAP 2000 to determine the surface area, pore size and pore volume.

C. Steam Gasification of PKS

Steam gasification of PKS was carried out in two staged reactors where the PKS was continuously introduced in the free fall reactor at a feeding rate of 2 g hr⁻¹ while the catalyst was placed in a fixed-bed reactor. The biomass to catalyst mass ratio was maintained at 3:1. The reactors were first purged with approximately 100 ml min⁻¹ of N₂ before both reactors were heated up to 700 °C at a heating rate of 150 °C hr⁻¹. Steam was injected to the first reactor when the desired temperature is reached. The steam to biomass (S/B) ratio was first maintained at 4 and the best catalyst was then used to study the effect of S/B between 2 to 4.

Product gas exiting the reactor was passed through a condenser to condense the liquid products. After 1 hr, the gases produced (H₂, CH₄, CO₂, CO and C₂ hydrocarbons) were analyzed using an online gas chromatography (Agilent 7890A) equipped with two thermal conductivity detectors (TCD) and a flame ionization detector (FID). H₂, CO and CO₂ were measured using TCD detectors fitted with Molsieve 5A and Hayesep Q columns. Meanwhile the C₂ hydrocarbons were analyzed using FID detector fitted with HP-AL/S and DB-1 columns.

III. RESULTS AND ANALYSIS

A. Catalysts Characterization

The textural properties of the BEA supported Ni and Fe catalysts are shown in Table 1. The bare BEA has the largest surface area (529.04 m² g⁻¹) and pore volume (0.15 cm³ g⁻¹). However, once BEA is impregnated with 5% metal loading, the surface areas of the catalysts are reduced to between 390-528 m² g⁻¹ while the pore volumes are reduced to below 0.15 cm³ g⁻¹. Ni/BEA showed little decrease in surface area when the catalyst was calcined at 500 and 600 °C, however the reduction in surface area becomes more drastic when the catalyst was calcined at 700 °C. Lesser reductions in surface area of Ni/BEA at low calcinations temperature may be due to the hydrophobic nature of high silica in the presence of Ni metal species [6].

TABLE 1
TEXTURAL PROPERTIES OF THE CATALYSTS

Calcination Temperature	Catalysts	BET Surface Area [m ² g ⁻¹]	Pore Volume [cm ³ g ⁻¹]	Average Pore Diameter [nm]
500 °C	BEA	529	0.15	4.30
	Ni/BEA	528	0.15	5.19
	Fe/BEA	474	0.13	5.43
600 °C	Ni/BEA	523	0.15	5.50
	Fe/BEA	471	0.13	6.55
700 °C	Ni/BEA	397	0.10	6.72
	Fe/BEA	492	0.14	6.02

In addition, the average pore diameter of bare BEA is 4.30 nm which is smaller than the prepared catalysts, ranging from 5.3 to 6.7 nm. This may be due to the acidic nature of the metal salts used for impregnation which attacked on the pore opening of the support leading to a bigger pore size and deformation of some of the continuous surface into smaller non-continuous surface [7].

The XRD patterns of the BEA supported Fe and Ni catalysts are displayed in Fig. 1. The bare BEA has two major diffraction peaks appeared at 8° and 22.5°. The intensity of bare BEA diffraction peaks is high and quite broad, illustrating that the peaks are corresponding to Si-O-Al. As reported in JCPDS cards, the catalysts demonstrated hexagonal structure (89-0596) for Fe₂O₃ and cubic structure (47-1049) for NiO, respectively. The Ni/BEA catalysts show two diffraction peaks corresponding to bunsenite, NiO phase while the Fe/BEA catalysts show two diffraction peaks corresponding to hematite, α -Fe₂O₃ phase.

Calcinations temperature affect the crystallization of the prepared catalysts as it can breaks up the precursor and eventually decelerates the crystallization. As the calcination temperature was increased from 500 to 700 °C, the diffraction peaks corresponding to BEA, NiO and Fe₂O₃ are slightly shifted to higher 2 θ values. The intensities of Fe₂O₃ and NiO peaks are found to decrease as the calcination temperature was increased, signifying that the active metal has been inserted into the support, resulted in interference to the BEA structure [8]. Hence, temperature contributes to the crystallization of the catalysts.

Fig. 2 (a) and (b) demonstrate the reduction profiles of BEA supported Ni and Fe catalysts calcined at 500 – 700 °C. The reduction of 5%Ni/BEA (Fig.2a) shows two reduction peaks in the region between 400 – 500 °C and 600 – 700 °C. The low temperature peak on the TPR curve is attributed to the reduction of NiO not bound with the support which is referred to as “free nickel oxide” [9]. The higher temperature peak corresponds to the reduction of nickel that has reacted with the support forming nickel aluminate, NiAl₂O₄ or so-called “fixed nickel oxide”. However, the existence of this nickel aluminate has not been detected in any of XRD diffraction peaks which may be due to its small crystallite size.

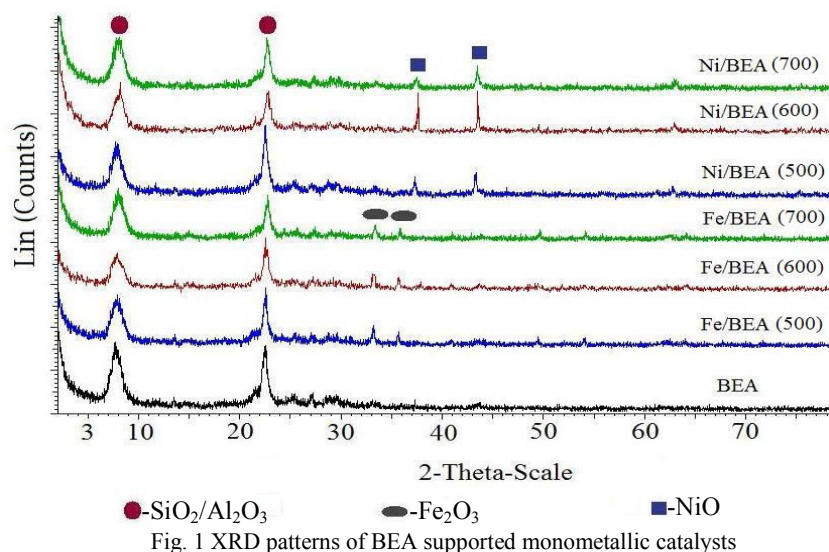


Fig. 1 XRD patterns of BEA supported monometallic catalysts

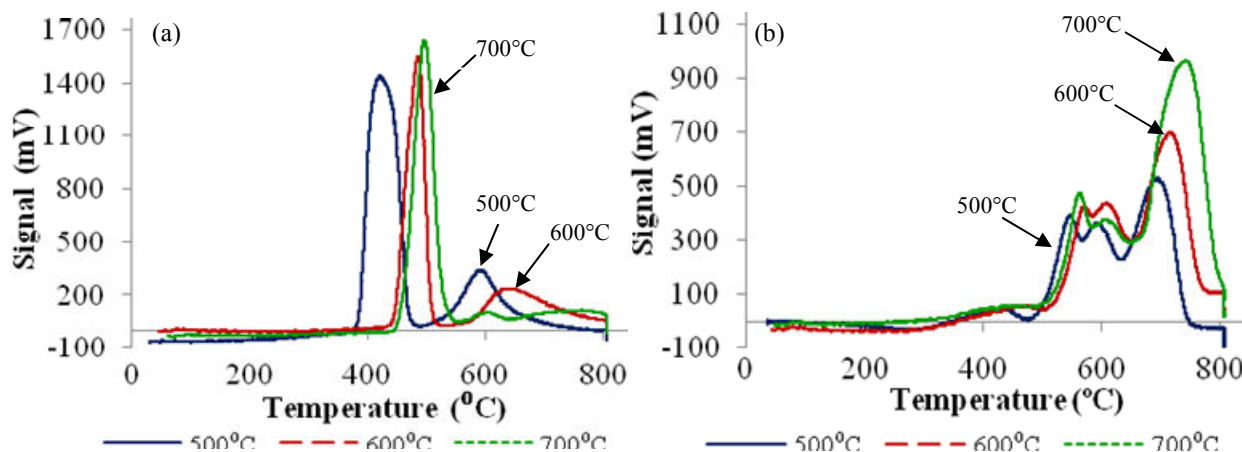


Fig. 2 Temperature programme reduction of Ni/BEA and Fe/BEA catalysts

Both reduction peaks of the Ni/BEA catalysts are shifted to higher temperatures as the calcinations temperatures increases. This indicates that the metals are becoming more difficult to reduce, thus Ni/BEA (500) has better reducibility as compared to Ni/BEA (600) and Ni/BEA (700).

The phase transformations of 5%Fe/BEA (Fig. 2b) show three main reduction peaks between 500 - 800 °C. It is observed that a lower broad peak between 300 - 500 °C shows the reduction of free iron oxides [10]. The reduction peaks between 500 - 650 °C are attributed to reduction of Fe_2O_3 which has weak interaction with the support. The first peak is attributed to reduction of Fe_2O_3 to Fe_3O_4 followed by reductions of Fe_3O_4 to FeO [11]. Reduction of Fe_2O_3 ends at FeO phase rather than Fe because FeO is a metastable phase of iron oxide on the support [12]. The reduction peak at higher temperatures between 650 - 800 °C corresponds to the reduction of iron species which has strong interaction with support, FeAl_2O_4 . The strong interaction between Fe- Al_2O_3 provided the stabilization of FeO phase on Al_2O_3 [13], which could further retard the transformation of FeO to Fe [11].

The reduction activity of Fe/BEA catalysts also increased with increasing calcinations temperature. It should be noted that the third reduction peaks, which represents the reduction of FeAl_2O_4 was largely shifted towards higher temperature as the calcinations temperature was increased. The strong interaction between Fe and BEA resulted in BEA to suppress the reduction metals in TPR process [11].

B. Catalytic Activity

1. Effect of Calcination Temperature

Catalytic performance of the Ni/BEA and Fe/BEA catalysts in the steam gasification of PKS are displayed in Fig. 3. Non-catalytic PKS steam gasification leads to production of (vol %) ~ 62% H_2 with 30% CO_2 , 5% CO and 2% CH_4 . When only BEA was used, the formation of H_2 , CO and CH_4 in the product stream increase slightly to 68.25%, 6.41% and 2.17% respectively whilst CO_2 formation decreases to 23.17%. The favorable performance of BEA in steam PKS gasification may be associated to its textural properties with high surface area ($529 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.15 \text{ cm}^3 \text{ g}^{-1}$).

Calcination temperature has an effect on the performance of Ni/BEA and Fe/BEA catalysts in steam gasification of PKS. The catalytic activity decreases with increasing calcinations temperature. In the case of Ni/BEA catalyst, the highest H₂ formation was obtained in the presence of Ni/BEA (500). As the calcinations temperature increases, the evolved H₂ and CO gas gradually decreased which is in contrast to the production of CO₂. However, only small concentration of CH₄ (<2.0%) was detected in the presence of Ni/BEA (500) and Ni/BEA (700). On the other hand, CH₄ was not detected in the product gas when Ni/BEA (600) was used as catalyst. CH₄ produced may have subsequently undergone steam reforming to produce CO and H₂ [14] or may have been oxidized to produce CO₂ and H₂O [15]. The latter may be the appropriate reason as the concentration of CO₂ produced increases whilst CO and H₂ formation decrease when Ni/BEA (600) was used as catalyst.

The Ni/BEA catalysts calcined at 500 °C has demonstrated its ability to produce higher concentration of H₂ as compared to the other Ni/BEA catalysts. This capability may be attributed to the catalysts properties where Ni/BEA (500) has better reducibility and higher surface area. For the catalysts calcined at lower temperature, these free metals oxide also exist at low temperature. As previously shown in H₂-TPR

(Fig.2a), Ni/BEA (500) reduced to NiO at 450 °C. These free metal oxides may actively react with PKS to generate more H₂. In the case of Fe/BEA catalyst, the evolution of H₂ from steam gasification of PKS increases with increasing calcination temperature from 500 to 600 °C but further increase in calcination temperature resulted in a decrease in H₂ production. The maximum hydrogen production is achieved in the presence of Fe/BEA (600) catalyst. It is suggested that Fe/BEA (600) promotes methane steam reforming instead of water gas shift reaction as the production of CH₄, H₂ and CO were increased. Water gas shift reaction may not be favorable in the process due to low transformation rate of CO [14]. Fe/BEA (600) which has relatively larger pore diameter has higher activity in H₂ production. The catalyst with larger pore diameter will alleviate PKS to penetrate the active sites and allow the reactions to occur.

On the other hand, the CO₂ production shows a decreasing trend as the calcinations temperature was increased from 500 to 600 °C and increases again as the calcinations temperature was further increased to 700 °C. Lesser efficiency of Fe/BEA (700) may be due to PKS undergoing combustion rather than promoting steam gasification.

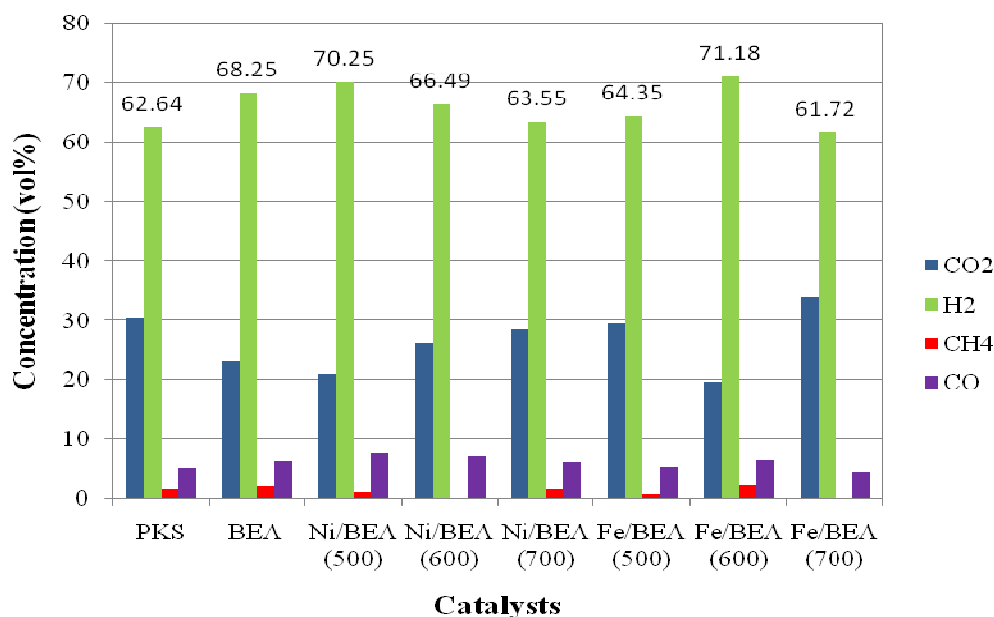


Fig. 3 Profile of gases produced in the presence of Ni/BEA and Fe/BEA catalysts

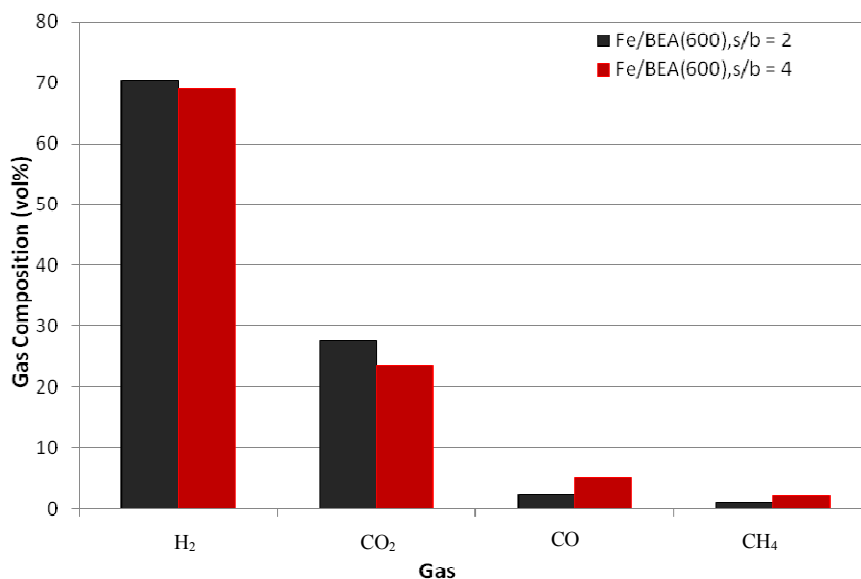
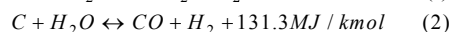
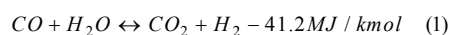


Fig. 4 Effect of steam to biomass ratio on gas composition

2. Effect of S/B ratio

Steam is used as gasification agent in order to obtain the good quality and high percentage of H₂. The introduction of steam facilitates the steam reforming of tar and hydrocarbons as well as the water gas shift reactions. The S/B ratio has been studied at ratio of 2 and 4 using Fe/BEA (600) catalyst only. The selection is based on its favourable catalytic activity shown earlier. The S/B ratio was varied while keeping all other parameters constant i.e. biomass feed rate and operating temperature of 700 °C. As shown in Fig. 4, it can be seen that the gas composition displayed a decreasing trend with increasing S/B ratio for H₂ and CO₂ production. H₂ slightly decreases from 70.5 vol% to 69.2vol%, while CO₂ changed from 27.7vol% to 23.6vol%. On the other hand, the formation of CO and CH₄ increase with increasing S/B ratio from 2.4 to 5.2 vol% and 1.0 to 2.0 vol% respectively. Increasing S/B ratio leads to higher steam pressure, which makes reactions (1) and (2) shifted to the left, resulting in the decreasing of H₂ and CO₂ contents while the CO and CH₄ concentration increase [16]. However, previous work by other researchers reported that an increase in S/B ratio would increase H₂ and CO₂ contents while CO formation dropped [17]. The contrasting findings observed in this work may be attributed to the different biomass used, the type and design of reactor and operating conditions.



Excessive steam would result in temperature drop in the reactor which led to the reduction of decomposition rate of steam, and thus not conducive for gasification reactions [16]. Therefore, there exists an optimum value for S/B in the steam gasification. In this work, it can be concluded that the optimum range for S/B ratio would be within 2 to 4.

IV. CONCLUSION

The effects of calcination temperature and steam to biomass (S/B) ratio on product gas distribution from steam gasification of PKS have been investigated. In general, the catalytic activity decreases with increasing calcinations temperature. In the case of Ni/BEA catalysts, the H₂ concentration is in the order of Ni/BEA (500) > Ni/BEA (600) > Ni/BEA (700). However, for Fe/BEA catalysts, the H₂ concentration is in the order of Fe/BEA (600) > Fe/BEA (500) > Fe/BEA (700). The capability of the developed catalysts to produce maximum H₂ may be attributed to their physicochemical properties i.e. reducibility and BET surface area.

The production of CO and CH₄ increased with increasing S/B ratio. The result is in contrast with the formation of H₂ and CO₂, that is increasing S/B ratio decrease H₂ and CO₂ contents in the product stream. As more steam was introduced to the reactor, the system will experience a temperature drop which leads to unfavourable condition for gasification reactions to take place. The optimum range of S/B ratio is within ratio of 2 to 4.

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