

Catalytic Gasification of Empty Fruit Bunch for Enhanced Production of Hydrogen Rich Fuel Gas

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ABSTRACT

Oil palm is widely grown in Malaysia. There has been interest in the utilization of oil palm biomass for production of environmental friendly biofuels. The gasification of empty fruit bunches (EFB), a waste of the palm oil industry, was investigated in this study to effectively and economically convert low value and highly distribution solid biomass to a uniform gaseous mixture mainly hydrogen (H₂). The effects of temperature, equivalence ratio (ER) and catalyst adding on the yields and distribution of hydrogen rich gas products were also investigated. The main gas species generated, as identified by GC, were H₂, CO, CO₂, CH₄ and trace amounts of C₂H₄ and C₂H₆. With temperature increasing from 700 to 1000 °C, the total gas yield was enhanced greatly and reached the maximum value (~90 wt. %) at 1000 °C with a big portion of H₂ (38.02 vol. %) and CO (36.36 vol. %). Equivalence ratio (ER) showed a significant influence on the upgrading of hydrogen production and product distribution. The optimum ER (0.25) was found to attain a higher H₂ yield (27.42 vol. %) at 850 °C. The effect of adding catalysts (Malaysian dolomite1, P1), Malaysian dolomite2 (GML), NaOH, NaCl, CaO, ZnO, NiO) as a primary catalyst on gas product yield was investigated, and it was found that adding dolomite showed the greatest effect with the maximum H₂ yield achieved (28.18 vol.%) at 850 °C.

Keywords: Biomass, hydrogen, gasification, catalyst adding

INTRODUCTION

Biomass is an important contributor to the world economy. Today, various forms of biomass energy are consumed all over the world. Biomass provides a clean, renewable energy source that could dramatically improve the environment, economy and energy security. In particular, conversion of non-edible biomass, such as agriculture residues, wood chips, and fruit bunches, stalks, industrial and municipal wastes, into fuels and useful chemicals would solve waste disposal and energy issues (Baratieri *et al.*, 2008). Palm oil wastes are the main biomass resources in ASEAN countries. In Malaysia alone, there were 9.66, 5.20 and 17.08 million tons for fibres, shell and empty fruit bunches, respectively (Nasrin *et al.*, 2008). Thus, to treat this tremendous amount of wastes, novel technologies with improved efficiencies and reduced environmental impacts need to be established timely.

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Biomass gasification is one of the most promising thermo-chemical conversion routes to recover energy from biomass. During gasification, biomass is thermally decomposed to solid charcoal, liquid bio-oil and bio-gases under partial oxidation condition. The yields of end products of gasification are dependent on several parameters which include temperature, biomass species, particle size, equivalence ratio and reactor configuration, as well as extraneous addition of catalysts (Demirbas, 2002). As two most important parameters, temperature and equivalence ratio (ER) (Wang *et al.*, 2008) have been investigated widely in bench scale reactors including fixed beds (Yang *et al.*, 2006), fluidized bed (Cao *et al.*, 2006; Lv *et al.*, 2004) and others (Sheth & Babu, 2009). Generally, H₂-rich gas products are favoured at high temperature and the H₂ yield from the gasification of biomass is acceptable as compared to fast pyrolysis, but they still contain high quantity of tar. It is known that the gas yield, especially H₂, could be improved by catalyst adding and at the same time, reducing the tar content in the gas yield. So far, various types of chemicals (such as dolomite, oxides and inorganic compounds) have been selected as catalysts to improve the overall efficiency of the system used in producing high quality fuel gases so as to increase the economic feasibility of the biomass gasification process. Furthermore, the humid weather in Malaysia could also show a great effect on gaseous products from biomass gasification when air is used as a gasification agent.

In this study, the catalyst effect on air gasification of EFB was investigated using a fluidized bed reactor in the attempt to achieve an improved performance of EFB conversion to energy with higher yield of H₂-rich gas and minimum tar content. The biomass gasification technologies used to produce hydrogen-rich fuel gas were found to present highly interesting possibilities for biomass utilization as a sustainable energy. In more specific, biomass used as an energy source can reduce CO₂ greenhouse effect, as well as SO₂ and NO_x atmospheric pollution (McKendry, 2002), due to its characterization of natural carbon and less sulphur and nitrogen contents.

MATERIALS AND METHODS

Biomass Samples and Catalysts

The feedstock used was empty fruit bunches (< 1mm, ~5.18 moisture). The physical and chemical properties of the EFB are presented in Table 1. The molecular formula of EFB can be expressed as CH_{1.66}O_{0.73} based on the ultimate analysis. Meanwhile, particle size reduction was required to allow gasification of the EFB on the available reactor. First, the bunches were manually chopped into small pieces that could be fed in a shredder. After that, a Fritsch grinder with a screen size of 1.0 mm was used to obtain the feedstock size of less than 1.0 mm. The cellulose, hemicelluloses and lignin contents of EFB were sent to MARDI for analysis. Acid detergent fibre (ADF), neutral detergent fibre (NDF) and acid detergent fibre (ADL) analyses were also carried out. The percentages of the cellulose, hemicelluloses and lignin of EFB are also given in Table 1. Among the EFB components, lignin is the most thermally stable and also the main source of tar.

Seven types of catalysts, including Malaysian dolomites P1 and GML, NaOH, NaCl, CaO, ZnO, NiO, were introduced into the thermal system as the catalysts to improve the yields of gas product from EFB gasification. The catalysts' surface areas were measured using nitrogen adsorption (BET) analysis by Quantachrome AS1Win with liquid N₂ at 77.3 K. It was found that NaOH and NaCl contain very low surface area (< 1 m²/g) while those of GML, CaO, ZnO and NiO are higher (2-9 m²/g), and Malaysian dolomite P1 shows the highest surface area (15.2 m²/g). The catalysts were directly dry-mixed with the EFB samples (Sutton, *et al.* 2001) and their weight ratio to EFB (C/W) was kept at 0.1.

TABLE 1
Properties of EFB

Component	Measured (wt. %)
Cellulose	22.24
Hemicellulose	20.58
Lignin	30.45
Elemental analysis	
C	46.62
H	6.45
N	1.21
S	0.035
O ^a	45.66
Proximate analysis	
M_{ad}	5.18
V_{ad}	82.58
A_d	3.45
FC_{ad}	8.79
Calorific value (MJ/Kg)	17.02

M : moisture content; V : volatile matters; A : ash;

FC : fixed carbon; ad : on air dried basis; d : on dry basis.

^a the oxygen (O) content was determined by difference.

Experimental Set-up

A fluidized bed bench scale gasification unit, operating at atmospheric pressure, was employed for all the runs. Fig. 1 shows a schematic diagram of this particular unit, which consists of three main systems, namely, reactor (gasifier and heating furnace), condenser and purification (condenser, glass wool filter and dryer) and gas storage (gasbags). The reactor is a cylindrical configuration that is made of stainless steel with a length of 600 mm and a diameter of 40 mm. Three thermocouples were inserted in the middle of the heating furnace, middle of the reactor tube and bottom of the reactor tube, respectively. Biomass was fed into the reactor by a feeder on the top of the reactor, which was continuously carried out at a constant flow rate. The feeding capacity of biomass was 10 g/min. The heating medium in fluidized bed gasifier was silica sand of a mean size of 0.1-0.15 mm. The density of sand material is approximately 1470 kg/m³. It is approximately 69.3% SiO₂, 26.5% CaO, and 1.7% Fe₂O₃ with the balance of the other trace amounts of oxides. The minimum fluidization velocity at atmospheric pressure for the sand material was measured to be 0.04 m/s.

Initially, the fluidized bed reactor was loaded with 100 g of inert sand as bed material. The air was injected from the bottom distributor to maintain the sand material to be fluidized. When the desired temperatures were achieved, a 20 min waiting time was allowed so as to make the system stable and to achieve a steady state, before the biomass feeding was started. The fuel gas produced was passed to the downstream cooling system, where the condensable vapours were collected by ice water condenser and caught by dichloromethane inside the neck flask, whereas the incondensable part of product gas left the cooling system and passed through a fibre glass-wool filter for more tar trapping and dried by silica gel before it was collected by 12 L gas sampling bags and taken every 1 min for gas chromatography (GC) analysis.

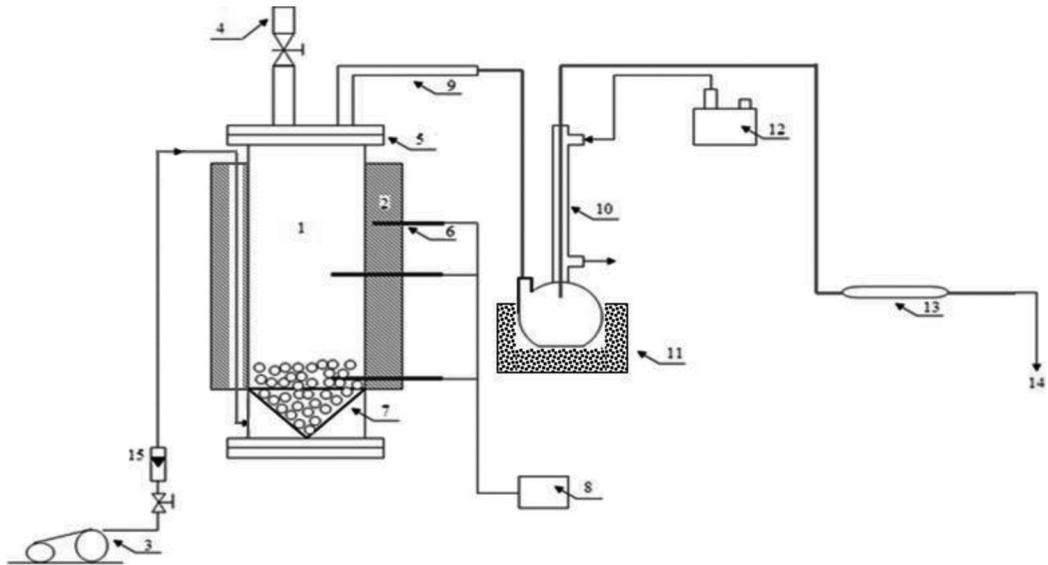


Fig. 1: The schematic of lab-scale fluidized bed biomass gasifier; (1) lab-scale gratefrier, (2) electric furnace, (3) air pump, (4) biomass feeder, (5) flange, (6) thermocouples, (7) air distributor, (8) furnace controller, (9) gas discharge, (10) water cooler, (11) ice trap, (12) cooling water pump, (13) glass wool filter, and (14) fuel gas

Fuel Gas Sampling and Measuring Procedures

After a steady state was achieved, the fuel gas stream was switched to downstream cooling system and glass wool filter. Then, the dry gas was sampled by a gas sampling bag and taken every 1 min. The permanent gas compositions and light hydrocarbon constituents (mainly C₂-C₆) of the fuel gas were analyzed by a gas chromatograph (Agilent HP6890N) with TCD and FID detectors using argon as a carrier gas. The standard gas mixture of H₂, CO, O₂, N₂ and CH₄ was used as a quantitative calibration of GC. Generally, 10 gas samples were taken for each test condition. The tar product was trapped in the cooling system condenser and fibre-glass wool filter. Dichloromethane (99.8 %) was used to dissolve the tar from the condenser walls and fibre-glass wool filter. The dissolved product was transferred to a ceramic tray and heated in an oven at 100 °C for about 12 hours to evaporate any water and solvent fractions and later weighted to get the tar mass.

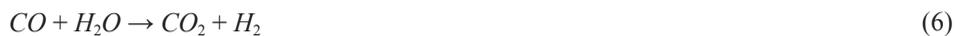
RESULTS AND DISCUSSION

The goal of this study was to produce H₂-rich gas with less tar formation from the air gasification process of a biomass. The experiments were conducted to investigate the impacts of the parameter variation, such as temperature profiles in the reactor, the equivalence ratio (ER) and catalysts that were adding on to gas composition and tar formation.

The Influence of Gasifier Temperature on EFB Gasification

The yields of the final products from the EFB gasification under different temperatures are illustrated in Fig. 2. With the temperature increasing from 700 to 1000 °C, the total gas yield increased sharply from 62.68 to 91.70 wt. %, while liquid, char and tar yields were found to have constantly reduced.

Meanwhile, varying the temperature showed a great influence on the gas product components. As shown in *Fig. 3*, the main gas products are H₂, CO, CO₂, CH₄ and some C₂ hydrocarbons traces (C₂H₄ and C₂H₆). Among them, the H₂ content increased steadily from 10.27 to 38.02 vol. % as the temperature was increased from 700 to 1000 °C. Meanwhile, the yield of CH₄ was also increased from 5.84 to 14.72 vol. %, whilst the CO₂ content generally decreased with the increase of the temperature, particularly at 1000 °C. The CO yield was initially increased from 21.87 to 33.35 vol. % as the temperature increased to 800 °C, before it decreased to 33.08 vol. % at 900 °C, and later increased again to 36.36 vol. % as the temperature continuously increased to 1000 °C. On the contrary, the C₂H₄ and C₂H₆ yields were relatively small and the influence of temperature was insignificant. As the temperature of the reactor increased, the tar content in the fuel gas produced decreased sharply from 8.05 wt. % at 700 °C to less than 2.12 wt. % at 1000 °C. The thermal cracking of gas-phase hydrocarbons at the high temperature might explain the variation of the gas product distribution observed (Dai *et al.*, 2000). At a high furnace temperature, the gas species generated from the biomass at pyrolysis zone could undergo further reactions (secondary reactions), such as tar cracking and shifting reaction, leading to much more incondensable gases (including H₂) generated. Therefore, the total yield of gas products increased significantly as the temperature increased from 700 to 1000 °C. The main reactions involved could be expressed using equations (1) - (10) (Dai *et al.*, 2000; Demirbas, 2001). Among them, equations (1) – (5) are the principle or heterogenous gasification reactions whilst equations (6) – (10) are homogenous and secondary reactions. In terms of increasing H₂ production, equations (6) to (10) are the main reactions of interest for the EFB gasification at atmospheric pressure and temperature between 700 and 1000 °C. The other gas components might increase or decrease with the occurring of secondary reactions. As a result, more H₂ could be obtained when secondary reactions occurred significantly. From the above analysis, it could be concluded that higher temperature (1000 °C) is favourable for thermal cracking of tar and shift reaction.



The lower heating value (LHV, MJ/m³) of the gas products can be calculated using the following equation (Dai *et al.*, 2000; Yang *et al.*, 2006):

$$LHV = (30xCO + 25.7xH_2 + 85.4xCH_4 + 151.3xC_nH_m) \times 4.2 \quad (11)$$

CO, H₂, CH₄ and C_nH_m in the above equation are the molar ratios of the CO, H₂, CH₄ and other hydrocarbon (C₂H₂ and C₂H₆) in the gas product. As shown in *Fig. 2*, the heating value of the total gas products increased steadily as the temperature increased. At 1000 °C, the LHV of gas products reached 15.55 MJ/m³, which could be grouped in the medium level of the heat values for gas fuels.

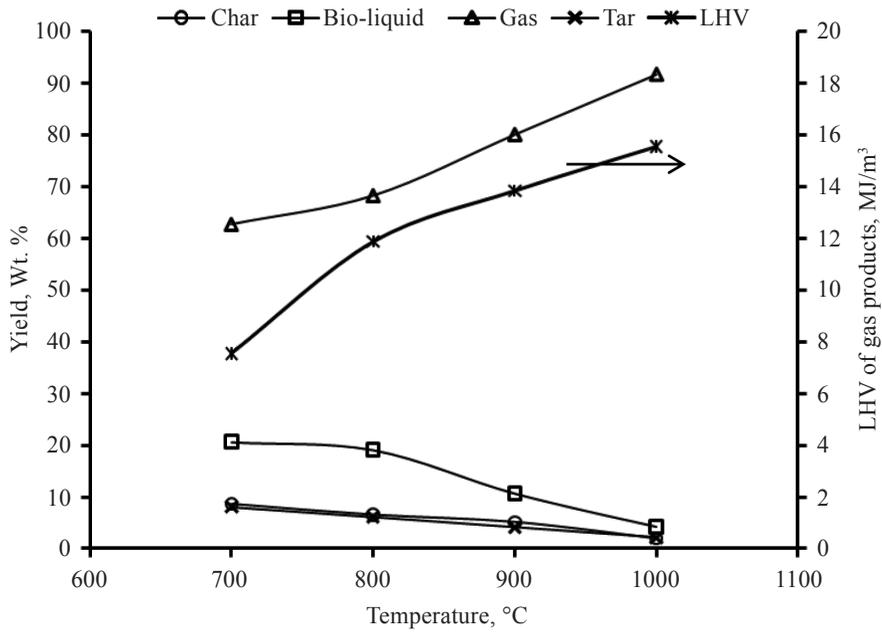


Fig. 2: The effect of gasifier temperature on the EFB gasification yields

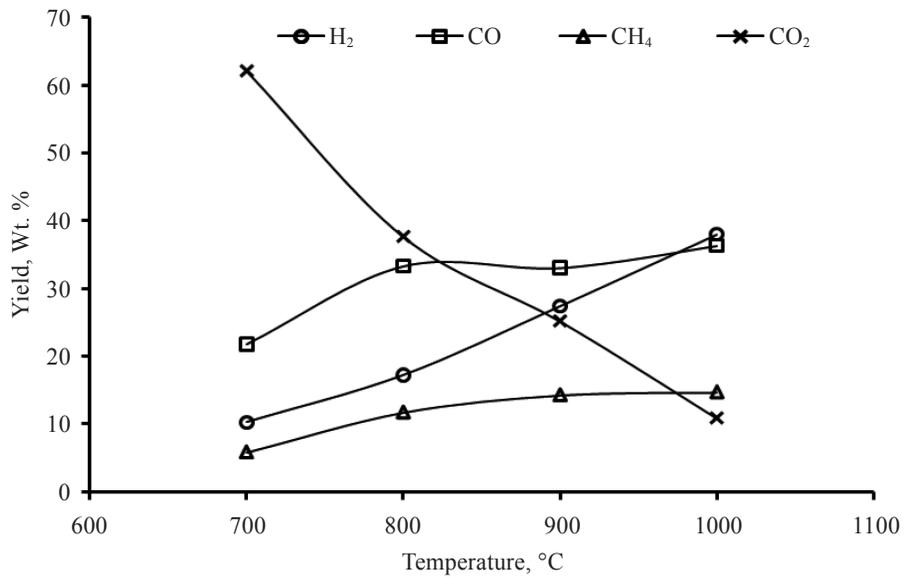


Fig. 3: The effect of gasifier temperature on the gas composition of EFB gasification

This LHV group can be directly used for gas engine, gas turbine or boiler for power generation. In addition, this group can also be applied for the chemical formation of methanol and methane (McKendry, 2002).

The Influence of Equivalence Ratio (ER) on Product Yields

The equivalence ratio (ER) is defined as the ratio of oxygen (air) that is required for gasification to oxygen (air) required for stoichiometric combustion of a given amount of biomass (Narvaez *et al.*, 1996). In this work, ER varied from 0.15 to 0.35 in an increment of 0.05, keeping the final temperature of the reactor at 850°C, and the feedstock particle size in the range of 0.3-0.5 mm. The air flow rate entering the reactor was varied to investigate the effect of ER. As shown in *Fig. 4*, with increased in ER, char and tar yield decreased from 13.65 to 2.12 wt. % and 9.83 to 2.82 wt. % respectively, while gas yield increased from 70.75 to 86.46 wt. %. The lower heating value (LHV) of the gases decreased slightly from 15.38 to 12.35 MJ/m³. The increase in ER increased oxidation reaction and decreased the product gas quality. However, too high ER causes low concentrations of H₂ and CO with a high CO₂ content in the product gas. As shown in *Fig. 5*, with ER varied from 0.15 to 0.35, the H₂ content increased to and reached the maximum value of 27.42 vol. % at ER of 0.25 and then dropped to 18.37 vol. % with a further increase in ER, while the CO₂ content increased steadily from 16.66 vol. % to 36.05 vol. %; however, CH₄ and other hydrocarbons traces content were found to have the contrary results. It can be explained that in the gasification process, the oxidization reactions are always strong, and oxidization reactions of combustible product gases

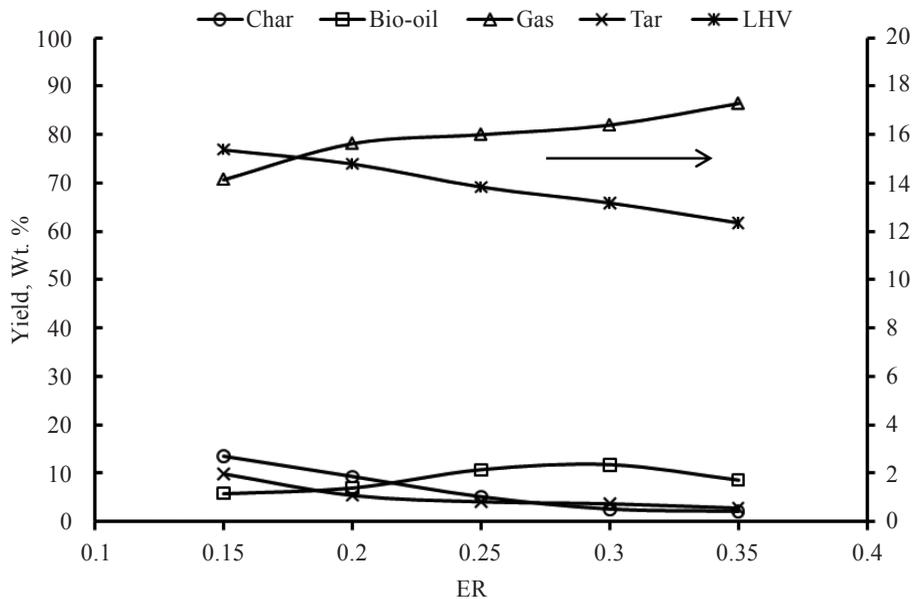


Fig. 4: The effect of ER on the EFB gasification yields

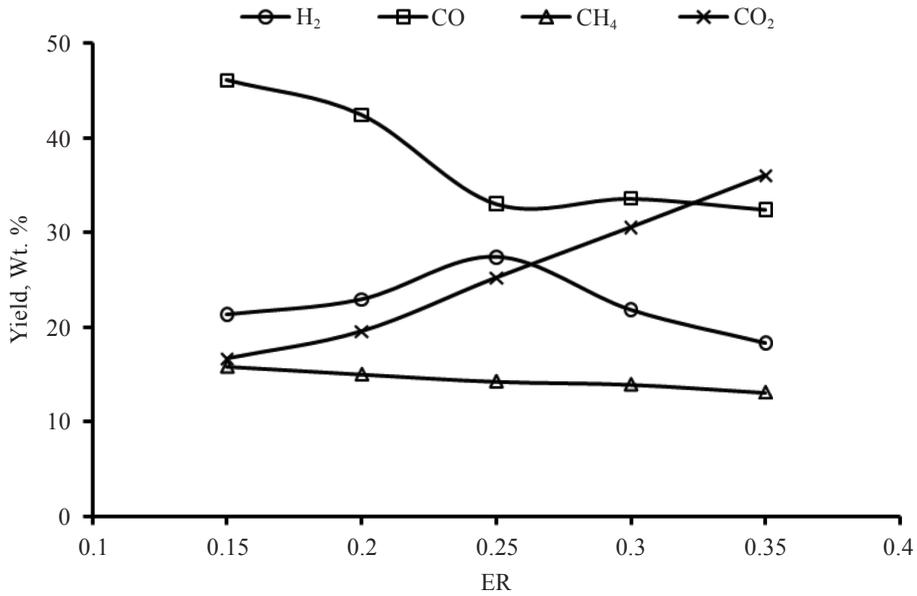


Fig. 5: The effect of ER on the gas composition of the EFB gasification

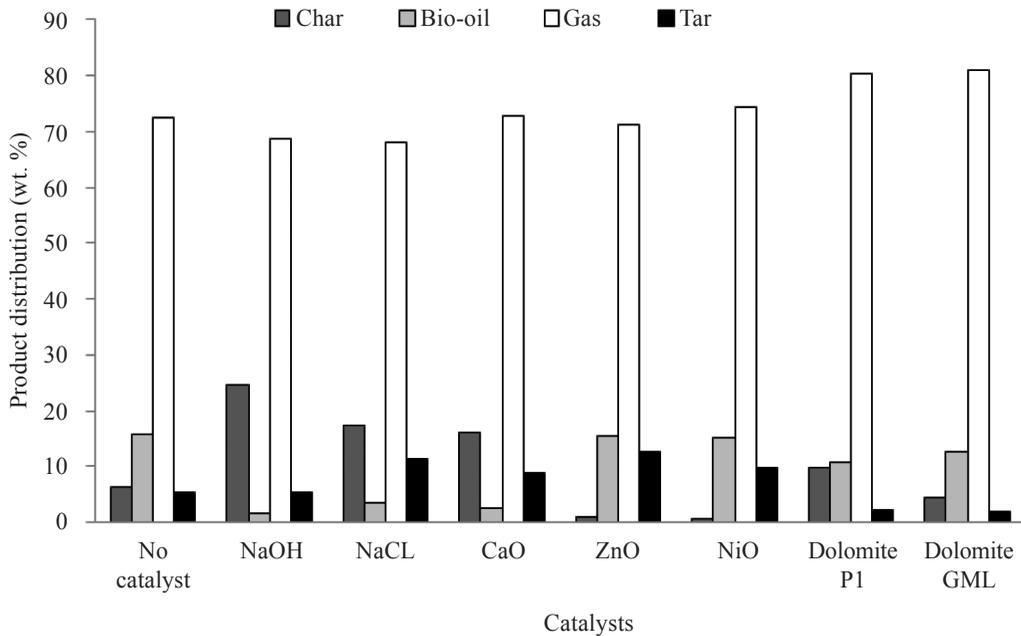


Fig. 6: Product distribution from the EFB gasification with different catalysts at 850 °C, ER=0.25 and C/W = 10 wt. %.

strengthen with ER, which results in more CO₂. Several research groups, such as Mansaray *et al.* (1999), Manyá *et al.* (2006) and Xiao *et al.* (2007), investigated the effect of ER in the air gasification of biomass in a fluidized bed gasifier, and found that with the increase in ER, H₂ and CO initially increased but later decreased, whereas CO₂, CH₄ and other hydrocarbon contents were progressively decreased, which are similar with the findings obtained in the current study. Through the analysis on the experimental results of varying ER, it could be understood that the optimum value for ER is 0.25, in which the maximum hydrogen content was obtained.

The Influence of Adding Catalyst

The results of the catalytic gasification of EFB at 850 °C and ER= 0.25 are reported in Fig. 6 and Fig. 7. All the catalysts with C/W of 10 wt. % showed a more or less positive influence on gasification yields and the total volume of gases produced. Malaysian dolomite P1 appeared to have the strongest catalytic effect than others; with the presence of dolomite, the total gas yield from EFB gasification was increased to reach 28.18 vol. % as compared with 24.78 vol. % without any catalyst. Meanwhile, the Malaysian dolomite GML and pure catalyst NiO showed less effect compared to dolomite P1. The sodium compounds (NaOH and NaCl) showed the lowest effect on EFB gasification, and this was possibly due to the strong sodium base which could extract some low molecular compounds in the biomass and also break the intermolecular hydrogen bridges under swelling or heating (Wang *et al.*, 2006). It could also react with cellulose, hemicellulose and lignin to make the devolatilization of biomass to occur earlier at a low temperature and that can increase

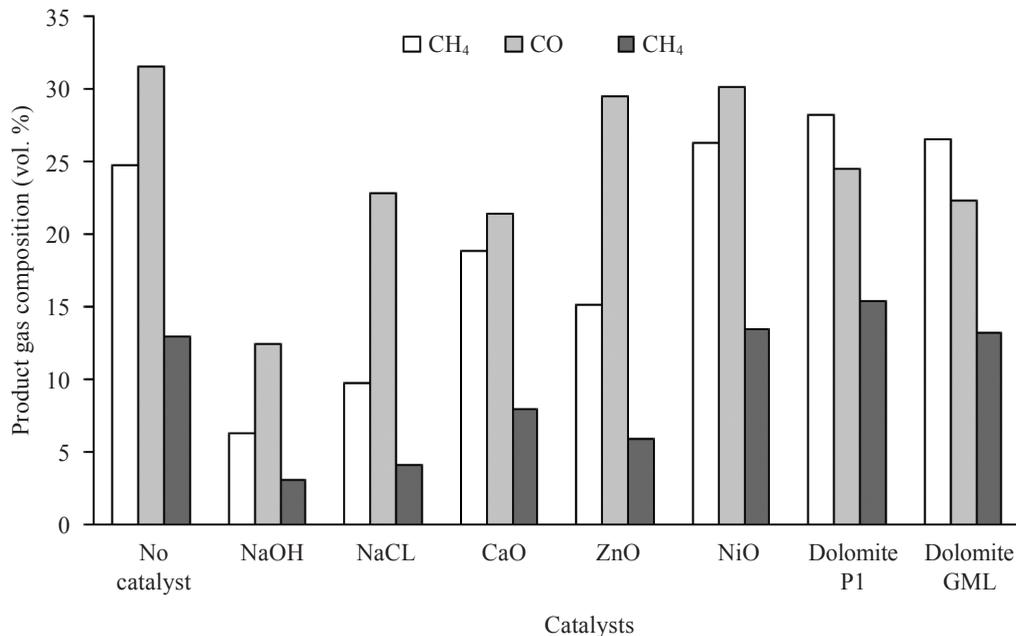


Fig. 7: Product gas composition (N_2 free) from the EFB gasification with different catalysts at 850 °C, ER=0.25 and C/W = 10 wt. %

char formation during gasification. The catalytic gasification of EFB, in terms of the yield of H₂ production, was Malaysian dolomite P1 > Malaysian dolomite GML > pure catalyst NiO > no catalyst > CaO > ZnO > sodium based catalysts NaCl and NaOH. Adding the catalysts to biomass (except for the sodium compounds) could improve the H₂ content, whilst the CO contents were found to have decreased in all the cases, and these were attributed possibly to the shifting reactions. This changing trend is consistent with that observed from the gasification process in some previous research (Haiping *et al.*, 2006; Perez *et al.*, 1997).

CONCLUSION

The main products of EFB gasification were solid charcoal, bio-oil liquids and gas products. Gas yield increased greatly whilst solid and liquid yields decreased constantly as the temperature was increased from 700 to 1000°C. The gas products mainly consist of H₂, CO, CO₂ and CH₄ and some C₂ hydrocarbons. The high temperature was found to be favourable for higher hydrogen/syngas production and for the enhancement of LHV of gas products. The optimum equivalence ratio was 0.25 for the fluidized bed gasifier studied. Several potential catalysts have been investigated on improving gas yield and quality. The Malaysian dolomites P1 and GML appeared to have the strongest effects on H₂ yield and tar removal. With the addition of dolomite P1 (10%), the total gas yield from the EFB gasification was improved and gas quality was upgraded, in addition to the great reduction of the tar yield.

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