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Enhancing Hydrogen Production From The Pyrolysis Of Oil Palm EFB by Alkali Metal Oxides.

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ABSTRACT

The pyrolysis gas of oil palm empty fruit bunches (EFB) was investigated in a fixed bed reactor. The yields and distributions of the pyrolysis products were studied under various operating conditions. In the absence of any additive, the amount and composition of volatile released from EFB depended mainly on the pyrolysis temperature. The pyrolysis gas was analysed for the fractional species distribution. The total yields of hydrogen, Methane, CO and CO_2 *were obtained through the reaction at a temperature range of 300-600 °C. The total yield of hydrogen were dramatically improved to almost 100% with the addition of Sodium Hydroxide (NaOH) and Calcium Oxide (CaO). Hydrogen without CO and* CO_2 *was produced through the reactions of EFB volatiles with NaOH and water to produce hydrogen, sodium carbonate (*Na_2CO_3*), and a small amount of methane as the by-product. The pyrolysis with inexpensive and abundant sorbent such as NaOH and CaO could produce hydrogen-rich gas which is free of CO and* CO_2*, and the process could be optimized at relatively low temperature of 400-500 °C, which is significantly lower than the normal temperature ranges for biomass gasification to produce syngas fuel.*

Keywords: *Bio-Hydrogen, Pyrolysis Gas, Oil Palm EFB.*

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Introduction

In a view of low carbon energy technology, alternative clean energy like hydrogen is expected to be one of the important resources in the near future. The need for a more sustainable and economical method for hydrogen production is crucial. Biomass which is abundant and renewable resources has been considered as one of the most probable source for hydrogen production [1]. The production of hydrogen from biomass resources can be said to be carbon neutral as the CO_2 released when the biomass is consumed is absorbed by the growing plant through photosynthesis.

Thermochemical biomass conversion

The main routes for biomass conversion to hydrogen gas (H_2) are either through bio-chemical or thermo-chemical processes. Figure 1 shows the possible ways of obtaining H_2 from biomass via thermal route. Gasification, which is heating in oxygen-deficient environments has shown as one of thermal routes which provides a competitive way to convert diverse, highly distributed and low-value lingo-cellulosic biomass to a uniform, hydrogen-rich syn-gas mixtures [2,3]. Gasification is normally conducted at a relatively high temperature of 700 – 900 ^oC. The gasification reactions of biomass may be simplified as:

$$\text{Biomass (heat)} \longrightarrow [H_2 + CH_4 + CO + CO_2](g) + HC(g) + Tar(l) + Char(s) \quad (1)$$

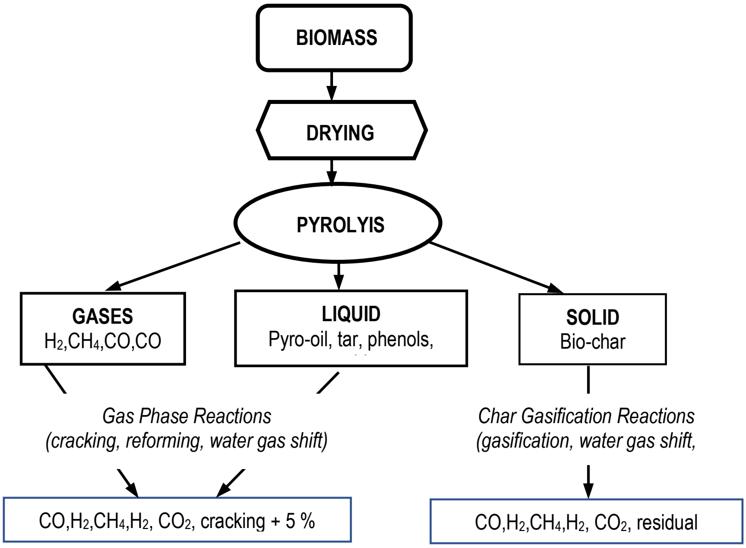


Figure 1: The possible routes for hydrogen production of biomass via thermal process. Adapted from [3]

Since hydrogen element (H) content in biomass ($C_xH_yO_z$) is comparatively low, the yield of hydrogen gas (H_2) from the biomass gasification is also relatively low (Approx. 6% H_2 vs. 25% CH_4) [4]. Several types of catalyst have been identified could play important role in enhancing the proportion of hydrogen fraction in the gasification syn-gas [3,4,5].

Pyrolysis is the thermal process of producing solid, liquid or gaseous fuels by transforming biomass in an oxygen-free environment. The process can be categorized as slow, mild or as fast pyrolysis in which the proportion of the final products (gas, liquid, solid) depend mainly on the resident time of volatiles. Fast pyrolysis has been considered as an efficient thermochemical route to transform biomass into liquid fuel. However, since the liquid yield through fast pyrolysis is high, the gaseous yield is reduced.

In recent years, low temperature, thermal catalytic conversion of biomass has been studied as an attractive alternative route for producing relatively pure hydrogen. Ishida et. al.[4] proposed a method for the synthesis of hydrogen without CO or CO_2 through the reactions of cellulose, alkali metal hydroxides and water vapour at relatively low temperatures (473-623 K) at atmospheric pressure. The main reaction for this process is expressed as:

$$C_6H_{12}O_6 \text{ (cellulose)} + 12NaOH + H_2O \rightarrow 6Na_2CO_3 + 12H_2 \qquad (2)$$

In their work, mixtures of cellulose and sodium hydroxide was injected with steam and heated linearly. The product were sodium carbonate and hydrogen gas. By using this method, hydrogen was formed at a relatively low temperature and little methane (CH_4) was produced as a by-product, but most importantly CO and CO_2 was not formed at all. When Ni catalyst was added to the reacting biomass, production of CH_4 was not observed and the hydrogen yield was almost 100%.

Since biomass is composed mainly of cellulose and hemicelluloses, high concentration of hydrogen could be generated from the thermal catalytic treatment of biomass at lower temperature range than those of normal gasification techniques. However, more fundamental researches are needed on how to enhance hydrogen fraction yield which include reactor performance studies and catalyst selection and utilization.

EFB as biomass feedstock

A large amount of biomass from the Malaysian agricultural-based industries by-products is produced annually. The palm oil sector alone produced approximately 83 million tonnes of solid dry biomass in 2012 and is expected to reach 100 million tonnes in 2020[6]. Empty fruit bunches (EFB), one of the main the oil palm processing wastes, is a suitable feedstock for biofuel productions due to its abundance and favourable physicochemical characteristics. Usually, palm oil industries have to dispose around 1.1 ton of EFB for per ton of palm oil produced [7]. With around 20 million tonnes of EFB produced in 2016, the utilization of this readily available feedstock into various product is greatly observed by those interested in turning biomass into value-added products. Table 1 shows the physical and chemical and properties of EFB

Table 1: Properties of EFB [7].

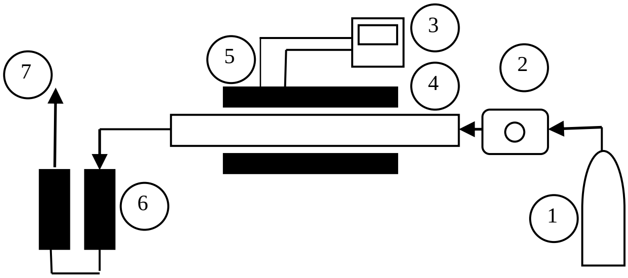
Properties	Fraction (%)
Moisture (%)	2.40 - 14.28
Proximate analysis (%)[a]	
Volatile matter	70.03 - 83.86
Fixed carbon	8.97 - 18.30
Ash	1.30 - 13.65
Ultimate analysis (%)[b]	
C	43.80 - 54.76
H	4.37 - 7.42
O[c]	38.29 - 47.76
N	0.25 - 1.21
S	0.03 - 1.10
Chemical composition (%)[a]	
Cellulose	23.70 - 65.00
Hemicellulose	20.58 - 33.52
Lignin	14.10 - 30.45
Extractive	3.21 - 3.70

[a] Weight percent on a dry basis.
[b] Weight percent on a dry and ash-free basis.
[c] By difference.

EFB has some certain amount of lignocellulosic contents like cellulose (42.7-65.0 % of weight), hemicelluloses (17.1-33.5% of weight) and lignin (13.2-25.3% of weight) [7]. As the ultimate analysis of EFB shows there is 4.37-7.42% (of weight) of Hydrogen in EFB which recommends that it can be an excellent raw material for hydrogen gas production. The moisture content is high enough (2.40-14.28% of weight) to decompose easily during the thermochemical conversion. Taking these into account, the aim for this experiment is to discover an alternative process for producing hydrogen from biomass, in this case empty fruit bunches, via a low temperature thermo-chemical process.

Experimental Setup

In the earlier work [9] a bigger Refuse-Derived Fuel-Pyrolysis system with reactor of internal volume of 9.4 L fitted with external heaters with maximum temperature of 1000 ºC was used. However, the infiltration of air reduced the reliability of the gas composition fractions. A smaller laboratory-scaled, horizontally fixed bed unit was used to pyrolyse the feedstock, with batch-feed of 50-100 g of EFB. The pyrolysis gas from the reactor is passed through a gas cleaning system prior to the gas collection for fraction verification. The gas samples were analysed using gas chromatographer by Agilent Technology Model 6890N GC. Figure 2 shows the schematic diagram of the system.



1-N_2 tank, 2-Digital gas rotameter, 3-Temperature controller, 4-Heaters, 5-SS Furnace, 6-gas scrubber, 7-gas collector bag

Figure 2: The Schematic diagram of the pyrolysis system.

The feedstock is palletised EFB from palm oil mill without additional binders. The work by Ishida [4] was based on a much specific materials (cellulose). This experiment proposed that it could present itself as a viable method for hydrogen production using a much more complex biomass. This work focused on the significance of the effect of various process parameters as a function of temperature with reference to the gas yields, gas compositions and hydrogen composition production. The experiment runs were initially based on batch feeding. Some of the parameters were initially set as constant; moisture content, particle size and heating rate. Sodium Hydroxide (NaOH) and Calcium Oxide (CaO), were later added with certain proportions to the feedstock.

Results and discussions

The effect of pyrolysis temperature on the pyrolysis gas yields and distributions in the absence of sorbent is shown in Figure 3. At temperature of less than 350 ^oC, CO_2 is the most dominant product. Hydrogen is produced at temperature of around 350 ^oC, and the yield increases to its peak of 60% vol. at around 500 ^oC. However, the yield of CH_4 and CO increases at temperature above 500 ^oC and hence, the fraction of H_2 decreases.

This result is in close agreement with those suggested ealier by Hao *et. al*. [8] who studied the pyrolysis of various wood samples, that the yields of low molecular weight products increase with the increase of pyrolysis temperature above 500 ^oC. The wood constituents, hemicellulose and cellulose, could be pyrolyzed at about 500 ^oC. Hao *et. al*.[8] concluded that at 500 ^oC, the primary decomposition reactions were almost completed. Tar and char were the main pyrolysis products in this process, and small amount of gas products was produced. With the increase of pyrolysis temperature, tar and the other high molecular weight products from the primary decomposition reactions will undergo secondary phase reactions. This enhanced the production of lower molecular weight products.

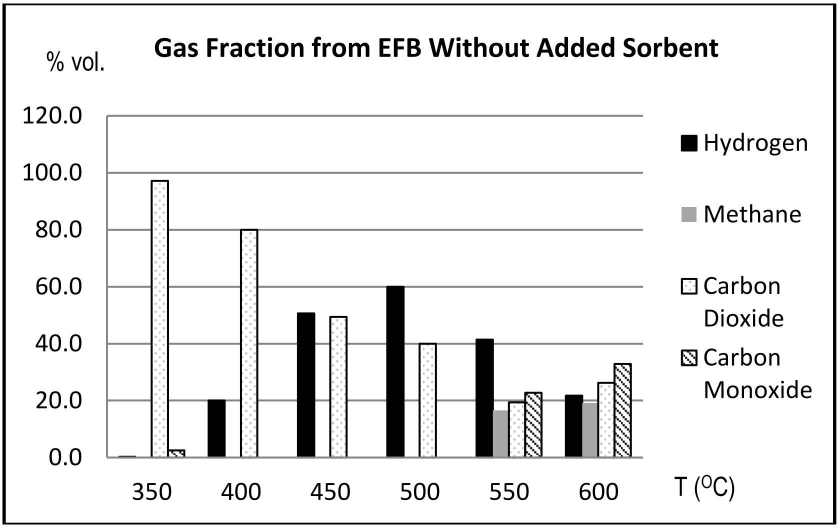


Figure 3. The pyrolysis gas composition fraction of EFB without any added Metal Oxides

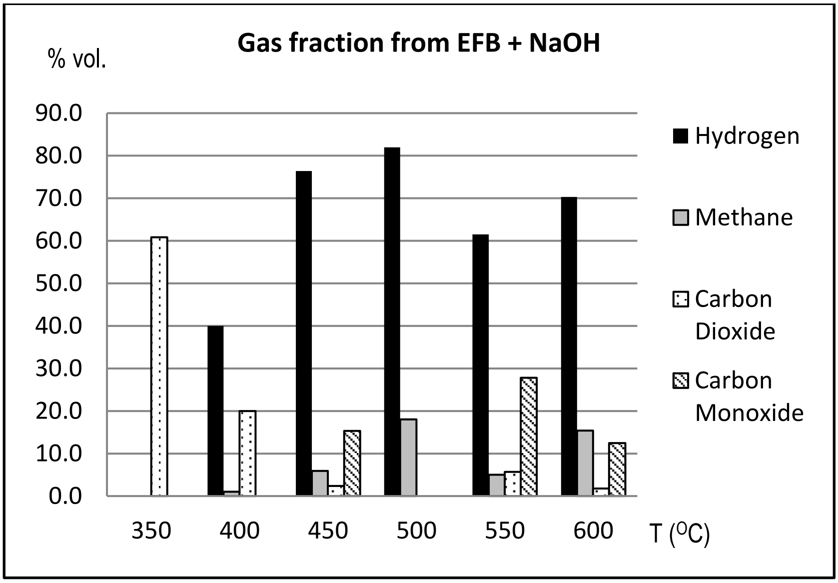


Figure 4. The pyrolysis gas composition fraction of EFB with NaOH.

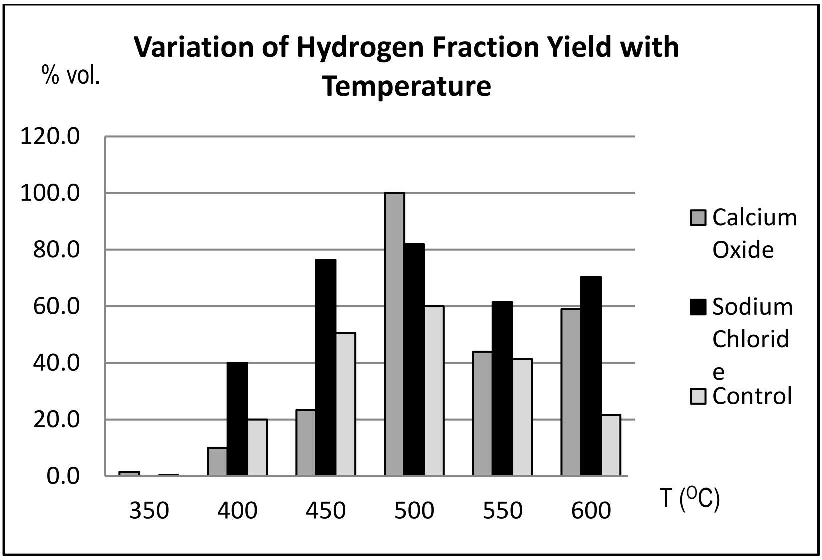


Figure 5. The hydrogen gas fraction of EFB pyro-gas with NaOH and CaO.

The effect of adding alkali metallic oxides/hydroxides in the feedstock on the pyrolysis gas yields and distributions is shown in Figure 4 and Figure 5. The total yield of hydrogen was significantly improved with the addition of NaOH. The total yield of hydrogen was dramatically improved further to almost 100% with the addition of CaO.

Hydrogen without CO and CO_2 was produced through the reactions of EFB volatiles with NaOH to produce hydrogen gas, sodium carbonate (Na_2CO_3), and a small amount of methane as the by-product. Hence, the pyrolysis with inexpensive and abundant sorbent such as NaOH and CaO could produce hydrogen-rich gas which is free of CO and CO_2,

In comparison to work by Ishida [4] using cellulose as feedstock and NaOH, the formation of hydrogen started peaking at lower temperature of 230 °C. However, the formation of methane starts at a temperature above 350 °C and it was concluded that pure hydrogen without CO, CO_2 and CH_4 could be obtained at around 330 °C. Since this experiment is using EFB as feedstock, a broader range of temperature has been selected at 300 °C – 600 °C. The experiment runs will narrow down the temperature range and will select the most optimum temperature for the highest fraction of hydrogen production.

Conclusions

The alternative method of hydrogen production from biomass via thermos-chemical route is still at its infancy stage. Many projects have not yet reached the commercially viable stage. However, it is anticipated that thermo-chemical route of bio-hydrogen production technique is able to progress as a competitive method to other commercially available systems, such as gas reforming and electrolysis, in the very near future. This experiment suggests an alternative method of hydrogen production from biomass such as EFB with readily available substances such as NaOH and CaO, which could be further developed for larger scale applications.

Acknowledgment

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