Parametric Analysis on the Study of Hydrogen Production From Biomass Using Mixtures of Pure Cellulosic Material and Adsorbent

by

Ignatius Benjamin Salip

Dissertation Submitted in Partial Fulfillment of

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UNIVERSITI TEKNOLOGI PETRONAS

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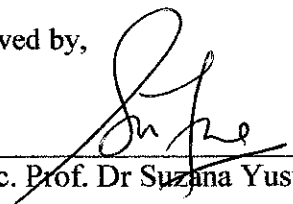
CERTIFICATION OF APPROVAL

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Approved by,

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(Assoc. Prof. Dr Suzana Yusup)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

DECEMBER 2010

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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IGNATIUS BENJAMIN SALIP

ABSTRACT

The energy consumption and demand in the world today has become a critical issue. The energy resources such as fossil fuels, that we currently relying on are very quickly depleting thus lies the need for research to develop alternative renewable resources that can cater to our demand and consumption. Biomass energy is the one of the best alternative energy sources that is needs to be studied in order to solve this issue. This is because biomass energy is renewable and environmental friendly. Furthermore, biomass materials are available in almost all of the countries that could reduce the dependence foreign resource for fuel requirements.

The steam gasification of biomass (cellulose) when coupled with in situ CO_2 capture using CaO is a promising pathway for the renewable production of Hydrogen (H_2). A H_2-rich steam results from the conversion of biomass with steam at moderate temperature (~400-700°C) by manipulating the equilibrium composition of the conversion product with the removal of CO_2 as soon as it formed. CaO react directly with CO_2 to form a solid $CaCO_3$. Optionally, the CaO can be regenerated from $CaCO_3$ by heating it around 700-950°C.

The main objective in this project is to optimize the parameters affecting the biomass gasification in maximizing the hydrogen yield from a local biomass, PKS (palm kernel shell).

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Biomass is a biological material derived from living, or recently living organisms. It contains stored energy derived from the sun, for example, plants absorb the sun's energy in a process called photosynthesis. This chemical energy is then passed to animal or human that eats them. When the biomass is burned, the chemical energy of the biomass will be released as a heat. In old use, biomass example like garbage and wood waste is burned to produce steam for making electricity. This biomass is a renewable source of energy, as we can always grow more trees, crops and waste will always exist.

Burning this biomass is not the only way to release its chemical energy. Nowadays, biomass can be converted to other useable form of energy such as methane gas, and most importantly to hydrogen. Generally, most hydrogen is used in refining process, treating metals and food processing. Furthermore, hydrogen is one of the main sources to generate electricity through fuel cells. Fuel cells are devices that directly convert hydrogen into electricity. Large hydrogen quantities are needed in the petrochemical industries, where hydrogen is used in ammonia production.

Gasification process is a viable route in converting biomass into simple fuel gases. The product produced from the gasification process depends on by the operating conditions such as, heating rate, pressure, gasifying medium, and types of adsorbent and catalyst used. Steam gasification of biomass is an attractive process for producing H_2 rich gas [36]. Furthermore, the excess steam in the product after the gasification can be easily separated by condensation.

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Biomass energy is highly emphasized in the 9th Malaysian plan [1]. There are many incentives given to the promotion of the use of renewable energy from biomass in Malaysia. The biomass technology range from the conversion of biomass in solid fuel such as briquettes and charcoal production to the direct combustion of biomass for use in the palm oil, rubber and brick making industries and the commercial use of biomass energy through Small Renewable Energy Program [1].

1.2 Problem statement

Taking fossil fuel depletion and pollutant emission into consideration, the promising hydrogen production should be based on renewable materials. Due to its abundant amount, CO_2 neutral, and low in sulphur, biomass has been known as the most potential materials for hydrogen production in the near future.

The necessity of the biomass application ware development has risen rapidly especially, the development of highly effective energy conversion technology and the practical use. This due to the increasing energy demand in the world as in 2008, total worldwide energy consumption was 474 exajoules (474×1018 J) with 80 to 90 percent derived from the combustion of fossil fuels [38]. Therefore, it is significant the world needs to reduce its reliance to the fossil fuels for the needs of our future generation. Furthermore, energy production from biomass would help to secure local energy supplies due to the diversity and abundance of renewable biomass resources, e.g. forest residues, agricultural crop waste, mill wood waste, logging waste and animal waste [2].

Moreover, the production of energy and fuels from biomass is receiving considerable interest, particularly due to concerns regarding regional energy security and the need to reduce greenhouse gas emission [3]. Nowadays, biomass has been widely acknowledged as a key renewable source for meeting future energy demand [4]. In addition, biomass utilization can expedite mitigation of green house gas emission and carbon sequestration cycles and promote "green" industries with associated growth in rural economies [6]. A highly promising way to exploit biomass resources involves converting biomass to a H_2 rich gas. H_2 produced from biomass could be utilized as a

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replacement energy carrier for fossil fuel in transport, industrial, commercial and residential sectors [2].

In more detail, factors that maximize the hydrogen production are needed to be studied and analyzed to make sure the biomass is converted efficiently to the fuel gas.

In a nutshell, the research and investigation of various biomass materials, for long term commercial global fuel use, is the challenge of today and the investment for the near future. These investigations are expected to produce the required materials and technologies to replace the fossil fuel, in particular crude oil, which will be exhausted sooner or later [5].

1.2.1 Significant of project

Steam gasification of biomass, with the presence of a calcium oxide (CaO) sorbent for carbon dioxide (CO_2) capture is a viable process for the renewable and sustainable production of rich Hydrogen (H_2).

fThe biomass conversion to H_2 will be at moderate temperature. The CO_2 produced from the gasification will be removed as soon as it formed in the product, using the sorbent where CaO reacts directly with CO_2 to form solid $CaCO_3$. Besides, a high temperature process can subsequently used to regenerate CaO, producing a pure stream of CaO.

Local biomass PKS (palm kernel shell) is selected and used as a biomass sample. The reason why palm oil shell is used as a sample is to study and analyze the potential of the local biomass waste in producing hydrogen gas. Furthermore, Malaysia as the world second largest producer of palm oil, relatively will have a huge palm oil industry waste. If these all of these waste is utilize efficiently, this would safeguard our energy supply, especially from clean and renewable resources such as PKS. Moreover, this also can reduce our reliance on fossil fuels, thus will preserve our very own oil and gas resources in Malaysia with this biomass as an alternative energy.

1.3 Objectives

The main objective of this project is to optimize and to study the effects of the parameters affecting H_2 production on the steam gasification. The key parameters that need to be studied and experimented are;

- Heating rate of the biomass steam gasification's
- Steam to biomass ratio
- Sorbent to biomass ratio

1.4 Scope of study

A number of processes can be utilized to convert biomass into H_2 including biological, chemical, and thermochemical pathways. The scope of study through this project will widely cover the biomass steam gasification process, which investigating the thermochemical conversion process, the steam gasification of biomass.

In this paper the steam gasification of biomass coupled with CO_2 capture is investigated using thermodynamic equilibrium theory. In addition, the optimal reaction parameters are identified for maximizing H_2 yield and concentration. Parametric analysis is an efficient method for identifying an operating window for maximizing H_2 yield, maximizing H_2 concentration and minimizing the presence of CO and CO_2. Rigorous experimental investigation is necessary in order to determine the influence of heat and mass transfer limitations on the overall efficiency of the proposed continuous H_2 production/CO_2 capture process. The studies also cover the literature review about the effect of key variables which includes the (i) reaction temperature, (ii) steam to biomass ratio, (iii) sorbent to fuel ratio.

The flowability and characteristics of the absorbent, CaO will also be studied. Seven of the sorbent powder characteristics will be determined, that include angle of repose, angle of spatula, angle of fall, angle of difference, compressibility, cohesion, dispersibility and three other auxiliary values aerated bulk density, packed bulk density, and uniformity.

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CHAPTER 2

LITERATURE REVIEW

2.1 Biomass energy

2.1.1 Introduction

As a result of environmental and other policy considerations, there is increasing world-wide interest in the use of biomass resources as feedstock for producing power, fuels, and chemicals. It is now widely acknowledged that combustion of fossil fuels contributes to the buildup of CO_2 in the atmosphere, which in turn contributes to the greenhouse effect, gradually warming the planet. In 2005, the CO_2 concentration was 379 ppm, approximately 180–300 ppm more than the equilibrium concentration of CO_2 in the atmosphere for the last 650 000 years [7]. Therefore, biomass resources are one of the major component of strategies to mitigate global climate change in the world.

Plant growth "recycles" CO_2 from the atmosphere, and the use of biomass resources for energy and chemicals results in low net emissions of carbon dioxide. The emissions of Nitrogen Oxide (NO_x) and Sulfur Dioxide (SO_x) from biomass facilities are also typically low. This helps biomass technologies meet local and regional environmental regulations and reduce emissions that contribute to acid rain. The use of these locally produced energy resources also results in new markets for agricultural and forestry products and provides a mechanism for rural economic development. As a result of these and other factors, many national governments are currently developing policies and regulations intended to expand the use of biomass over the next decade and beyond.

2.2 History of the biomass energy

Historically, development of biomass gasifiers has focused on small-scale units for a variety of uses. The biomass energy has been proven reliable and had been extensively

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used for transportation and on farm systems during World War II is wood or biomass gasification [13]. The interest in small-scale gasifiers began over a century ago and has continued into the present. Over the past two decades, there has been increasing interest in large-scale biomass gasifiers that can reliably be used to commercially produce heat, power, or other products.

2.3   H$_2$ production from biomass

Biomass is a diverse and renewable resource, which can be exploited for the production of H$_2$. Hydrogen is a colorless, odorless gas that accounts for 75 percent of the entire universe's mass. Biomass is defined broadly as contemporary organic matter formed by the photosynthetic capture of solar energy, which is stored as chemical energy [2]. Suitable forms of biomass for H$_2$ production can be categorized as: (i) energy crops, or (ii) waste materials. The sources will include the mill wood waste, forest residues, woody energy crops, agricultural crop waste, animal waste, industrial waste and sewage sludge.

Generally, H$_2$ is produced via: (i) steam methane reforming (SMR) (48%), (ii) coal gasification (18%), (iii) oil reforming (30%), and (iv) electrolysis (3.9%). Together, fossil fuel sources amount to 96% of total H$_2$ production [14]. These production pathways are non-renewable and result in significant CO$_2$ emissions [15].
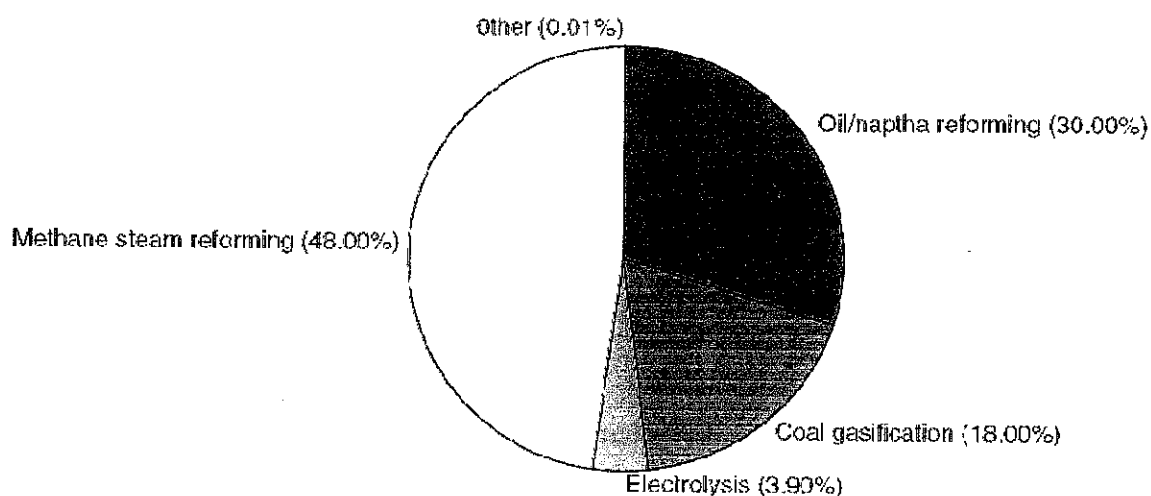
Figure 1: Distribution of primary energy sources and production methods for hydrogen production [14]

Thus, clean and renewable resources and sustainable pathways are necessary if H_2 is to become a fundamental energy resource for the future.

Furthermore, there are a number of methods in extracting hydrogen from biomass. These include: (i) thermochemical gasification, (ii) fast pyrolysis, (iii) solar gasification, (iv) supercritical conversion and (v) biological hydrogen production [8-11]. The most suitable conversion is dependent on nature of the biomass species.

2.4 Biomass steam gasification for hydrogen production

Biomass gasification technologies are expected to be an important part of the effort to meet these goals of expanding the use of biomass. Gasification technologies provide the opportunity to convert renewable biomass feedstock into clean fuel gases or synthesis gases. These gaseous products can be burned to generate heat or electricity, or they can potentially be used in the synthesis of liquid transportation fuels, hydrogen, or chemicals. Gasification offers a combination of flexibility, efficiency, and environmental acceptability that is essential in meeting future energy requirements [12].

Biomass gasification generally refers to the thermochemical conversion of solid biomass fuels using a gasifying agent (e.g. steam, air (partial-oxidation) or CO_2) to a mixture of combustible product gases, including: H_2, CH_4, CO and CO_2, plus heat to

continue the endothermic gasification process. A generalized reaction describing biomass gasification is as follows;

Biomass + H_2O (or O_2) $\rightarrow$ CO, CO_2, H_2O, H_2, CH_4 + other hydrocarbons
$\rightarrow$ Tar + char + ash
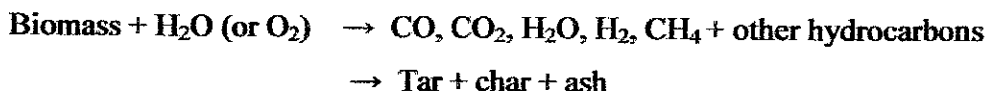
The actual biomass gasification product gas composition depends heavily on the gasification process, the gasifying agent, and the feedstock composition [22]. When thermochemical combustion of biomass is undertaken, using steam as the gasifying agent, the resulting product is rich in H_2 [2]. The use of steam instead of air will yield more H_2 gas as the additional H_2 produced from the decomposition of H_2O.

Previous researches have been done in comparing the best gasification agent in biomass gasification. Biomass gasification can be made in at least in three main gasifying agents; steam, steam + O_2 mixtures, and air (air including with some steam). Oxygen enriched air has not been proved yet as gasifying agent for biomass [16]. Air is cheap and widely used gasifying agent. Unfortunately, the large amount of nitrogen from air dilutes in the syngas and thus lowering its heating value.

The equivalent ratio (ER), which is the ratio of oxygen required for gasification to oxygen for full combustion for a given amount of biomass, is usually $0.2 - 0.4$ [18]. The equivalent ratio of the reaction is defined according to Eq. 1(1):

$$CnHmOp + (n + m/4 - p)O_2 \rightarrow nCO_2 + (m/2)H_2O \quad \text{(exothermic reaction)} \quad (1)$$

If pure oxygen is used as a gasifying agent, the heating value of the syngas will increase but the operating cost will also increase due to the requirement of oxygen production. Heating value and hydrogen content of syngas can be increased if steam used as the gasifying agent [19]. Heating value of product with steam as the gasifying agent is about $10 - 15$ MJ Nm^{-3} [20], compare to $3 - 6$ MJ Nm^{-3} for air gasification of biomass [21] and 38 MJ Nm^{-3} for natural gas. In the absence of O_2, conventional steam gasification is endothermic, which means that an additional heat source is required to drive the reaction system. This is a challenge because, obviously, this input of energy reduces the maximum efficiency of the process.

In the gasification of biomass, biomass is converted to a mixture of gases, at moderate temperature (500 − 800°C) and in the presence of steam. This conversion process is according to Eq. 2;

$$C_nH_mO_p + (n-p)H_2O \rightarrow (n + m/2 - p) H_2 + nCO \qquad \text{(endothermic)} \qquad (2)$$

The reaction temperature and steam-to-biomass ratio are reported to be the dominant experimental parameters, influencing both the concentration of H_2 in the product gas and the total yield. However, a broad range of H_2 concentrations are reported, from 20 to 60%-mol and even the highest levels are likely to be insufficient for commercial application [2]. In addition, one of the major issues in biomass gasification is to deal with the tar formation that occurs during the process. The operation parameters, such as temperature, gasifying agent and residence time, play an important role in formation and decomposition of tar. On this basis, there is need for further work to significantly increase the output of H_2 from biomass.

2.4.1 Steam gasification coupled with CO_2 capture.

In this research, it demonstrated that the H_2 yield can be increased using CaO to capture CO in situ. The basic idea is to remove CO_2 as soon as it formed, as can be seen in Eq. 2, alters the equilibrium composition of the product gas and promotes the production of H_2-rich gas.

Table 1: Important chemical reaction in the steam gasification of biomass [29, 36]

Name of reaction	Chemical Reaction	ΔH°_{923} (kJmol-1)	Eq. No
Water-gas shift	$CO + H_2O \rightarrow CO_2 + H_2$	−35.6 (exothermic)	(3)
Methane reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	225 (endothermic)	(4)
Water–gas (i)	$C + H_2O \rightarrow CO + H_2$	136 (endothermic)	(5)
Water–gas (ii)	$C + 2H_2O \rightarrow CO_2 + 2H_2$	100 (endothermic)	(6)
Oxidation (i)	$C + O_2 \rightarrow CO_2$	−394 (exothermic)	(7)
Oxidation (ii)	$C + 0.5O_2 \rightarrow CO$	−112 (exothermic)	(8)
Boudouard	$C + CO_2 \rightarrow 2CO$	171 (endothermic)	(9)
Methanation	$C + 2H_2 \rightarrow CH_4$	−89.0 (exothermic)	(10)

CaO is capable in removing CO_2 to very low concentrations at moderate temperatures (450 – 750°C), and under atmospheric pressure. Furthermore this CaO can be easily derived from a range of abundant and low cost precursor including limestone ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and calcium hydroxide ($Ca(OH)_2$). This is achieved by heating the material beyond its calcination temperature (~400°C for limestone and dolomite; ~ 400°C for calcium hydroxide in an inert atmosphere).

CO_2 is captured in the form of $CaCO_3$, a common and stable species according to the following Eq. 11:

CO_2 capture reaction:

$CaO(s) + CO_2 (g) \rightarrow CaCO_3 (s)$,

$\qquad H^o_{923} = -170.5 \, kJ \, mol{-}1$ \hfill (exothermic reaction) \hfill (11)

The Heat generated from this exothermic gas-solid absorption reaction, taking place in situ, and then the energy from this reaction is available to drive any of the endothermic biomass conversion reaction showed in Table 1.

When the CaO sorbent reach its conversion capacity, then it can be regenerated by heating beyond its decomposition temperature (~ 973 K), according to Eq. 12,

Sorbent regeneration reaction;

$CaCO_3 (s) \rightarrow CaO (s) + CO_2 (g)$,

$\qquad H^o_{923} = 170.5 \, kJ \, mol{-}1$ \hfill (endothermic reaction) \hfill (12)
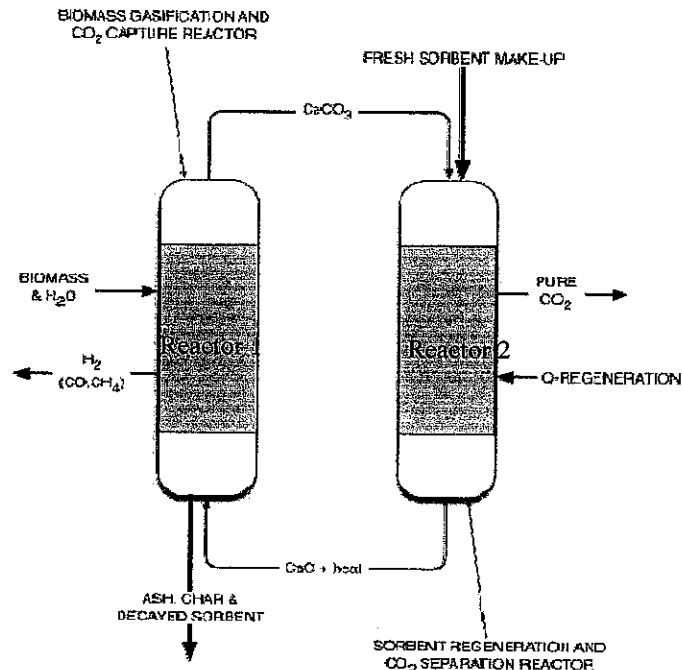
Figure 2: Simple diagram representing the biomass gasification coupled with CO_2 capture a CaO sorbent. First Reactor (1) Biomass gasification and CO_2 capture reactor; Second Reactor (2) Sorbent regeneration and CO_2 separation reactor.

The carbonation reaction of CaO to separate CO_2 from hot gases (T > 600°C) is very fast and the regeneration of the sorbent by calcining the $CaCO_3$ into CaO and pure CO_2 is favored at T > 900°C (at a partial pressure of CO_2 of 0.1 MPa) [23]. The overall biomass steam gasification reaction sketch is presented in Figure 2;

The biomass, steam and CaO is continuously feed to the first reactor, where after the biomass gasification reaction take place, the CO_2 is captured according to Eq. (11). The unconverted char, ash, and fines will be removed from the reactor. Then, the CO_2 captured in form of $CaCO_3$ is cycled to the second reactor, where the CO_2 is released, according to Eq. (12). The regenerated CaO from this reactor then will be fed to the first reactor.

2.5 Influence of biomass properties on the gasification process

The different elemental composition and chemical properties of biomass feedstock have a significant effect on the performance of the gasification process especially the yield and product gas composition. It includes; (i) moisture content; (ii) amount of

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volatile matter; (iii) inherent material content; (iv) thermochemical composition (amount of cellulose, hemicelluloses and lignin) (v) physical qualities (particle size, shape and density).

Biomass fuel with moisture content above about 30% makes ignition difficult and reduces the conversion of the product gas due to the need to evaporate the additional moisture before combustion/gasification can occur [24]. During gasification, high moisture contents lead to lower raw product gas heating values, in part through the dilution of the product gas with additional water vapor. Partial oxidation gasifiers require a greater degree of combustion to provide heat for additional drying, increasing carbon dioxide levels.

The feed particle size also has a big influence to the product gas yield. Previous study proved that smaller particle feed size will increase the product gas yield. The size of particle affects the heating rate of the biomass, whereas the heating rate is higher in the small particle than the bigger particle. Experiment conducted by Herguido et al.[25] where pine saw dust (mean particle diameter 500mm) and pine wood chips (approximate particle dimension 100mm^3) gasified and compared. The experiment conducted in an atmospheric pressure, fixed bed reactor (FBR), with an internal diameter of 150mm, temperatures at (650 – 780°C). The result, maximum of 1.2 kg-gas per kg-biomass was reported for the pine sawdust compared to 0.7kg of gas per kg of biomass for the wood chips at 780°C.

The main compositions in the biomass consisted of cellulose and lignin. The cellulose and lignin content in the biomasses was one of the important parameters to evaluate the pyrolysis characteristics. Asri Gani and Ichiro Naruse [26] reported that for the biomass with higher cellulose content, the pyrolysis rate became faster while, the biomass with higher lignin content will result a slower pyrolysis rate.

2.6   Effect of temperature on the gasification of biomass

Temperature has been identified as an important reaction variation. An increase in reaction temperature is expected to enhance the extent of conversion of a biomass fuel to gas product.

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It is also expected that, the increase in temperature during the gasification process led to higher gas yields with a reduction in the amounts of char and liquids formed which could be due to further cracking of liquids and enhanced char reaction with the gasifying medium. This increase in gas yield with temperature, could be due to various reasons, such as: (i) higher production of gases in the initial pyrolysis step, whose rate is faster at higher temperatures, as pointed out by Herguido et al. [25], (ii) the production of gas through the endothermic char gasification reactions, which are favorable at elevated temperatures and, (iii) the increase of gas yield resulting from the steam reforming and cracking of heavier hydrocarbons and tars.

For example C. Franco et al. demonstrated the influence of temperature on the gas composition for three biomass species, pine, holm-oak and eucalyptus. Hydrocarbon concentrations were joined together as C_nH_m, with the exception of methane, due to its higher concentration. The other hydrocarbon formed in appreciable amounts was C_2H_4, but its concentration was much lower than CH_4. The result shown in Fig. 3, the effect of temperature on gas composition produced from pine gasification is shown. The rise in temperature was found to increase H_2 formation from 26 to 33 mol%, whilst CO decreased from 41 to 38%. Hydrocarbon concentration was also observed to decrease and no significant changes were detected in CO_2 formation, which was around 14%.

These trends agree fairly well with the results reported by other researchers, for instance Corella et al. [27] and Walawender et al. [28]
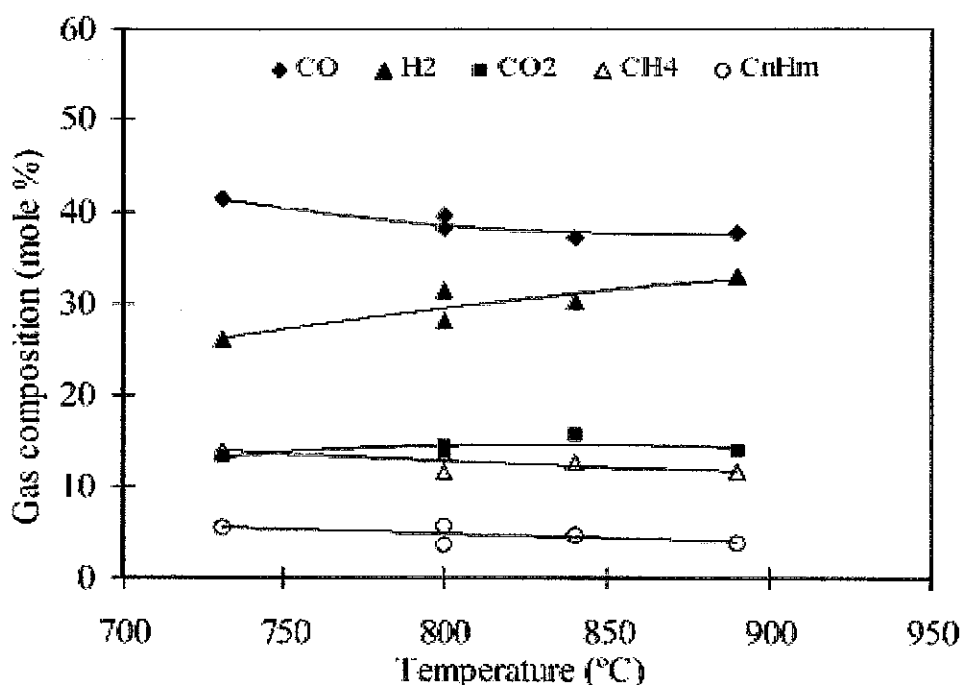
Figure 3: Effect of temperature on gas composition for pine wastes and a steam/biomass ratio of 0.8 w/w.

However, with regards to enhancing H_2 yield, the selection of reaction temperature involves a compromise between kinetic and thermodynamic limitations, noting that Eqs. (2), (4) – (7), (9) are endothermic, whereas Eqs. (1), (3), (8), (10) are exothermic. Hence, the selection of a suitable reaction temperature for H_2 production requires establishing a balance between the maximum available H_2 yield and the conversion of char to gas.

2.7 Influence of the steam to biomass ratio on the gasification of biomass

An increase in the ratio of reactant steam to the biomass fuel, fed to the gasifier, is expected to lead to an increase in the H_2 output according to the water–gas shift reaction, Eq. (3), and the steam reforming reaction, Eq. (4). In addition, in practice, excess steam is often used to drive the cracking and reforming reactions, according to Eqs. (4)–(6). Nevertheless, regarding process efficiency, an upper limit is expected due to an increase in the H_2O (g) in the product gas and energy penalties associated with the generation of steam, when excess steam is input to the system. Such considerations demonstrate the importance of selecting the optimal steam-to-biomass ratio.

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The trend and analysis of the steam to biomass ratio effect to the H_2 gas yield have been reported from the previous literature from Herguido et al. [25] and Turn et al. [29]. The increase in H_2 concentration, corresponding to an increase in steam-to-biomass ratio, observed in two studies is illustrated in Fig. 4. Turn et al. [29] studied the effect of the steam-to-biomass ratio from 1.1 to 4.7 at 800°C and Herguido et al. [25] varied the steam to biomass ratio from 0.5 to 2.5 at 750°C. Note that a direct comparison cannot be made between these two studies, considering the steam-to-biomass ratio, because different biomass species with different H-contents were used. However, it is possible to obtain general insight into the relationship between the ratio of the feed streams to the gasification reactor and the H_2 output by comparing this data.

The trends from the both date series shows that an increase in H_2 corresponding with an increase in the steam to biomass ratio. However, the rate of increase is slower for the higher steam to biomass ratios for more than 2, (>2). On the basis of these results it appears there is a maximum effective steam to biomass ratio for maximizing H_2 output .
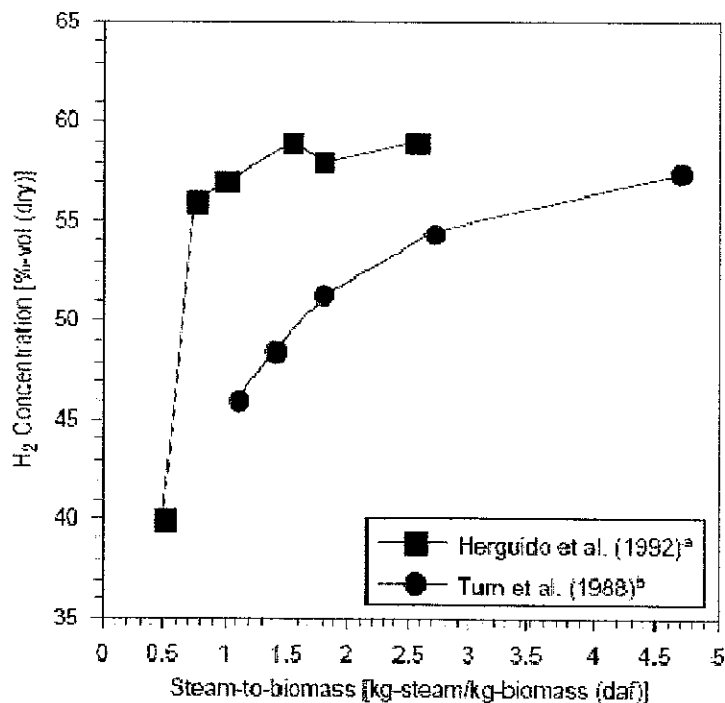
Figure 4: The effect of steam to biomass ratio on the concentration of H_2 in the product gas during biomass gasification. a) Constant temperature: 750°C, b) Constant temperature: 800°C.

Previous studies by Florin et al. [32] reported that the steam biomass ratio of 1.5 – 2.0 is considered optimal for maximizing the concentration of H_2 output without compromising the concentration of H_2 in the product gas. The experiment was conducted with varying the steam to biomass ratio, 1, 1.5, 2, and 5, and observed across range temperature of (600-1600K). The H_2 yield was most sensitive to an increase in the steam to biomass ratio in the low temperature range (600–900 K) and a maximum H_2 yield was predicted when the steam-to-biomass ratio was 2, at a temperature of 900 K. He also concluded that for temperature more than 900K (>900K) there will be a decrease in H_2 yield which corresponds with the decomposition of $CaCO_3$, according to Eq. (12).

A H_2 production process operating with such a high steam to biomass ratio is not likely to be energy efficient due to the high energy penalties associated with generating the large amounts of steam. The energy used to generate the steam is not likely to be recovered when the steam condenses.

2.8   Effect of the calcium oxide on the decomposition of cellulose

The presence of CaO has a significant influence on the rate of cellulose decomposition. Florin et al. [2] investigated the influence of CaO on the decomposition of cellulose, conducting an experiment with and without using the CaO in the biomass steam gasification. He concluded that the presence of CaO is expected to effect the decomposition of cellulose at least in two ways, i) primarily the removal of CO_2 as soon as it formed according to Eq. (11) influence the equilibrium balance, by pushing the water-gas shift reaction to the right, according to reaction Eq. (3). In addition the exothermic CO_2 capture reaction provides additional heat to drive the endothermic decomposition process. ii) CaO may influence the decomposition of cellulose by acting as a decomposition catalyst thus dramatically changing the nature of the decomposition way.

In the other way, the CaO may also enhance the dehydration of cellulose by rapidly absorbing the evolved H_2O and the additional heat generated by the exothermic

reaction, according to Eq. 13, where it would promote the endothermic conversion process.

Cellulose dehydration;

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad \text{(exothermic reaction)} \qquad (13)$$

2.9 Sorbent to biomass ratio

Florin et al. [32] reported that in order to determine the influence of the sorbent to biomass ratio, the Ca:C molar ratio is varied from 0 to 2, based on his experiment. Based in Fig. 4, the predicted H_2 yield as a function of the Ca:C molar ratio and reaction temperature and reaction temperature is displayed.
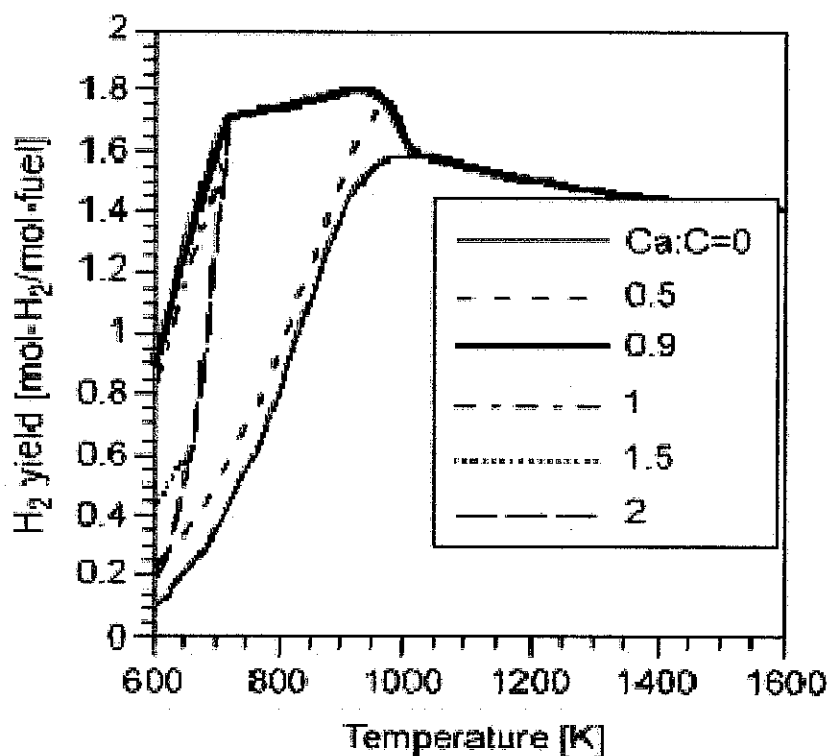
Figure 5: The H_2 yield as a function of the Ca:C molar ratio and temperature (steam to biomass ratio = 1.5 on a molar basis).

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In the absence of CaO (Ca:C=0), the H_2 yield increases from 0.1 to a maximum of 1.6 mol-H_2/mol-fuel, at 1000 K. When CaO is introduced to the reaction system, with a Ca:C ratio of 0.5, the H_2 output increases from 0.2 to a maximum of 1.7 mol-H_2/mol-fuel, at 980 K. A further improvement in the H_2 output achieved when the Ca:C molar ratio was increased to 0.9. At this ratio, consistently higher yields are predicted for a range of temperatures from 700 to 1000 K, presenting a broad process operating window. Maximum output of 1.8 mol-H_2/mol-fuels was predicted at 940 K. From the report, Florin et al. [32] concluded that the Ca:C molar ratio of 0.9 should be viewed as the optimal loading based.

Another experiment done by H. Guoxin et al. [37] where the experiments were conducted in the absence ([Ca]/[C] = 0) and presence ([Ca]/[C] = 0.1, 0.3, 0.5, 0.7, and 1). The reaction conditions were in temperature of 923K, steam to biomass ratio of 0.9 with 2 minutes holding time. The test results are shown in Fig. 6.
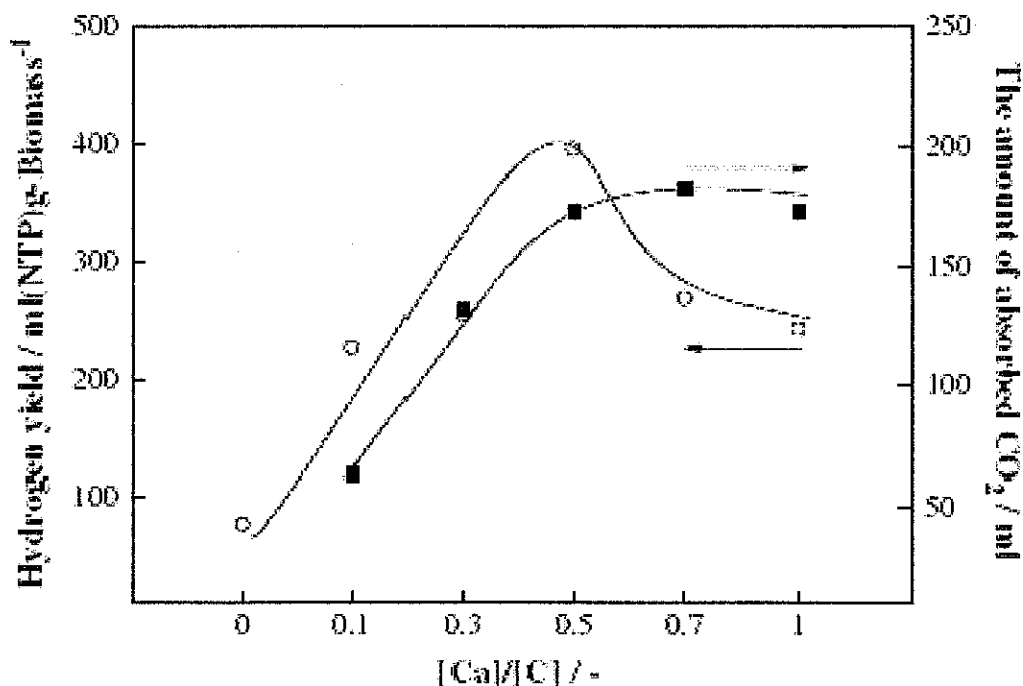
Figure 6: Effect of [Ca]/[C] on H_2 yield and the amount of absorbed CO_2

Fig. 6 shown that the effect of [Ca]/[C] on the H_2 yield and the amount of absorbed CO_2. On comparison with the case ([Ca]/[C] = 0) it can be found that the H_2 yield increases dramatically in the presence of the sorbent. At [Ca]/[C] = 0.1, the H_2 yield has more than trebled (from around 75 to 227 ml g^{-1}) and at [Ca]/[C] = 0.5, it increases over 4 times (from 75 to almost 400 ml g^{-1}). In these experiments, CaO plays an important role, as a CO_2 sorbent. On the one hand, CO_2 capture by CaO would result in an increase in the H_2 content as CO_2 capture by CaO will change the original equilibriums of gas phase and push reactions, water-gas shift reaction and methane steam reforming, Eq. (3), and (4) to take place on the direction of hydrogen production to produce the additional H_2.

H. Guoxin et al. [37] also concluded that based from Fig. 6, it can be found that the effect of [Ca]/[C] can be divided into two stages. In the first stage [Ca]/[C] increases from 0 to 0.5 and in the second stage [Ca]/[C] varies from 0.5 to 1. In the first stage, both the H_2 yield and the amount of absorbed CO_2 increase as a result of the enhancement of the contact frequency of CaO and the intermediate products. In the second stage, the H_2 yield decreases while the amount of absorbed CO_2 varies slightly, indicating that beyond a certain [Ca]/[C] the amount of absorbed CO_2 increases only marginally with the most of supplied CaO going unreacted.

2.10 Sorbent improvement

2.10.1 CaO sorbent hydration

There are many types of solid base catalyst such as hydroxides and alkaline line-earth metal oxides and. CaO falls down on the alkaline metal oxides. Based on the findings from Cantrell et al. [42] and Seki et al. [43],the reactivity order of the alkaline metal oxides is arranged from BaO > SrO > CaO > MgO. Among the alkaline metal oxides, CaO is the most well searched of heterogeneous catalyst and adsorbent [41]. There are also four reasons which account for this, high basicity, lower solubility, cheapest price among all and it is easier to handle [41].

Others have reported, for example Moran D.L et al. [42] , reported that hydration of calcined lime with methanol/water mixtures produced sorbents that had higher

reactivity, compared to the same lime hydrated with water only. Thus, sorbent improvement, as a minor project this study, the sorbent CaO hydration with ethanol solution is proposed will be further improve the surface area and the reactivity of the sorbent.

2.11 Sorbent characteristics.

2.11.1 Flowability of a powder

A simple definition of powder flowability is the ability of the powder to flow. Flow behavior is multidimensional in nature, and it depends on many physical characteristics. Flowability, in fact, is a consequence of the combination of the physical properties of material that influence flow, environmental conditions, and the equipment used for handling, storing, and processing these materials [39].

The capability of predicting powder flowability is helpful for preventing production stoppages in all bulk solid handling. However, no one test could ever fully quantify the flowability of a powder. Some of the factors that affect the flowability of bulk solids and powders include particle size, moisture content, humidity, flow agents, temperature, and pressure.

When dealing with powder, it is important to understand the flowability characteristics of the given powder. In general, there are seven characteristics of a powder and three auxiliary value. The seven characteristics are; Angle of Repose, Compressibility, Angle of Spatula, Cohesion, Angle of Fall, Dispersibility and Angle of Difference. Three auxiliary values, Aerated Bulk Density, Packed Bulked Density and Uniformity. Furthermore, the particle size and particle-size distribution plays a significant role in flowability as do as the other properties.

2.11.2 Seven Powder Characteristic

1. Angle of Repose

Angle of repose in other words is the maximum slope, measured in degrees from the horizontal, at which loose solid on material will remain in place without sliding.

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This measurement is carried out by subjecting the standard sieve to vibration and letting the samples pass through the funnel.

Powders with good flowability have a small angle of repose and reproducibility is also good. Powders which have high adhesion tendency have a high angle of repose, and tend to have poor flowability.

2. Angle of Spatula

The angle of spatula provides an indication of the internal friction between particles. This measure the angle of the powder accumulates on top of the spatula. In other words, it is determined by inserting a flat blade into a pile of granular material and lifting vertically. The new angle of repose, which the material forms relative to the blade surface, is known as the Angle of Spatula. This value is normally larger than the angle of repose. The greater the angle of spatula, the poorer is the powder's flowability. Generally, bulk solids with an Angle of Spatula less than approximately 40 degrees are considered free flowing. It is possible to have an Angle of Repose of 60° and angle of spatula 100°.

3. Angle of Fall

When a material lies in a pile at rest, it has a specific Angle of Repose. If the supporting surface experiences vibrations, impacts or other movement, the material on the sloped sides of the pile will dislodge and flow down the slope. The new Angle of Repose that forms is referred to as the Angle of Fall. This parameter provides an indication of particle size, shape, uniformity and cohesion—and thus the flowability of the material.

4. Angle of Difference

This Angle of Difference indicates the differences between the Angle of Repose and the Angle of Fall. This parameter is related to the internal cohesion of the granular particles. Large Angle of Difference can occur when the Angle of Fall is fairly small, and this can be used to conclude that the powder or the material is more flowable.

5. Compressibility

In brief, compressibility is a measure of the relative volume change of a fluid or solid as a response to a pressure (or mean stress) change. The compressibility can be obtained by measuring the aerated bulk density and the packed bulk density then making the ratio of these two measurements. The compressibility is the value which has the greatest effect on flowability of a powder.

6. Cohesion

Cohesion is the intermolecular force that holds together the molecules in a solid. This is measured by taking the standard sieves and subjecting them to vibration for a constant time at a constant force, and measuring the cohesion from how much powder passes through.

7. Dispersibility

Dispersibility is a measure of the propensity for a granular material to form dust and thus lose mass to the surrounding air. The more dispersible a material, the higher the potential for mass loss due to dust generation.

2.11.3 Three Flowability Supplementary Values.

1. Aerated Bulk Density.

Bulk density parameter is defined as the mass of a granular material that will occupy a specific volume. This bulk density does not include only particle mass but also the air entrained in the void spaces between the particles. Bulk density is used to determine the effective capacities of the particles for storage bins or containers.

Aerated bulk density is the density at which the powder in its most loosely packed form. This is measured by sieving the sample through the vibrating chute to fill a measuring cup.

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2. Packed Bulk Density.

The packed bulked density is the density of the powder when it is packed. The powder sample is filled in the measuring cup and reaches a height, then is it tapped for a set number of times under a constant condition. The packed bulk density then is measured after the tapping has caused the sample to consolidate.

3. Uniformity.

The relative homogeneity of the size and shape of the particles within a bulk solid (i.e., uniformity) has a direct effect on a material's ability to flow. This can be quantified by determining the screen size that will allow 60 percent of a sample to pass through (which is generally a relatively large mesh size) and the screen size that will allow 10 percent to pass through (which is generally a relatively small mesh size). Uniformity is then calculated by dividing the 60 percent mesh size by the 10 percent mesh size. Thus, the smaller the uniformity value, the more homogeneous the particle sizes and shapes. A material that is more uniform will have a tendency to have better flowability than a material with a wide range of particle sizes.
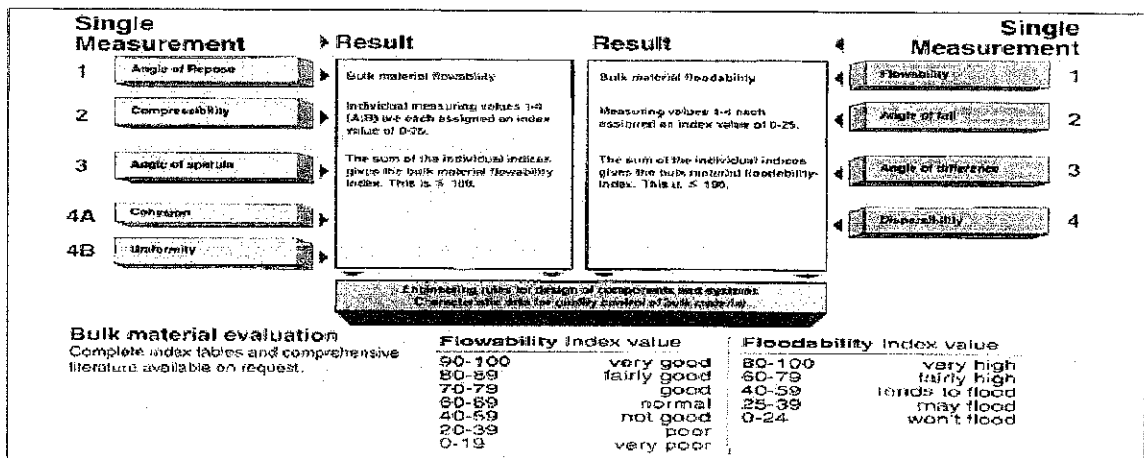
Figure 7 Bulk material evaluation index table

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CHAPTER 3

METHODOLOGY

3.1 Proposed experimental method

3.1.1 Experimental Apparatus

Experiment will be carried out using a modified thermogravimetric analyzer coupled with a mass spectrometer (TG-MS). Thermogravimetric–mass spectrometry (TG–MS) has been a well established technique for the analysis of evolved gases since the late 70s [34]. The main advantage of the technique is the acquisition of multiple information during one TG run, such as, the weight loss of the sample as a function of the temperature, the detection of the volatile pyrolysis products with a highly sensitive detector (MS) as a function of the temperature and the ability of quantitative determination of the evolved gases. The combination of MS and a thermogravimetric analysis system offers several advantages in thermal gas emission determination such as real-time analysis and qualitative and quantitative analysis [33].

3.1.1.1 Modified Thermogravimetric-Mass Spectrometry (TG-MS)

The TG-MS measures the pyrolytic weight loss using a thermobalance (sensitive to 0.01mg). More specifically, thermogravimetric analysis (TGA) is performed on samples to determine changes in weight in relation with the change in temperature. This analysis relies on a high degree of precision in three measurement; weight, temperature, and temperature change.

This analyzer usually consists of a high-precision balance with a pan (generally platinum). The samples is placed into the platinum sample pan and flushed one hour before the run by argon or helium carrier gas (inert gas) to prevent oxidation or any undesired reaction. A computer is used to control the instrument. Analysis is carried

out by raising the temperature gradually and plotting weight (percentage) against temperature. The temperature in many testing methods routinely reaches 1000°C or greater. The oven is greatly insulated that an operator would not be aware of any change in temperature even if standing directly in front of the device.

The Samples are kept at 100°C for 10 min to eliminate the adsorbed water and heated at 20°C min^{-1} (depending on the heating desired heating rate) and up to 950°C. The evolved pyrolytic gases flushed from the vicinity of the decomposing solid fuel with high Argon gas (Ar) purge flow. A sample of these evolved pyrolysis gases are rapidly delivered to the ion source of the mass spectrometer via a heated capillary. The mass spectra of the evolved gas are recorded as a function of temperature using the mass spectrometer. It should be noted that the relatively low molecular weight products will be detected, since the tar fraction is condensed in the apparatus. The mass spectrometer usually operated in electron impact ionization mode with 70 eV electron energy. The ion intensities are normalized to the sample mass and to the intensity of the ^{38}Ar isotope of the carrier gas.

The simple illustrate of the experimental apparatus can be seen at Fig. 5.
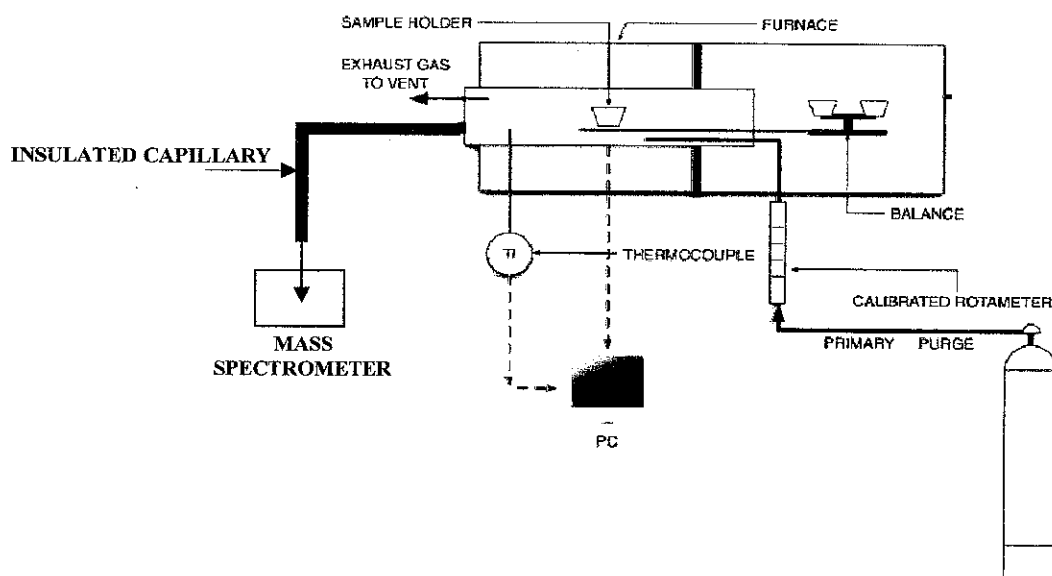
Figure 8: Modified thermogravimetric analyzer/mass spectrometer (TG-MS) for the decomposition of biomass fuels and the simultaneous of evolved product gas species.

Figure 9: Thermogravimetric Analyzer (TGA)

3.1.2 Biomass samples

Cellulose is the major component of typical biomass, usually greater than 50%-wt. Palm kernel shell (PKS) is selected as a biomass sample in this experiment.

3.1.3 Experimental procedure

Approximately 1mg of PKS sample will be loaded in the sample holder for all experiments, and placed inside the thermogravimetry (TG). The adsorbent used in the experiment is the modified CaO. The entire resulting product gas yield will be analyzed in the mass spectrometer.
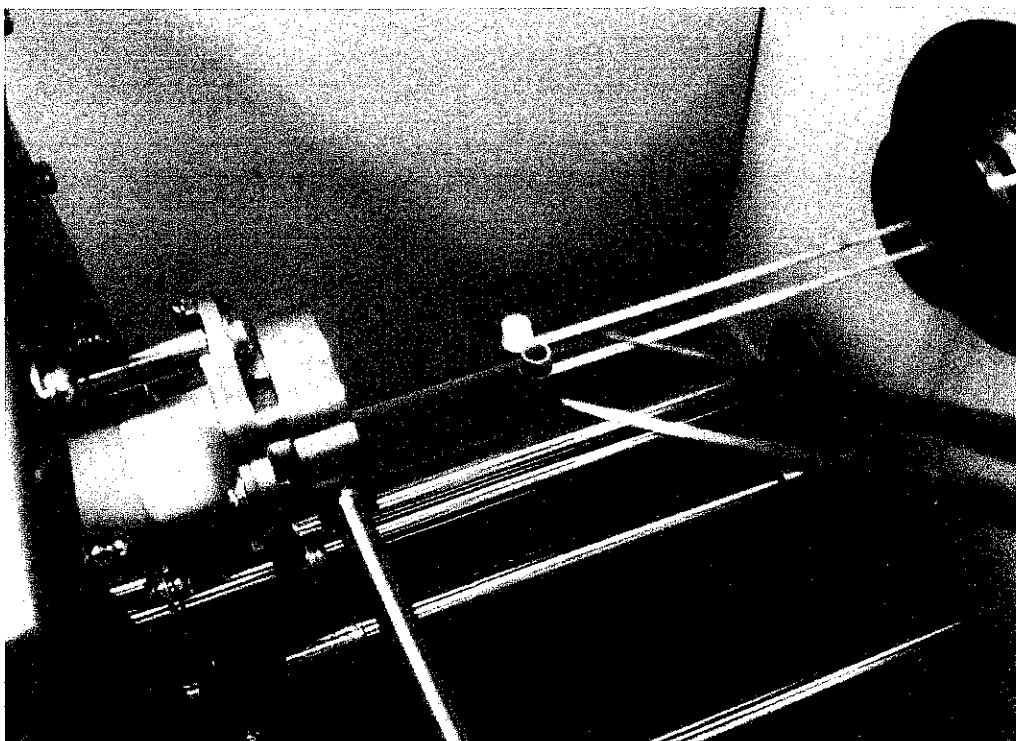
Figure 10: Placing the sample inside the TGA.

3.1.3.1 Experimental key parameters

In the meantime, these are the key parameters that were conducted in the experiment. There are 3 factors and 3 level of variation.

1. TG-MS analysis over heating rate

The pyrolytic decomposition will be carried out at three different heating rates: $20°C/min$, $50°C/min$ and $100°C/min$.

2. TG-MS analysis over steam to biomass ratio

The gasification process will be conducted with steam to biomass ratio, with 0, 1 and 2

3. Influence of sorbent to biomass ratio

In order to determine the influence of CaO on the decomposition of cellulose, experiment will be conducted in the absence of CaO ([Ca/C] = 0) and in the presence of CaO ([Ca/C] = 1, 2).

3.2 Design of experiment

There are quite number of experiments that are required in order to determine the effect of key parameters in optimizing the H_2 yield. Therefore, 'Minitab' software is required to design the experiments, which perform the statistical problem and minimize the number of experiments to be carried out. Statistical design of experiment (DOE) with Taguchi's design approach will be used.

The DOE is based on 3 factors and 3 levels of variations. The DOE using Taguchi approach is shown below.

Table 2: DOE using Taguchi approach using Minitab software

Experiment Order (Run)	Parameters		
	Heating Rate (°C/min)	Steam to Biomass Ratio	Sorbent to Biomass Ratio
1	20	0	0
2	20	1	1
3	20	2	2
4	50	0	1
5	50	1	2
6	50	2	0
7	100	0	2
8	100	1	0
9	100	2	1

Therefore, each run of experiment is conducted with the respective parameter condition specified. The experimental procedure is simplified in a flow chart as shown below.

```
┌─────────────────────────┐
│   Weigh PKS and CaO into │
│      the desired mass    │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐
│    Sample placed on the  │
│       sample holder      │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐
│   Set the heating rate and│
│  amount of steam required │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐
│     Start the gasification│
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐
│       Analyze the gas    │
│  composition result obtained│
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐
│     Finalizing the result│
└─────────────────────────┘
```
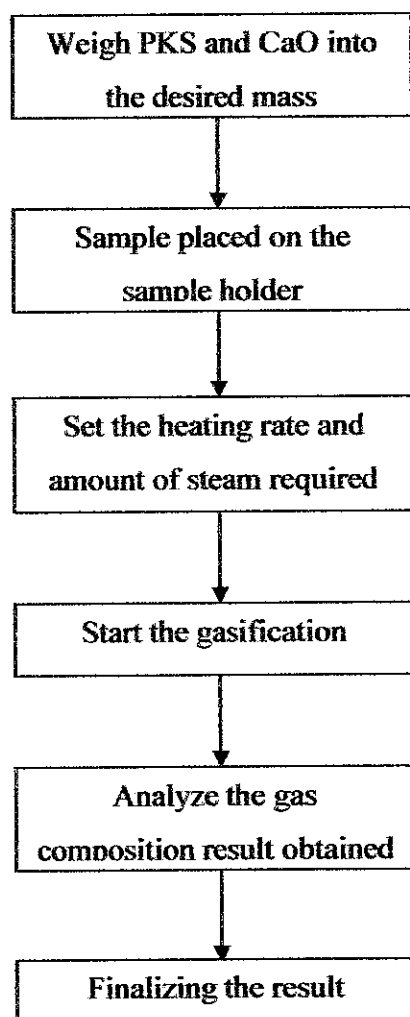
Figure 11: Simplified flowchart for PKS gasification

3.3 Powder Characteristic Testing

In order to measure and determine the characteristic of a powder, a Powder Characteristic Tester Model PT-S developed from Hokogawa will be used. This powder tester is usually coupled with a standard computer.

The instrument provides seven mechanical measurements and three supporting measurements of dry bulk powders.

Figure 12 Hosokawa powder characteristic tester

Seven characteristics were measured;

- Angle of Repose
- Angle of Spatula
- Angle of Fall
- Angle of Difference
- Compressibility
- Cohesion
- Dispersibility

Another three auxiliary values;

- Aerated Bulk Density
- Packed Bulk Density
- Uniformity

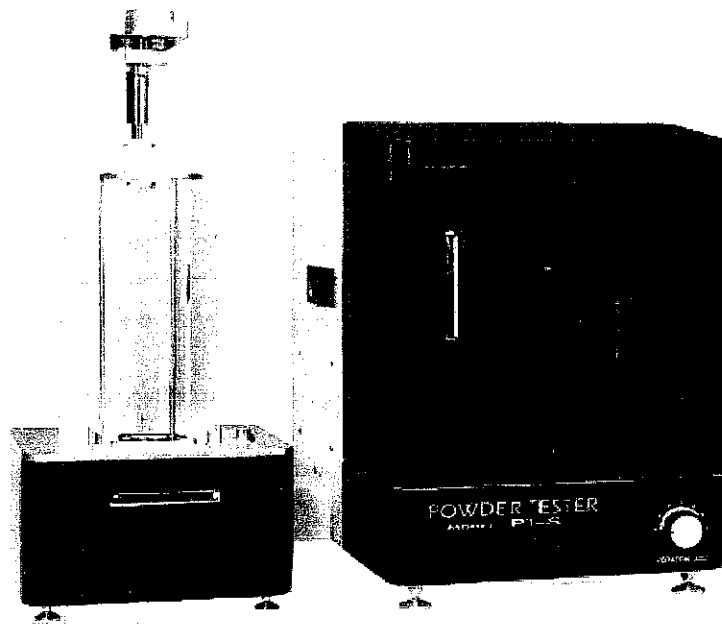This PT-S analytical instrument was developed so that key measurements are performed using a single convenient unit, providing an additional basis of data for quality control of powdered products, and numerical evaluations of flow behavior "Flowability" and flood behavior "Floodability" of dry solids.

3.3.1 Sample sorbent (CaO) preparation

In the powder characteristic testing, two sorbent samples will be tested which are CaO (original sorbent, 99.7% purity) and modified CaO.

The modified CaO is prepared through this method. The original CaO is used and mixed it with ethanol (EtOH) solution. The EtOH solution is made from 80% of EtOH (99.9% purity) and 20% of water. In this case, EtOH with 99.9% is used in the solution. 1 Liter of the EtOH solution is then mixed with 100 g of CaO.

Then, the mixed solution then placed in a beaker and stirred for 3 hour so that the solution will be evenly mixed. Next, the solution is placed inside an oven for 1 day with 110°C temperature in order to remove the EtOH and water in solution.

The dried CaO is then mashed and pressed inside the grinding sieving machine, with a mesh filter (150 μm size) so that only < 150 μm CaO particle passed through it.

3.4   Sorbent (CaO) testing procedures

In this experiment, two types of samples is used which are the original CaO and the modified CaO.

The CaO sorbent powder is filled in the cup with a sieve in the bottom of it and placed in a particular elevated position in the powder tester. The sample is then vibrated and the powder will drop or flow down through a glass funnel and accumulates unto the

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horizontal plate. Then, a Charge-Couple device camera (CCD) is used to capture the image of the heap profile and will calculate the angle of repose, as shown in Figure 10.
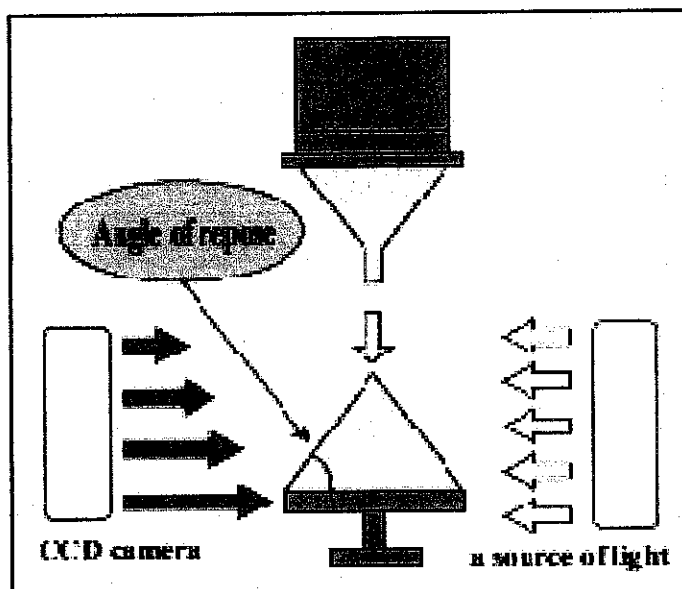
Figure 13 Angle of Repose measurement

Next, in default procedure, the shocker in the powder tester will impact the horizontal plates in two times. Once again, the angle of the slope is measured as the angle of fall.

For the angle of spatula, the powder is filled into a rectangular container with a flat blade inserted into it. The flat blade then is lifted upward and the slope of the powder which stayed on the top of the blade is measured. The new angle of repose which the material forms relative to the blade surface is the angle of spatula.

The angle of difference is calculated from the difference of angle of repose and angle of fall.

For the cohesion test, the powder is subjected to a series of sieves and how much of the powder pass can through it. In standard procedure, 2 g of CaO is place on top of three layers of sieves varied from 250, 200 and 150 micron. The sample is then vibrated at a constant force in default time, 180 seconds. The sample left on each sieve is weighed and the cohesion will be calculated by the powder tester.

Next, for the dispersibility test, approximately 10 gram or CaO is weighed, and placed on top of a cylinder. Then, the powder is released from the top of the cylinder and the sample left on the bottom of the cylinder will be collected and weighed.

Lastly, for aerated bulk density test, CaO sample is placed on the sieves, vibrated and the sample will flow through a glass funnel onto the measuring cup. The weight of the measuring cup is weighed and recorded. After the measuring cup is completely filled, then once again the measuring cup with the powder is weighed. Next, for packed density test, the procedure follows from the previous method except, after the measuring cup is completely filled, the sample is impacted to 180 seconds. Next, the powder testing procedures is repeated for the modified CaO.

All of the calculation is calculated by the powder tester and the results are generated automatically after performing the experiment.

CHAPTER 4

RESULTS AND DISCUSSION

4.1   Powder characteristic testing result

4.1.1   Powder Tester Overall evaluation result comparison

Table 3: CaO powder characteristic comparison result

Characteristic	Normal CaO		Modified CaO	
	Value	Index	Degree	Index
Angle of Repose	93.1 °	0	70°	2
Angle of Spatula	81.7°	7	67.8°	12
Angle of Fall	78.3 °	0	108.8 °	0
Angle of Difference	14.8°	15	- 38.8°	0
Compressibility	46.3 %	0	21.40%	17
Cohesion	60.8 %	2	86.90%	0
Dispersibility	11.2 %	12	56.90%	35
Aerated Bulk Density	0.615 g/cc	nil	0.32 g/cc	nil
Packed Bulk Density	1.146 g/cc	nil	0.407 g/cc	nil
Uniformity	nil		nil	

The results obtained from the powder characteristic tester between normal CaO and modified CaO is tabulated as shown above.

4.1.2   Discussion on CaO powder characteristic

The angle of repose value for normal CaO is 93.1 degrees (index = 0) which is higher than modified CaO, 70 degrees (index = 2). As shown from the flow properties angle of repose below, this indicates the both original CaO and modified CaO powder has a

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very, very poor flowability. In contrast, we can observe that the angle of repose is improved for modified CaO compared to the normal CaO powder.

The flow property angle of repose can be referred from the table below.

Table 4 Flow properties angle of repose

Flow Property	Angle of Repose (degrees)
Excellent	25–30
Good	31–35
Fair—aid not needed	36–40
Passable—may hang up	41–45
Poor—must agitate, vibrate	46–55
Very poor	56–65
Very, very poor	>66

All the powder characteristic result obtained in table 3 is analyzed with referring to the Carr's index table as shown below.

Table 5 Carr's index table – Flowability index for the powder

Degree of Flowability	Flowability Index	Necessity of Bridge-breaking measures	Angle of Repose		Compressibility		Angle of Spatura		Uniformity		Cohesion	
			Degree	Index	%	Index	%	Index	No.	Index	No.	Index
Very Good	90-100	Not required	≤25 / 26-29 / 30	25 / 24 / 22.5	≤5 / 6-9 / 10	25 / 23 / 22.5	≤25 / 26-30 / 31	25 / 24 / 22.5	1 / 2-4 / 5	25 / 23 / 22.5		
Fairly Good	80-89	Not required	31 / 32-34 / 35	22 / 21 / 20	11 / 12-14 / 15	22 / 21 / 20	32 / 33-37 / 38	22 / 21 / 20	6 / 7 / 8	22 / 21 / 20		
Good	70-79	Sometimes Vibrator is required	36 / 37-39 / 40	19.5 / 18 / 17.5	16 / 17-19 / 20	19.5 / 18 / 17.5	39 / 40-44 / 45	19.5 / 18 / 17.5	9 / 10-11 / 12	19 / 18 / 17.5		
(Normal)	60-69	Bridging will take place at the marginal point	41 / 42-44 / 45	17 / 16 / 15	21 / 22-24 / 25	17 / 16 / 15	46 / 47-59 / 60	17 / 16 / 15	13 / 14-16 / 17	17 / 16 / 15	≤6	15
(Not Good)	40-59	Required	46 / 47-54 / 55	14.5 / 12 / 10	26 / 27-30 / 31	14.5 / 12 / 10	61 / 62-74 / 75	14.5 / 12 / 10	18 / 19-21 / 22	14.5 / 12 / 10	6-9 / 10-29 / 30	14.5 / 12 / 10
Bad	20-39	Powerful measures should be provided	56 / 57-64 / 65	9.5 / 7 / 5	32 / 33-36 / 37	9.5 / 7 / 5	76 / 77-89 / 90	9.5 / 7 / 5	23 / 24-26 / 27	9.5 / 7 / 5	31 / 32-54 / 55	9.5 / 7 / 5
(Very Bad)	0-19	Special apparatus and techniques are required	66 / 67-89 / 90	45 / 2 / 0	38 / 39-45 / >45	45 / 2 / 0	91 / 92-99 / >99	4.5 / 2 / 0	28 / 29-35 / >35	45 / 2 / 0	56 / 57-79 / >79	4.5 / 2 / 0

Note:

Modified CaO characteristic result

Normal CaO characteristic result

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Table 6 Carr's index table – Floodability index for the powder

Degree of Floodability	Floodability Index	Measures For Flushing Prevention	Flowability Index From Table1	Index	Angle of Fall %	Index	Angle of Difference %	index	Dispersibility No.	Index
(Very high)	80-100	Rotary seal must be used	≥ 60 59-56 55 54 53-50 49	25 24 22.5 22 21 20	≤ 10 11-19 20 21 22 - 24 25	25 24 22.5 22 21 20	≥ 30 29 - 28 27 26 25 24	25 24 22.5 22 21 20	(≥ 50) 49 - 44 43 42 41 - 36 35	25 24 22.5 22 21 20
Fairly High	60-79	Rotary seal is required	48 47-45 44 43 42-40 39	19.5 18 17.5 17 16 15	26 27 - 29 30 31 32 - 39 40	19.5 18 17.5 17 16 15	23 22 - 20 19 18 17 - 16 15	19.5 18 17.5 17 16 15	34 33 - 29 28 27 26 - 21 20	19.5 18 17.5 17 16 15
Tends to flush	40-59	Sometimes rotary seal is required	38 37-34 33	14.5 12 10	41 42 - 49 50	14.5 12 10	14 13 - 11 10	14.5 12 10	19 18 - 11 10	14.5 12 10
May flush	25-39	Rotary seal is necessary depending on flow speed and feeding conditions	32 31-29 28	8 6.25	51 52 - 56 57	9.5 8 6.25	9 8 7	9.5 8 6.25	9 8 7	9.5 8 6.25
(Won't flush)	0-24	Not required	27 26-23 < 23	6 3 0	58 59-64 (64)	6 3 (0)	6 5 - 1 (0)	6 3 (0)	6 5 - 1 0	6 3 0

Note:

◯ Modified CaO characteristic result

Normal CaO characteristic result

From table 5 and 6, it is shown that, most of the CaO characteristics are improved on modified CaO compared with to the original CaO powder which are the angle of repose, compressibility, angle of spatula, and dispersibility. Based from the overall result, the CaO powder demonstrates a very poor flowability, and will not flush on degree of floodability.

It is proved that the modified CaO has better flowability and floodability. The better the degree of flowability, the easier the particles or powder to flow. Moreover, the higher the degree of floodability of the sorbent, the higher the resistant of the sorbent to resist from flooding. This also increased the tendency to liquid-like flow of the powder. Moreover, this also corresponds to the surface area of the sorbent. With the modified

CaO, the improvement on the degree of flowability, which means it has higher surface area, compared to the pure CaO particle. The higher the surface area of the sorbent, it reflects that the size of the modified CaO particle must be smaller than the previous CaO sorbent. Therefore, with smaller particle size, it makes the particle ease to flow, and has a higher resistant on flooding.

This enhancement of the CaO sorbent is due to the calcination which will remove the water content inside the CaO particles. Back to its definition, the purpose for the calcination is mainly to drive of water content, which present as absorbed moisture inside the particle. Thus, the hydrated CaO will have no or less water or moisture, which will make it lighter and easier to flow and harder to flood inside the gasification machine. This study of powder characteristic is really important when it comes to industrial production as the less flowability and floodability of powder used. This will affect the whole process as it will cause the powder to easily get stuck and jammed inside the pipeline, valve or funnel. Consequently, the problems will increase the capital cost as the process needs regular shutdown and maintenance.

Therefore, the modified CaO will be used as an adsorbent in the steam gasification of biomass.

4.2   Biomass gasification experimental results

To obtain an optimum of H_2 production from the PKS biomass sample, these parameters, the temperature of the reaction (heating rate), steam to biomass ratio, and sorbent to biomass ratio will be studied. Results will be analyzed and tabulated in the table below.
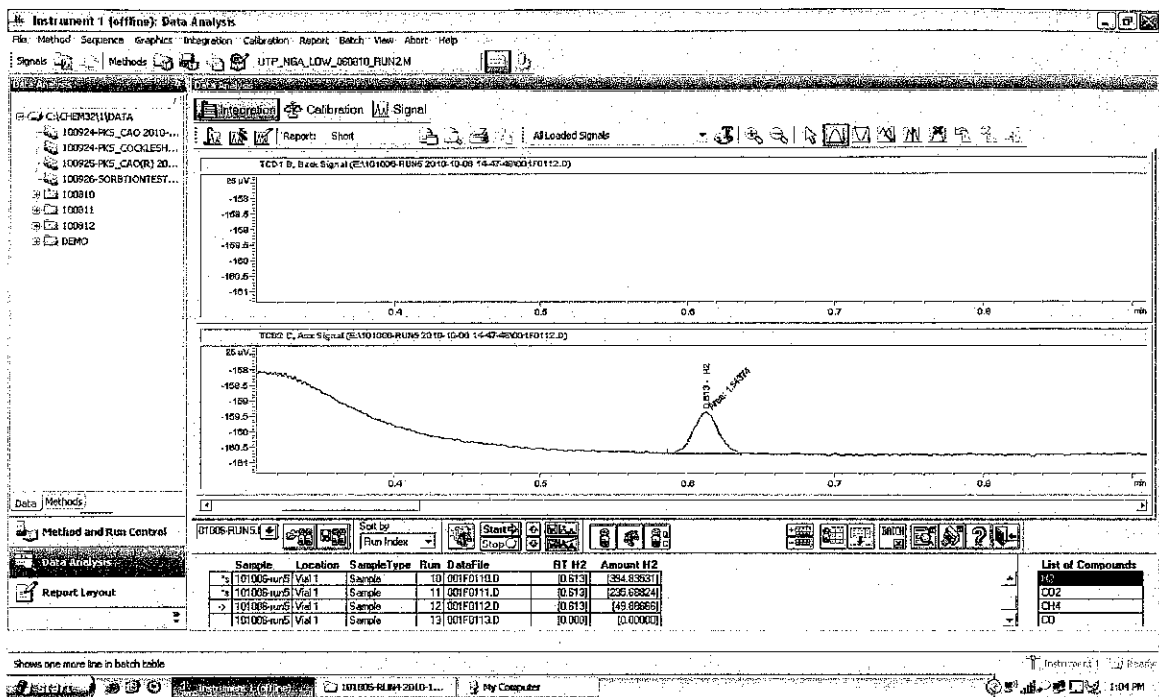
Figure 14: Analyzing data using the TGA software.

In addition, each of the run of experiment will be done twice to obtain average data in yielding more precise data.

Table 7: Mean gas yield composition results of biomass steam gasification

Experiment Order (Run)	Parameters			Gas Composition (vol%)			
	Heating Rate (°C/min)	Steam to Biomass Ratio	Sorbent to Biomass Ratio	H_2	CO_2	CO	CH_4
1	20	0	0	49.23	18.63	38.44	0.0
2	20	1	1	54.30	24.50	13.22	7.98
3	20	2	2	43.98	30.48	25.54	0.0
4	50	0	1	39.09	8.59	52.32	0.0
5	50	1	2	38.53	13.23	48.24	0.0
6	50	2	0	55.23	9.72	35.04	0.0
7	100	0	2	50.19	21.13	28.86	0.0
8	100	1	0	40.72	29.59	29.70	0.0
9	100	2	1	61.16	16.65	21.18	0.0

4.3 Discussions and data analysis

The results is plotted and shown as below. The experiment is repeated in two times so that an average and more precise data can be obtained.
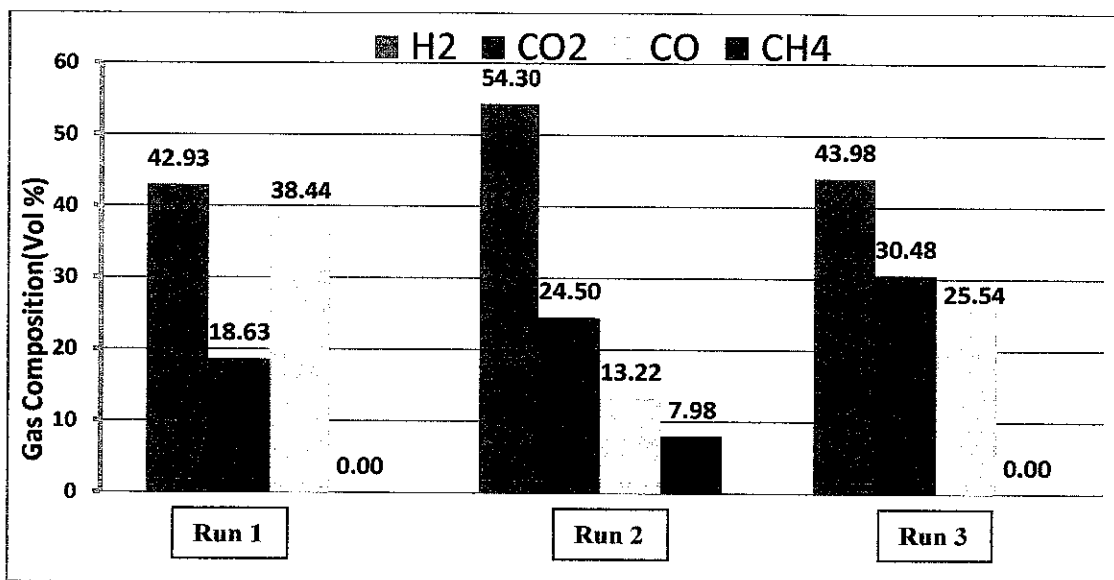

Figure 15: The effect of [H₂O/Biomass] and [CaO/Biomass] ratio on gas composition result (reaction condition; 20°C/min heating rate, 900°c reaction temperature, 20 mins holding time)

Figure 16: The effect of [H₂O/Biomass] and [CaO/Biomass] ratio on gas composition result (reaction condition; 50°C/min heating rate, 900°c reaction temperature, 20 mins holding time)
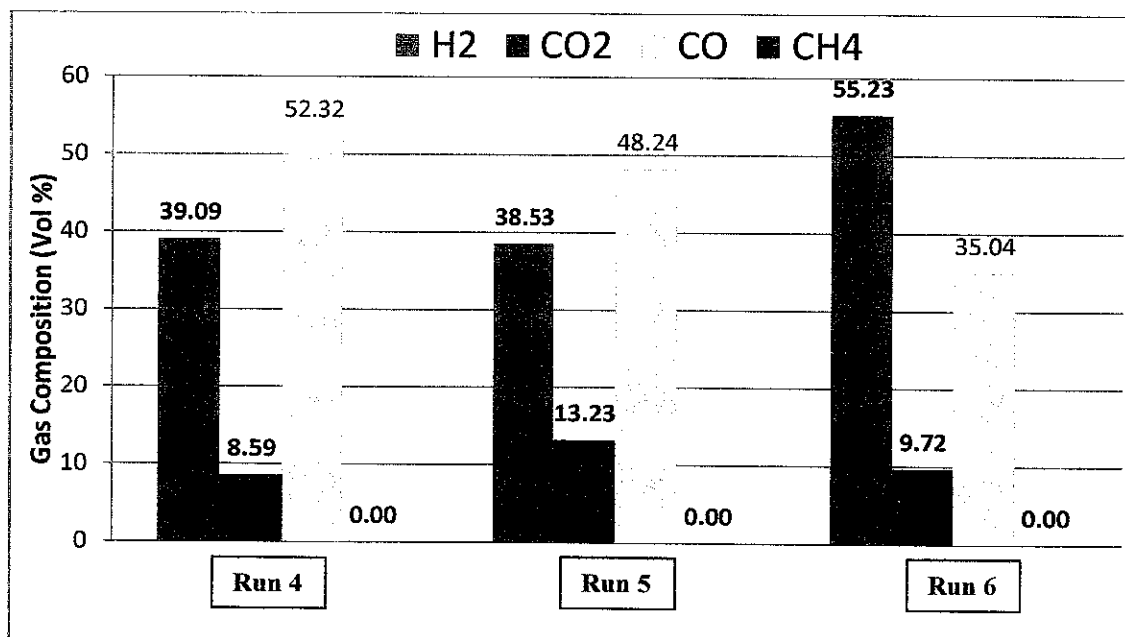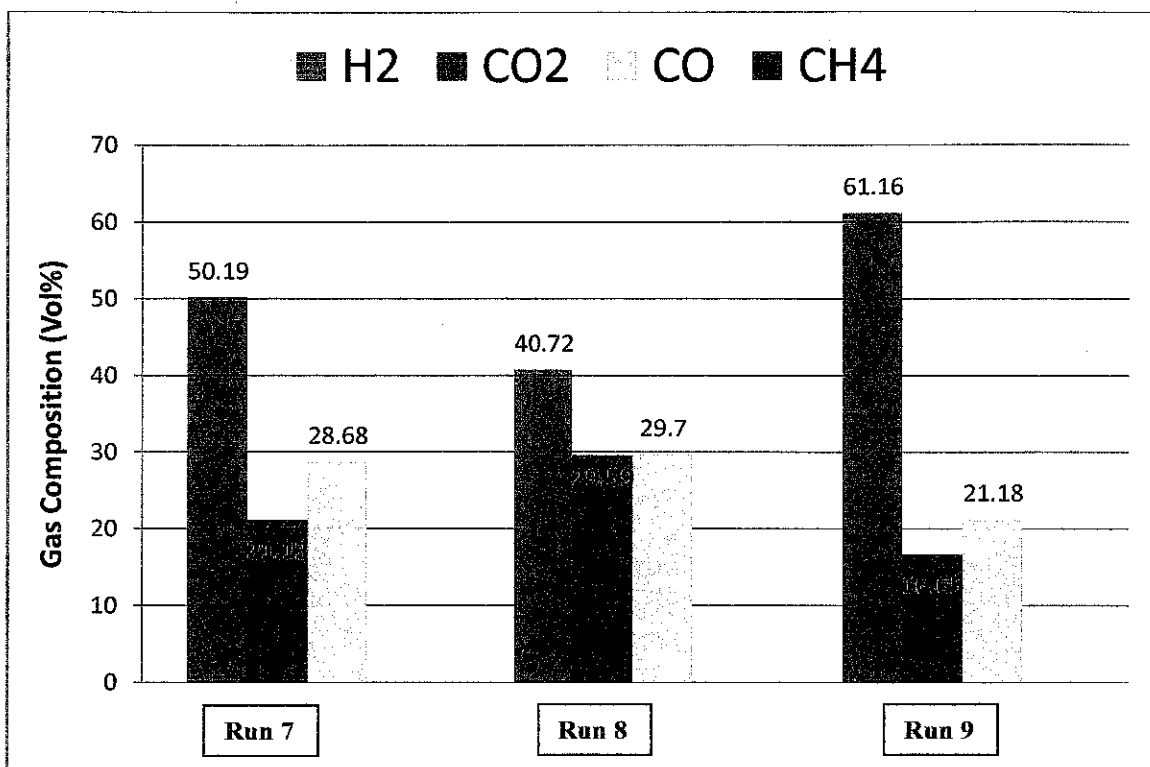
Figure 17: The effect of [H₂O/Biomass] and [CaO/Biomass] ratio on gas composition result
(reaction condition; 100°C/min heating rate, 900°c reaction temperature, 20 mins holding time)

Steam to biomass ratio of 0 means that there is no steam introduced during the experiment, and corresponds with sorbent to biomass ratio 0 means there is no sorbent introduced.

From the bar chart figure above, it is shown that the highest H_2 gas result is on run 9 (61.16 vol %), with ratio of [H₂O/Biomass] and [CaO/Biomass] = 2, 1 ratio at 100°C/min heating rate.

This result also supported from the Taguchi analysis from the Minitab software. The figure below showed the analysis result from Minitab.
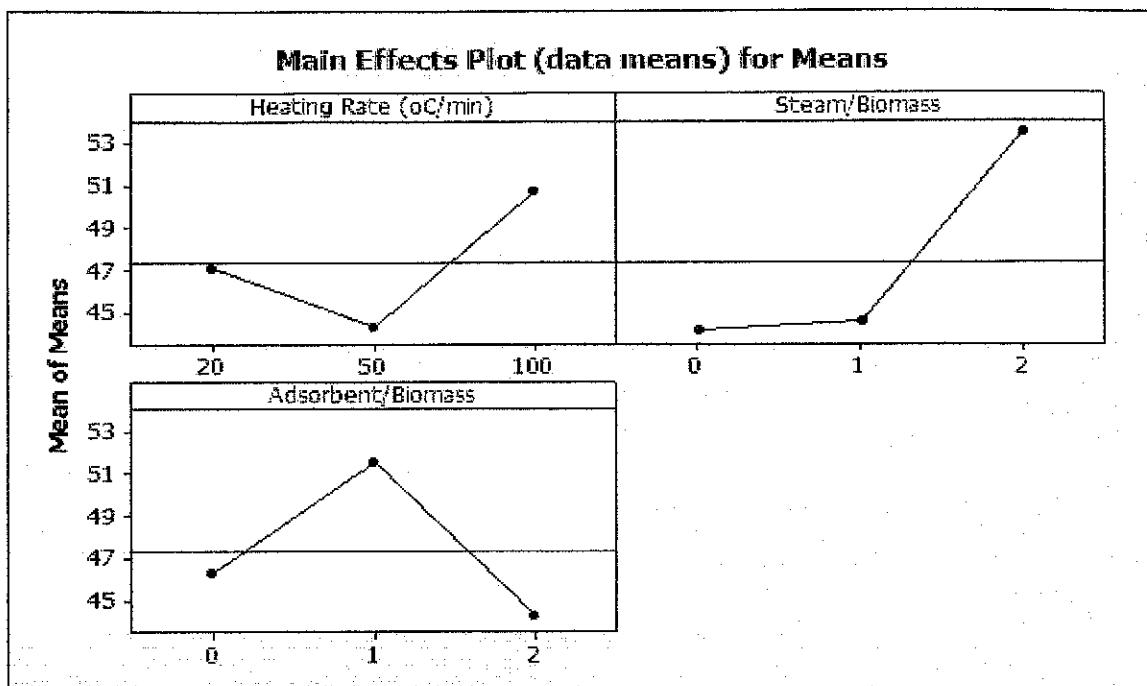
Figure 18: Overall main effect plots from Minitab software.

In this case, high value of H_2 yield is desired, therefore the highest value from each of the main effects plot will be chosen. Based from the Fig. 17 above, the highest means of means value fall on 100°C/min for heating rate, ratio of 2 for steam to biomass ratio, and ratio of 1 for adsorbent to biomass ratio. Then, this condition should be check back from the DOE table, whether the condition is already on the table or not. If the condition 100°C/min for heating rate, ratio of 2 for steam to biomass ratio, and ratio of 1 for adsorbent to biomass ratio is not in the DOE, new experiment should carried out based on the new condition found. If the specified condition is already there inside the DOE, the condition should be chosen and viewed as the optimal condition for the overall experiment.

4.3.1   The effect of steam to biomass ratio

Referring to Figure 12, as seen in run 5 and 6 (heating rate 50°C/min), the experiment is done with increasing the steam to biomass (S/B) ratio from 1 to 2; the H_2 yield is increased from 38.53 vol% to 55.23 vol%. From the result in Figure 13, the same behavior also observed in run 8 and 9 (heating rate 100°C/min) with increasing biomass to steam ratio from 1 to 2. The H_2 yield is also increased significantly from

40.17 vol% to 61.16 vol%. Therefore, this result proved the statements studied in previous report from Herguido et al. [25] and Turn et al. [29], which stated that the H_2 concentration yield will increased, with corresponding to an increase in steam to biomass ratio. However, this theory is not applied when the experiments using steam to biomass ratio from 0 to 1 as seen from run (5-6) and run (8-9) as the H_2 yield is decreased in the experiment. This must be caused from the insufficient steam supplied in the reaction after the steam is introduced.
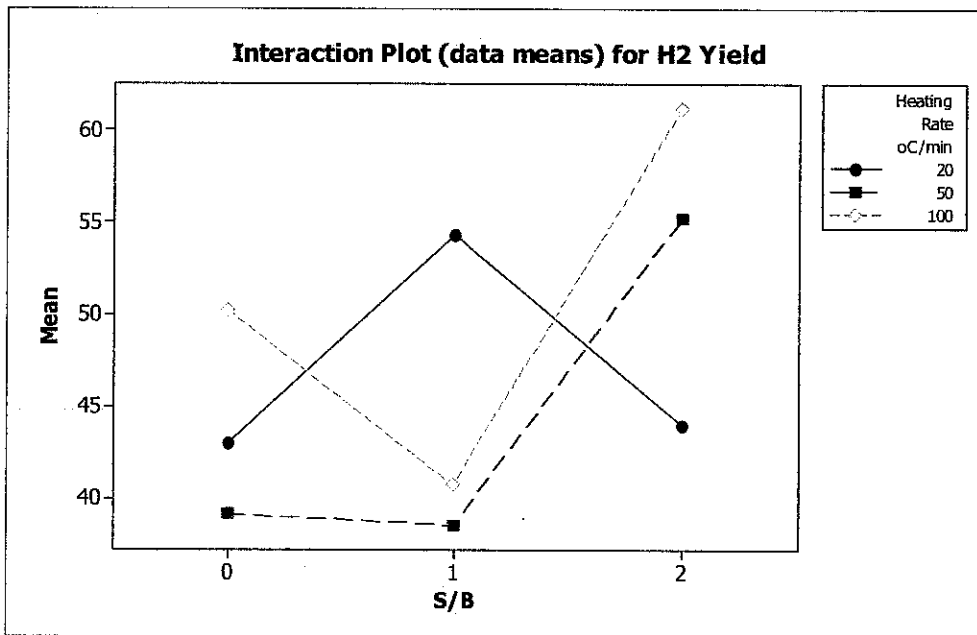
Figure 19: Interaction plot of H_2 yield (mean) and S/B ratio at different heating rate.

As we can see from the Figure 14 above, the higher H_2 yield in this experiment is also found to be at steam to biomass ratio of 2. Therefore, steam to biomass ratio of 2 can be considered as an optimum ratio for steam PKS (biomass) gasification in yielding maximum H_2 concentration. Furthermore, based on the previous report from Herguido et al. [25], he found that the rate of H_2 yield will become slower for the ratio of steam to biomass ratio for more than 2. Moreover, this also supports the previous study from Herguido et al. [25] and Turn et al. [29] which states that the optimum ratio of steam to biomass ratio should be between 1-2 in maximizing H_2 output.

4.3.2 The effect of adsorbent to biomass ratio.

With referring to Figure 11, in run 8 and 9, the sorbent to biomass ratio is from 0 to 1, with the same reaction condition at 100°C/min heating rate, H_2 yield has increased rapidly from 40.72 vol% to 61.16 vol%. The increased of H_2 yield must be due to the introduction of CaO inside the reaction. Removal of CO_2 from reaction especially on the water-gas shift and methane reforming reaction, thus shift the equilibrium reaction to the right, resulting more H_2 yield.
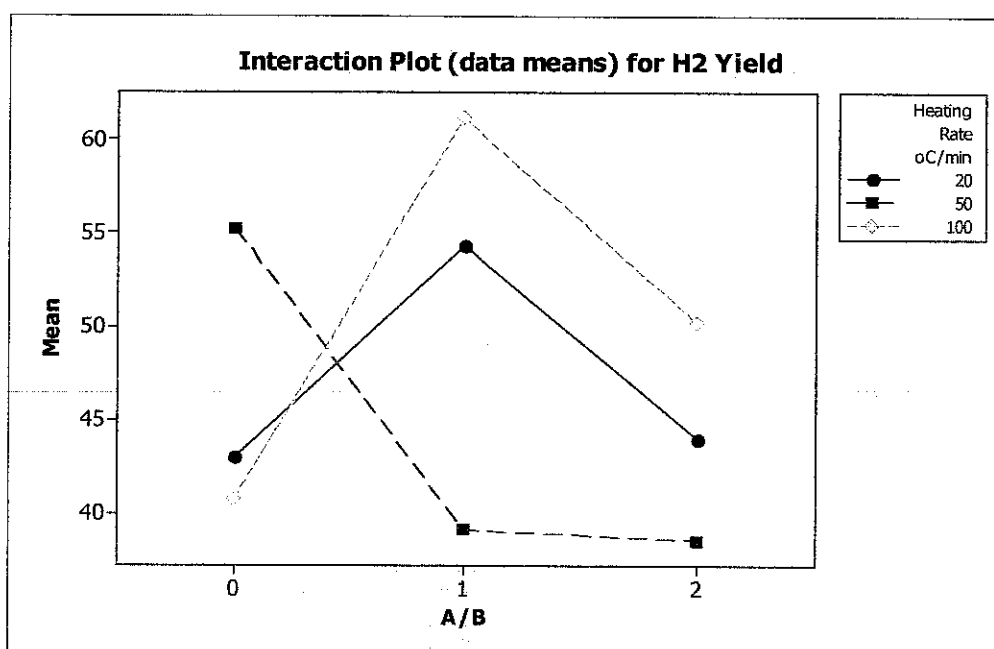

Figure 20: Interaction plot of H_2 yield (mean) and A/B ratio at different heating rate.

From the interaction plot shown in the Figure 5 above, for H_2 yield at 20 and 100°C/min heating rate, the H_2 yield is increased as the adsorbent to biomass (A/B) ratio is introduced from 0 to 1. This indicates that when CaO (adsorbent) is introduced in the reaction, the H_2 yield would be increased. However, H_2 yield is decreased when the adsorbent to biomass ratio is increased from 1 to 2. This may be due to excess CaO supplied makes the most CaO supplied is going unreacted. This result also supports from the previous study from H. Guoxin et al. [37]. Therefore, there must be a (A/B) ratio around 0.5 – 1.5, that will produce that maximum H_2 yield. In another findings from Florin et al. [32] which concluded that 0.9 sorbent to biomass ratio should be

considered for optimal H_2 yield. In this experiment, the highest H_2 yield for PKS steam gasification condition is found to be at (A/B) ratio of 1 which yielding 61.16 vol% of H_2. Therefore, this finding is also supports the previous result found by Florin et al. [32] as the (A/B) ratio obtained is not much difference.
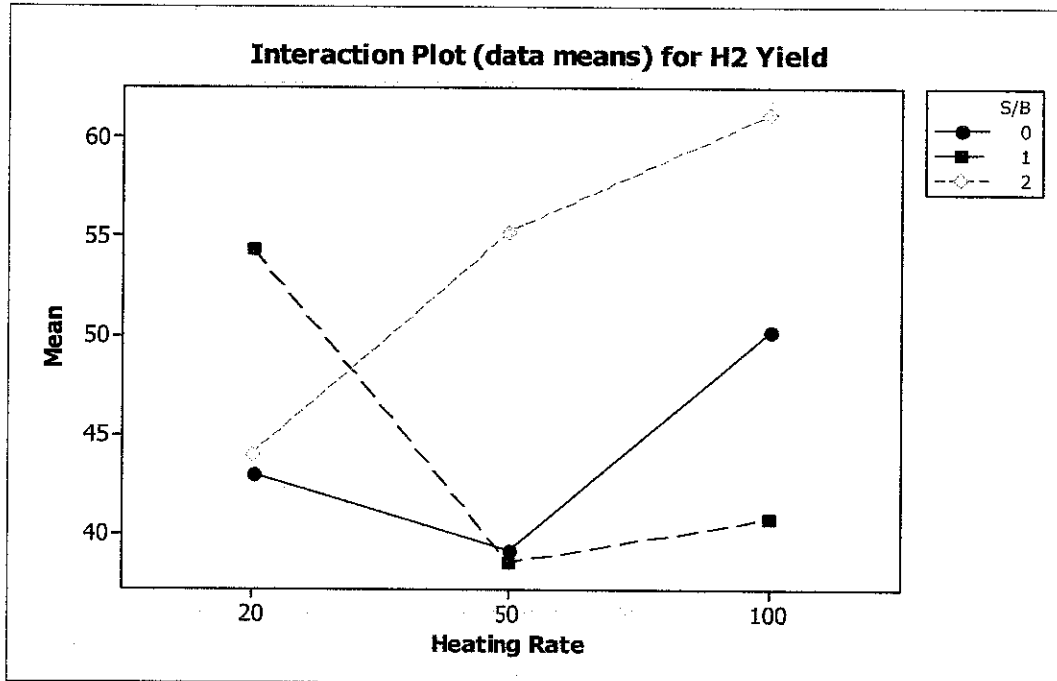
4.3.3   The effect of heating rate

Figure 21: Interaction plot of H_2 yield (mean) vs Heating rate

Referring to Figure 16, we can conclude that the H_2 yield is only increased with the increment of the heating rate from (20 to 100°C/min) as the S/B ratio is increased from 1 to 2. In fact, the highest H_2 yield (61.16 vol %) in this experiment which is also found to be at 100°C/min heating rate. This is because as expected, usually the increase in temperature in the gasification process will lead to higher production of gases at the initial pyrolysis step, where the rate is faster at higher temperatures as pointed out by Herguido et al. [25]. Furthermore, an increase in reaction temperature is expected to enhance the extend the biomass conversion to gas products. Therefore, the optimal heating rate for PKS steam gasification would be at 100°C/min.

CHAPTER 5

CONCLUSION

The parameters affecting the amount of hydrogen produced from the reaction was studied and experimented to determine the optimum condition in maximizing the hydrogen production which are the heating rate, steam to biomass ratio and adsorbent to biomass ratio. The results were analyzed and discussed in details. In this paper, it is proved that the steam gasification of PKS, coupled with CO_2 capture, is a promising process for exploiting renewable biomass, resources for the H_2 production.

Based on the powder characteristic testing, the sorbent CaO demonstrated a very poor flowability, which needs a special apparatus or modification in order to improve its flowability. Based from the findings from the experiment, with the modified CaO, the flowability and floodability of the sorbent were improved. Moreover, with the modified CaO, the surface area of the sorbent can be increased, thus will speed up the reaction. In the future, more tests should be done in comparing both of the sorbents, especially in steam biomass gasification.

The presence of CaO inside the steam gasification of biomass in most of the runs will reduce the amount of CO_2 produced and also increased the H_2 yield. Other than that, with increasing the amount of steam in the gasification reaction also increased the H_2 yield.

In a nutshell, the optimum condition found for the steam PKS gasification in producing maximum H_2 yield are heating rate at $100^\circ C/min$, with [H_2O/Biomass] ratio $= 2$, and [CaO/Biomass] ratio $= 1$

CHAPTER 6

RECOMMENDATION

There are few recommendations that are needed to be done in this project. Firstly, more steam and sorbent ratio should be studied and conducted in order to find the precise optimal parameter ratio in yielding maximum H_2 yield. The ratio should be selected around the optimal ratio found in this experiment. Next is to repeat all the experiment runs for more than two times in order to get more precise data.

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APPENDIX 1

APPENDIX

No	Detail / Week Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	FYP 2 work continues																
2	Preliminary Research Work																
3	Submission of Preliminary Report																
4	Seminar 1																
5	Project Work																
6	Submission of Progress Report								■								
7	Pre-EDX poster presentation																
8	Project Work Continues																
	Submission of Dissertation Report													■			
9	Final Draft															■	
10	Oral Presentation																

■ Suggested Milestone

☐ Progress