

Parametric Analysis on Hydrogen Production using Mixtures of Pure Cellulosic and Calcium Oxide

N.A. Rashidi, S. Yusup, and M.M. Ahmad

Abstract—As the fossil fuels kept on depleting, intense research in developing hydrogen (H_2) as the alternative fuel has been done to cater our tremendous demand for fuel. The potential of H_2 as the ultimate clean fuel differs with the fossil fuel that releases significant amounts of carbon dioxide (CO_2) into the surrounding and leads to the global warming. The experimental work was carried out to study the production of H_2 from palm kernel shell steam gasification at different variables such as heating rate, steam to biomass ratio and adsorbent to biomass ratio. Maximum H_2 composition which is 61% (volume basis) was obtained at heating rate of $100^\circ C \text{min}^{-1}$, steam/biomass of 2:1 ratio, and adsorbent/biomass of 1:1 ratio. The commercial adsorbent had been modified by utilizing the alcohol-water mixture. Characteristics of both adsorbents were investigated and it is concluded that flowability and floodability of modified CaO is significantly improved.

Keywords—Biomass gasification, Calcium oxide, Carbon dioxide capture, Sorbent flowability

I. INTRODUCTION

At present, hydrogen (H_2) production is mainly via the utilization of the fossil fuel, either through steam methane reforming or coal gasification. According to Ewan and Allen, the conventional H_2 production consumes approximately 96% of fossil fuel sources in which 48% of steam methane reforming, 18% of coal gasification, 30% of oil reforming, and 3.9% of electrolysis process [1]. However, these routes associates with its non-renewable pathway and may emit significant amount of carbon dioxide (CO_2) into the ambient air, which contribute to increase concern of greenhouse effect and ultimately, global warming issue. Thus, considering pollutant emission and fossil fuel depletion, biomass gasification is an alternative to the direct use of the fossil fuel energy derived from petroleum, natural gas or coal. Therefore, extensive interest has been focused on the production of pure and clean H_2 . In this work, production of H_2 and simultaneous CO_2 capture via the sorption enhanced steam reforming process of biomass is considered [2]. In addition, with consumption of steam as the gasifying agent instead of air or CO_2 , higher production of H_2 can be produced due to additional H_2 generated from the decomposition of water [3]. Besides, the utilization of steam as the gasification agent will enhance the heating value of the product gases ($10\text{-}14 \text{ MJ/Nm}^3$) due to absence of nitrogen dilution as compared to the utilization of air as the gasifying agent [4].

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In contrast, utilization of oxygen (O_2) as gasification agent will increase the heating value of the product gas but will consume higher cost due to pure O_2 requirement for the process to occur [4]-[5].

Due to the abundance and variability of the biomass in the worldwide, it is difficult to predict the H_2 production from each type of biomass consumed during the process. Therefore, continuous effort should be done to further investigate the capability and suitability of the available biomass as the starting materials for energy production. Until now, there have been quite few studies that investigate the suitability of raw lignocellulosic materials in the steam gasification process in producing the syngas, since the feedstock composition directly affect the H_2 production. In addition, the characteristics of the biomass involves the determination of chemical composition, elemental composition, inherent mineral content, amount of volatile materials, moisture content and their physical properties such as particle shape, size and density [3]. Besides, common criterion possessed by the starting materials is high carbon content and low moisture content [5]. Therefore, almost all of the carbonaceous materials can be converted to bio-fuel in the thermochemical gasification process. However, high moisture content of the feedstock may bring adverse impacts towards the gasification process meanwhile high ash content result in various operating problems due to sintering and slagging problems. Therefore, pre-treatment (i.e. heat treatment) of these biomass wastes is appropriate because excess moisture content or inorganic content can be removed.

Besides, the selection of calcium oxide (CaO) as the solid adsorbent in the gasification process is due to its prominent advantages such as wide availability of the precursor. These calcium-based adsorbents in general can be easily derived from cheap and plentiful sources such as limestone ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and calcium hydroxide ($Ca(OH)_2$). The other reason on the selection of CaO as the solid adsorbent is due to their high reactivity possessed by them at the elevated temperature. The criterion is in contrast with the other types of solid adsorbents such as activated carbon and zeolite, in which the CO_2 capture is limited to ambient condition due to weaker binding forces between adsorbent-adsorbate [6]. Although metal oxide is already an established adsorbent for an elevated temperature process, but not all of the oxide materials can be further utilized as the adsorbent in the steam gasification process. Unlike the $CaCO_3$ which is decomposed at temperature greater than gasification operating temperature, other metal carbonates show different characteristics that make them unsuitable to be applied in the gasification process. For example, magnesium carbonate which will readily decompose at temperature of $385^\circ C$, zinc carbonate decomposes at $340^\circ C$, and the lead carbonate at

350°C makes them incompatible for the process because their decomposition temperature is still within the gasification operating condition [3].

Even though lithium zirconate and hydrotalcite are capable to capture CO₂ at the elevated temperature, but their CO₂ capture capacity is still low compared to CaO [6]. This is because CaO is capable to act as the adsorbent and catalyst simultaneously and thus, results an improvement of the CO₂ removal [7]. In addition, the energy release from the CaO carbonation can compensate the energy required for the endothermic gasification process which will increase the effectiveness of the process [8]. Therefore, considering the superior characteristics of CaO as adsorbent, few experimental works have been established previously to study the effectiveness of these calcium-based solid sorbents with in-situ steam gasification process and the findings disclose that the process is well-dependent on the temperature and pressure [8]-[10].

Even though the combination of steam gasification with CO₂ capture has been done previously, but continuous and further effort should be implemented to study the process on the local biomass waste. Thus, the core objective of the work is to evaluate the H₂ production through the implementation of thermochemical gasification process. Besides, the CaO adsorbent in this case will undergo the hydration process prior of being utilized in the gasification process, which is claimed as a promising pathway to further enhance the adsorption process. The effects of solid adsorbent to biomass ratio, heating rate, and steam to biomass ratio are investigated in order to optimize these process parameters. Apart from that, the flowability and floodability characteristics of both the original and modified solid sorbents are examined. The physical characteristics of the sorbent powder comprise of angle of repose, angle of spatula, angle of fall, angle of difference, compressibility, cohesion, dispersibility in addition to the other three auxiliary values such as aerated bulk density, packed bulk density, and uniformity.

II. EXPERIMENTAL METHODS

A. Materials Preparation

Modified CaO adsorbents were prepared through the hydration process by mixing 100 grams of original CaO (99.7% purity from Sigma Aldrich) with 1L of ethanol (EtOH) solution. In addition, EtOH solution was prepared through mixing of ethanol (99.9% purity from MERCK) and distilled water with the ratio of 8:2, respectively. The mixed solution then was placed in a beaker and stirred for 3 hours to ensure thorough mixing. Upon completion of the mixing process, the solution was heated inside an oven for a day at 110°C temperature in order to remove the excess EtOH and water in the solution. The modified CaO was ground and filtered using mesh opening of 150 µm. On the other hand, local palm kernel shells (PKS) were selected as the biomass sample for the work and were obtained from a local mill in Perak, Malaysia.

B. Characterization of CaO Adsorbent

The flowability and floodability characteristic of both the original and modified CaO is an important parameter because it will directly influence its performance in capturing CO₂. Thus, Hosokawa Micron Powder Characteristic Tester Model PT-S was applied to evaluate their characteristics, inclusive of angle of repose, angle of spatula, angle of fall, angle of difference, compressibility, compression, and dispersibility measurement. Besides, the aerated bulk density, packed bed density, and uniformity of these adsorbents were also investigated by using the equipment. The PT-S analytical instrument was developed so that the key measurements are performed using a single and convenient unit, and providing an additional basis of data for quality control of powdered products as well as numerical evaluations of flow behavior of dry solids.

C. Steam Gasification Procedures

Thermogravimetric analyzer (EXSTAR TG/DTA 6300) coupled with the mass spectrometer (MS) has been utilized to study the steam gasification process with PKS as the selected biomass samples. 1 mg of mixture of PKS and hydrated CaO adsorbents was loaded into platinum sample pan. Prior of the gasification process, the sample was loaded with argon (99.999% purity from MOX-Linde) as a carrier gas for an hour to avoid any oxidation from occurring inside the reactor. Then, the sample was heated to 100°C to remove any remaining moisture and further heated up to 900°C, with the heating rate is varied. The products which consist of low molecular weight gases such as H₂, methane (CH₄), carbon monoxide (CO) and CO₂ were analyzed by using the mass spectrometer. In addition, the experiment was conducted with the assistance of Taguchi optimization approach, as shown in Table 1.

TABLE I
 L₉ ORTHOGONAL ARRAY

Experimental Orders (Run)	Heating rate (°C/min)	Parameters	
		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

III. RESULTS AND DISCUSSIONS

A. Physical Characteristics of the CaO Adsorbent

The physical characteristics of commercial and developed CaO adsorbents are given in Table 2. The result of the powder characteristics as tabulated in Table 2 was based on Carr's floodability and flowability index table, respectively [11]. Overall, the developed CaO provides better characteristics in terms of angle of repose, compressibility, angle of spatula, and in the dispersibility. These properties are significant for understanding the powder's flowability and floodability in the

real gasifier system. Floodability in general is a sum of angle of fall, angle of difference, dispersibility and flowability index meanwhile flowability index is indicated by five parameters; compressibility, angle of repose, angle of spatula, uniformity and cohesion [12]-[14].

TABLE II
 COMPARATIVE STUDY BETWEEN THE CHARACTERISTICS OF COMMERCIALIZED AND MODIFIED ADSORBENT

Characteristics	Commercialized CaO		Modified CaO	
	Value	Index	Value	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	46.30%	0	21.40%	17
Cohesion	60.80%	2	86.90%	0
Dispersibility	11.20%	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

The significance of powder characteristic is imperative especially when it comes to the industrial or mass production. Consumption of less flowability and high floodability of powder will terribly affect the whole process as it will cause the powder to easily get stuck and jammed inside the pipeline, valve or funnel. Accordingly, it will increase the capital and operating cost and the process will not run smoothly due to regular shutdown and maintenance requirement. Thus, for the subsequent biomass gasification experimental works, the modified CaO has been chosen as the solid adsorbent due to its higher surface area, which is proposed to enhance the CO₂ adsorption capacity apart from its ease in handling process.

In addition, hydration method utilizing ethanol-water mixture has been employed in the research work to enhance the CO₂ capture capacity and recyclability of the material in continuous process [15]. It is reported that hydration with the alcoholic solutions yield sorbents with higher surface area, smaller particle size and better pore distribution that affect the sorbent reactivity [16]. Arpin *et al.* reported that the surface area and pore volume of modified CaO is much higher as compared to the original materials, which is from 2.18m²/g to 29.22m²/g and 0.006cm³/g to 0.157cm³/g respectively [15]. According to previous works, mesoporous sorbent structure is ideal because it maximizes the porosity in range of 5-20nm and will prevent pore blockage, pore plugging and minimize the pore diffusion resistance [16]-[17].

B. Steam Gasification of PKS with In-Situ CO₂ Capture

The results of the steam gasification of PKS with in-situ CO₂ capture in terms of product gas composition were plotted in Fig. 2. The data are repeated at least twice for reliability and repeatability. The ultimate goal of the research work is to maximize the total amount of H₂ production and simultaneously, minimize the production of CO and CO₂. Based on the Taguchi design L₉ orthogonal array, steam to biomass ratio of 0 indicates the absence of steam inside the gasifier system meanwhile adsorbent to biomass ratio of 0 shows no introduction of CaO inside the steam gasification process. According to Fig. 2, experimental run number 9 shows the greatest production of H₂ (in volumetric basis) which is about 61%. The results were also strongly supported based on Taguchi analysis using Minitab 16 statistical software (Minitab Inc., PA), as shown in Fig. 1.

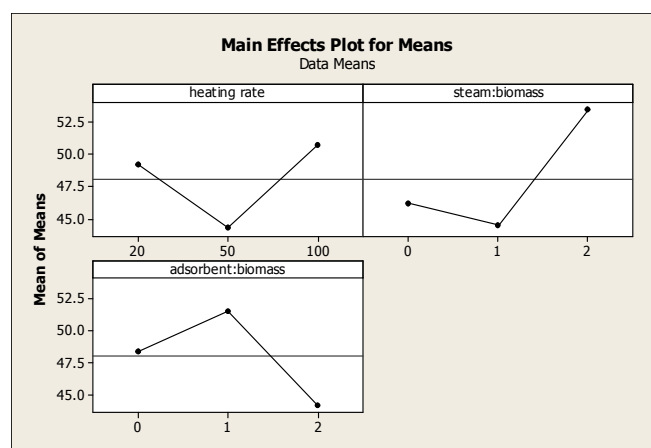


Fig. 1 Overall main effect plots from Minitab 16.1.1 software

Therefore, it can be concluded that the optimal condition for the process is at heating rate of 100°C min⁻¹, steam to biomass ratio of 2:1 and adsorbent to biomass ratio of 1:1. In gasification process, it is desirable to maximize the production of H₂ over CO, which can be applied by further promoting the reforming and water-gas shift reaction. Thus, Table 3 provides the comparative study of H₂/CO and H₂/CO₂ ratio for each of the experimental runs. Also, the gas composition is different at various experimental designs. Therefore, the simultaneous reaction that take place at each of the process design will contribute to various product gas compositions. Thus, the effect of each parameters (heating rate, steam to biomass fed ratio and amount of adsorbent) on H₂ production and yield is thoroughly analyzed and discussed in the following sections.

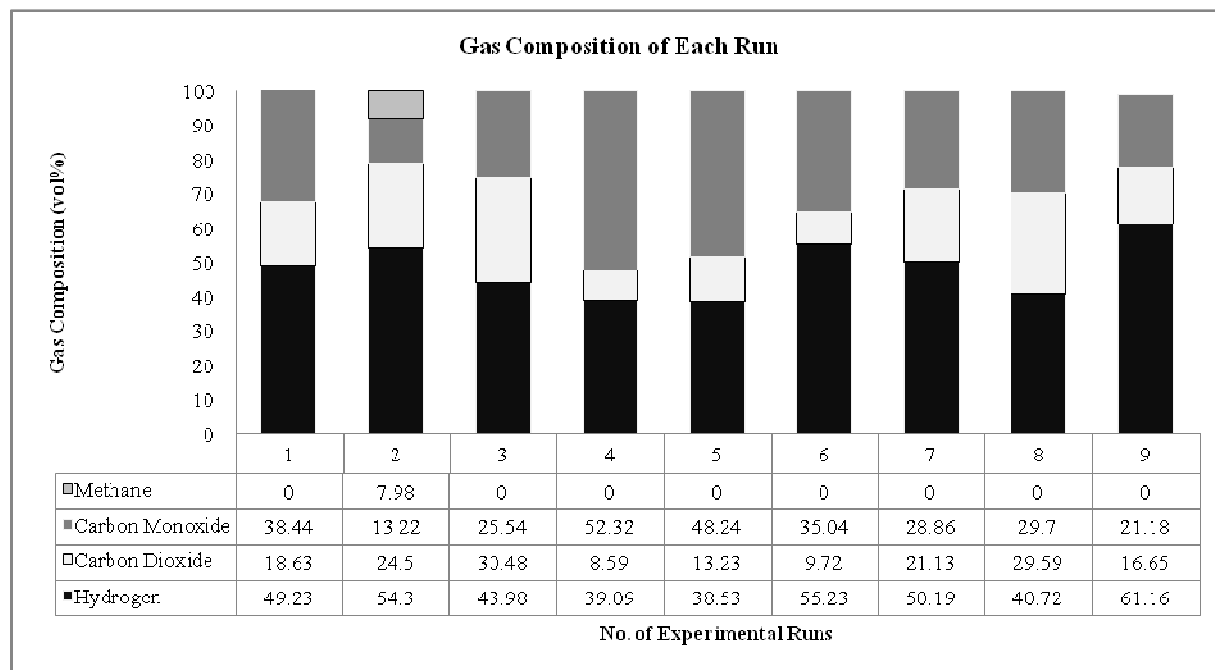


Fig. 2 Gas composition at each experimental run, based on Taguchi Design of Experiment

TABLE III

H₂/CO AND H₂/CO₂ FOR EACH OF THE EXPERIMENTAL WORKS

Experimental run	H ₂ /CO ratio	H ₂ /CO ₂ ratio
1	1.28	2.64
2	4.11	2.22
3	1.72	1.44
4	0.75	4.55
5	0.80	2.91
6	1.58	5.68
7	1.74	2.38
8	1.37	1.38
9	2.89	3.67

C. Effect of Steam to Biomass Ratio

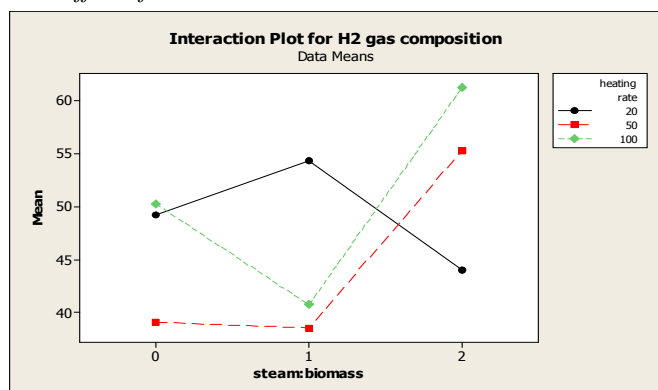
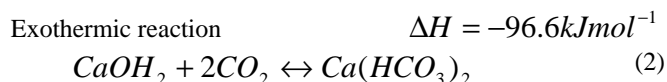
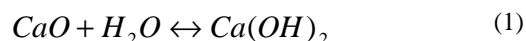


Fig. 3 Interaction plot of H₂ yield versus steam to biomass ratio (Unit for heating rate: °C/min)

Based on Fig. 3, H₂ production is significantly increasing correspond to the increase in steam to biomass fed ratio to the system. However, drastic reduction of H₂ production can be seen from Fig. 3 when increasing the steam to biomass ratio from 0 to 1 at heating rate of 50°C min⁻¹ and 100°C min⁻¹, respectively. This scenario is probably due to insufficient steam supplied to the gasification process, results in the ineffectiveness of the process. In addition, according to Fig. 3, the greatest H₂ composition was found at steam to biomass ratio of 2:1. Therefore, the ratio of 2:1 was identified to be the optimal point for steam gasification process. At the optimal point, the reaction attain the equilibrium condition in which H₂ released reach the maximum [18].

According to previous work by Xiao *et al.*, the presence of steam as the gasification agent helps to improve the carbon conversion, selectivity of H₂ and the lower composition of CH₄ and CO through steam methane reforming and the water-gas shift reaction of CO [19]. Steam also has the tendency to enhance the CO₂ capturing process in such a way that the steam react with CaO to form Ca(OH)₂ and the product will further promote the carbonation process to take place [20]. The reaction formula is as given in (1) and (2):



Since steam is the only agent used in the gasification process, the reactions that involve steam will be highly dependent on its concentration, up to a certain extent. Thus,

the selection of optimal steam to biomass ratio is significant since it affects the whole process reaction. From the research work, the optimal ratio of 2:1 is parallel with the recent literature that proves the slower rate of H₂ for the steam to biomass fed ratio above 2 [21]. The circumstance is due to the excess steam inside the process led to the temperature reduction inside the gasifier, attributed by the heat absorption [22]. In addition, based on Chen *et al.* [23], insufficient steam supply minimizes the H₂ production and the undesirable chemical reaction will take place (CO and CH₄ as the dominant product) and meanwhile, the high steam flow rate into the gasifier will tend to decline the H₂ yield and the surplus steam will be a waste of heat load and results in energy penalty. Also, according to Luo *et al.*, higher steam to biomass ratio cause increment in steam pressure and cause the reversible reaction shift towards the left, resulting declined in H₂ and CO₂ and increase CH₄ and C₂H₆ contents [24]. On this basis, it is concluded that a maximum value of the ratio of steam at each experimental conditions is crucial to maximize the composition of H₂ as the output.

D. Effect of Adsorbent to Biomass Ratio

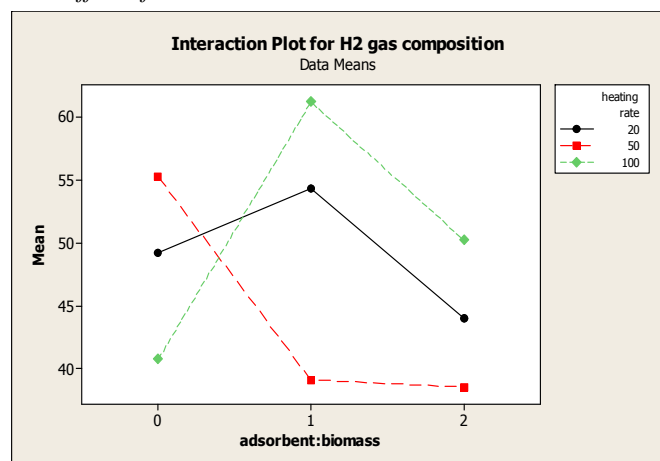
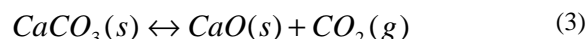


Fig. 4 Interaction plot of mean H₂ yield versus adsorbent/biomass ratio (Unit for heating rate: °C/min)

Based on Fig. 4, the introduction of CaO adsorbent into the steam gasification system was proved to enhance the H₂ composition in the product gas, especially at the heating rate of 20 °C min⁻¹ and 100 °C min⁻¹. However, drastic declined of H₂ production was shown at the heating rate of 50 °C min⁻¹, when varying adsorbent to biomass ratio of 0 to 1. The circumstances might be attributed by the unsuitable process parameters (combination of heating rate, steam to biomass fed and adsorbent to biomass ratio) for the gasification process to occur. The increment of H₂ yield can be explained by the movement of water-gas shift reaction according to the Le Chatelier principle. Due to the CaO carbonation reaction, the partial pressure of product CO₂ is lowered, making the process to be shifted forward and results an improvement of H₂ production [4].



Endothermic calcination $\Delta H = 170.5 kJ / mol$



Exothermic carbonation $\Delta H = -170.5 kJ / mol$

Apart of being a CO₂ adsorbent, the enrichment of H₂ production is attributed by the catalytic effect of these materials. Due to the catalytic effect possessed by the CaO, tar and hydrocarbon reforming will be further enhanced [22], [25]. Besides, the scenario can be explained as follows: the carbonation process and cellulose dehydration which is exothermic release heat during the CO₂ capture and thus, will enhance the gasification temperature. The increment of temperature will further assists in cracking of tar, char conversion and compensate the energy required by other endothermic processes [25]. Moreover, finding of this experiment study in which the optimal point is at ratio of 1:1 can be supported from the previous result found by Florin *et al.* as the adsorbent to biomass ratio obtained is approximately 0.9 and thus, there is not much differences between these two [3].

However, beyond the optimal condition, the excess of solid sorbent to biomass ratio will bring an adverse impact towards the H₂ production, as shown in Fig. 4. This is because beyond the optimal point, most of supplied CaO will be unreacted and the heating and decomposition of the excessive sorbents will reduce the reactor temperature and subsequently, reduce the H₂ yield [25]. As reported in the literature, the selection of suitable adsorbent to biomass ratio is highly dependent on the energy balance between regenerator and gasifier, target product, type of biomass, activity of catalyst, as well as efficiency of CaO-based adsorbent [8].

E. Effect of Heating Rate

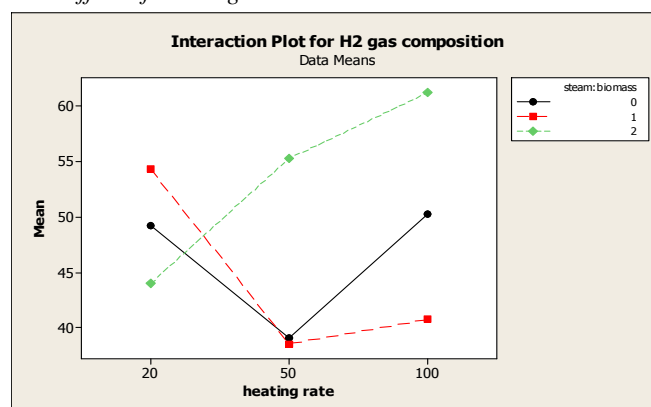


Fig. 5 Interaction plot of mean H₂ yield versus heating rate (Unit for heating rate: °C/min)

According to Fig. 5, H₂ yield increase with the increment of heating rate from 50 to 100 °C min⁻¹ as the steam to biomass ratio increase from 0 to 2. Based on Fig. 1, Fig. 2, and Fig. 5 respectively, the greatest H₂ production is at heating rate of 100 °C min⁻¹. The findings from this research study are parallel

with the recent work by Fushimi *et al.* whom states that the H₂ yield increased with the enhancement of heating rate because there will be a rapid evolution of volatiles due to bond breaking of biomass samples and subsequently, produce a porous char which has high reactivity to enhance the reaction rate [26]-[27]. Table 4 summarizes the effect of heating rate towards the coal's porosity.

TABLE IV
EFFECT OF HEATING RATE TOWARDS THE POROSITY [27]

Coal	Conditions		Specific pore volume (cm ³ g ⁻¹)	BET surface area (m ² g ⁻¹)
	Temperature	Heating rate		
SS005: high volatile bituminous coal	1473K	10 K/min	0.00473	4.92
		Rapid	0.01531	16.3
	1673 K	10 K/min	0.00799	4.94
		Rapid	0.06822	61.9
SS021: medium volatile bituminous coal	1473K	10 K/min	0.0026	3.19
		Rapid	0.00296	3.02
	1673 K	10 K/min	0.00504	4.91
		Rapid	0.00717	6.61

Basically, heating rate of the gasification process is known to have an influence on the surface morphology of the samples and their reactivity during the process [28]. Therefore, it is reported that slow heating rate produces smooth coal surfaces meanwhile at the rapid and high heating rate; rough and porous structure was obtained. The scenario is attributed by the drastic release of volatile matter during the initial pyrolysis (decomposition of the biomass samples) [29]. In addition, Fushimi *et al.* reported that rapid heating increased the reactivity of char in steam gasification due to formation of macropore on the char surface; prevent char agglomeration and condensation of fragments onto the char surface [26].

Therefore, it can be concluded that rapid heating rate favor the steam gasification of the biomass samples and complete the conversion of volatiles into low molecular weight gases (i.e. H₂, CO, CH₄, and CO₂) at the low temperature during the initial biomass devolatilization steps. Hence, the investigation on the impact of heating rate on the evolution of gas output during the steam biomass gasification is very important.

IV. CONCLUSION

Product gas composition through the steam gasification of biomass samples, PKS was examined and evaluated through TG-MS analysis by varying three process parameters namely heating rate, steam to biomass fed ratio, and adsorbent to biomass ratio. The effect was captured in terms of H₂ production and yield throughout the process. From the analysis, more than 60% of PKS samples were converted to H₂ with combination of heating rate at 100°C, steam/biomass of 2:1 ratio, and adsorbent/biomass of 1:1 ratio. All of the parameters in general are very significant because the heating rate will assist the devolatilization of the biomass samples and

conversion of volatiles into gases and the other two parameters will enhance the reforming and water-gas shift reaction. By capturing CO₂, the H₂ production was enhanced since the water-gas shift reaction is shifted forward. Meanwhile, the enhancement of CO₂ sorbent in terms of flowability and floodability was demonstrated by the modified CaO. The study of powder characteristics is vital especially in the industrial production as it will affect the material handling process. Overall, biomass represents clean and renewable resources for the H₂ production, provided that the steam gasification process is accompanied with in-situ CO₂ capture.

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