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Production of Hydrogen from Biomass using Pyrolysis

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Abstract: The pyrolysis of some selected biomass samples Palm Kernel Shell (PKS), Empty Fruit Bunch (EFB), Sugarcane Bagasse (SCB), Rubber Seed Shell and Kernel (RSSK), and Rubber Seed Shell (RSS), were carried out with the aim of producing Hydrogen using fast pyrolysis in a non iso-thermal pyrolysis temperature of 700°C, 800°C, with the other pyrolysis parameters to be kept constants at 100ml/min inert gas flowrate, 100°C/min heating rate. Both non catalytic and ex-situ catalytic pyrolysis using mesoporous Alumosilicate (Al-MCM-41) as catalyst under the same process parameters. It was observed that the hydrothermal instability structural collapse of Al-MCM-41 affected hydrogen yield at 800°C, but suitable at 700°C. The various biomass showed different variation in the proportion of hydrogen yield at different pyrolysis temperatures, strongly indicating hydrogen yield depends on the biomass elemental composition and pyrolysis temperature and among the few biomass samples experimented on SCB and EFB showed to be promising feedstock with their Hydrogen yield at all the process conditions remarkably above all other samples on the value of 47.17vol% for EFB at 800°C non catalytic pyrolysis, and 50.21vol% for SCB at 700°C catalytic pyrolysis.

Keywords: *Pyrolysis, Al-MCM-41, Hydrogen, Biomass, RSSK, PKS, EFB, SCB, Syngas.*

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I. INTRODUCTION

Finding sustainable sources of energy as hydrogen is a global problem as the world is driving towards reducing CO_2 emission to net-zero, hydrogen from Biomass is a promising, clean, renewable energy source due to its abundance, wide distribution, and CO_2 neutrality as it is formed from biogenic carbon via the photosynthesis process [1]. Long-term projections show that by 2050, hydrogen will play a significant role in the world economy and provide up to 20% of the world's energy needs. Hydrogen is crucial for many industrial processes, including the manufacturing of chemicals, fertilisers, steel, and other industrial products, in addition to being used as a fuel. The demand for hydrogen in its pure form is around 70Mton/year [12]. Hydrogen can be produced from different processes as shown in Fig.1, which are namely Electrolysis of water, through biological processes, hydrogen is produced by microorganisms like bacteria and microalgae, and Thermochemical processes which consist of pyrolysis, bio-derived liquid reformation, biomass gasification solar thermochemical hydrogen, using feedstock like natural gas, coal, or biomass to release hydrogen from their molecular structure, natural gas reforming [8].

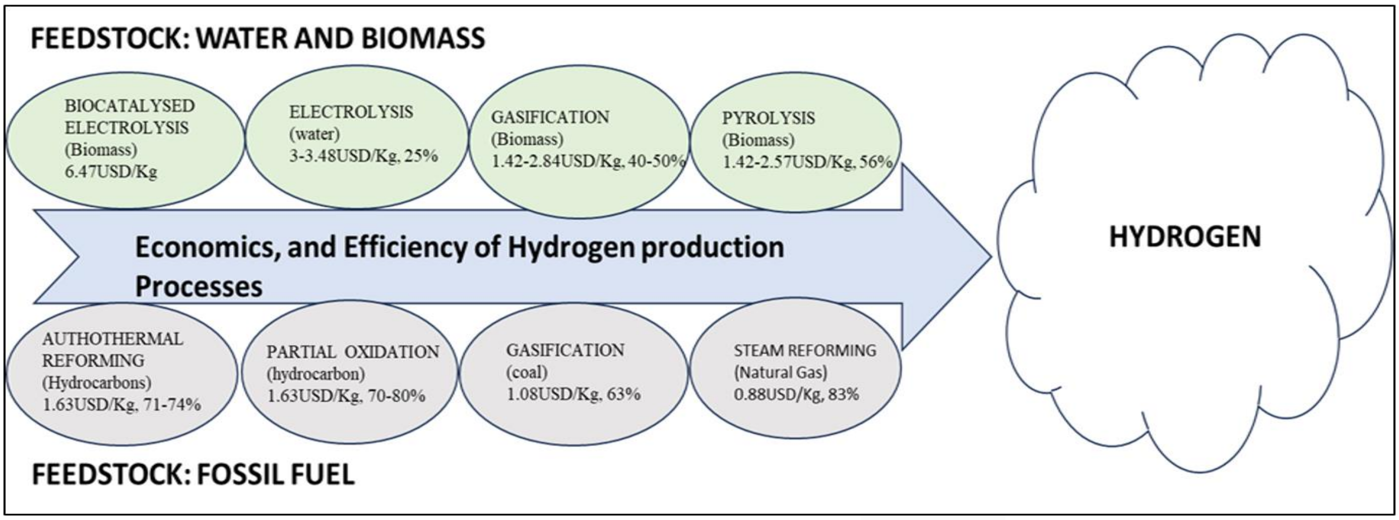

Fig 1 Hydrogen Production Processes, Modified from Parthasarathy et al., [13]

At the worldwide level, natural gas accounts for 48% of the production of H_2, oil for 35%, and other sources for the rest. Natural gas is the primary feedstock to produce hydrogen using a variety of technologies, The major drawback of these route lies in the amount of CO_2 emitted to the atmosphere, which accounts for 2.7% of global CO_2 emissions [9], the depletion of oil and gas reserves and, to a lesser extent, methane emissions, this method of producing hydrogen is deemed to be unsustainable. If the conflict between Russia and Ukraine continues, the levelized cost of manufacturing H_2 from natural gas will continue to climb. Therefore, the best and most sustainable alternative to using natural gas as a feedstock to manufacture hydrogen is regarded to be sustainable H_2 generation from organic biomass [11]. The number of articles suggesting an increase in the thermochemical H_2 generation of organic biomass over time (2000 to 2020), the research on publications revealed a steady increase in articles on the thermochemical conversion of biomass to H_2 using pyrolysis from (2010 to 2020), there was a sharp growth [10].

➢ *Overview of Pyrolysis.*

According to the operating parameters used throughout the process, conventional pyrolysis may be divided into three basic categories: (i) slow pyrolysis; (ii) fast/rapid pyrolysis; and (iii) flash pyrolysis.

The slow pyrolysis process, which typically produces biochar as the primary product and bio-oil and syngas as byproducts, is a batch process. Most of the slow pyrolysis occurs at moderate temperatures (300–700°C), ramping rate (5min), the reactors most frequently employed in slow pyrolysis process include auger reactors, rotary kilns, and drum reactors [23]. The main drawback of these processes is that the yield greatly depends on the feedstock's characteristics, the pace and temperature of heating, the choice of purging gas, and the bed material. While the breakdown of cellulose and hemicellulose occurs at higher temperatures, which results in less char production.

Fast pyrolysis is a result of the rising need for biomass liquid product production. Temperatures between 450 to 800°C and a brief holding period of 0.5 to 10sec are optimal for fast pyrolysis [20]. By preventing volatiles from taking part in secondary reactions and inhibiting primary products from participating in cracking reactions, these high process temperatures and brief holding durations increase the yields of bio-oil and gas. Before char is generated, the biomass is converted into liquid products and condensable gases [23]. A high rate of heat transmission is necessary for the efficient use of fast pyrolysis and may be achieved by maintaining tiny particle size, ideally 1mm [23]. Chemical kinetics, rate of mass and heat transport, and transition phenomena all play important roles in fast pyrolysis since it is anticipated that the reaction would occur in a relatively short period of time [23]. Fast Pyrolysis can be improved to Flash Pyrolysis, which has higher heating rates than fast pyrolysis. Process temperatures of 800-1200°C, particle sizes of less than 0.1mm, heating rates of more than 1000°C/sec, and residence periods of less than 2sec are the operating parameters that are often used in flash pyrolysis [19].

In recent years, a unique type of pyrolysis known as intermediate pyrolysis—which occurs halfway between slow and quick pyrolysis—has been established [21]. Pyrolysis heating rate, temperature and duration, volatiles' residence time, and feedstock size are the control factors that set the four groups apart. The distribution of products as well as the category of the pyrolysis process may both be determined by the heating rate [23].

Intermediate pyrolysis A stand-alone synthesis method with a residence time of 2-4 seconds, a process temperature range of up to 500°C, and a duration range of 30–1500sec has been developed [22]. The primary result is the liquid fraction (40–60%), which is followed by the gases (20–30%) and the solid biochar (16–25%). Low tar concentrations and lower viscosity are benefits of using intermediate pyrolysis. However, the main difficulty regarding the experimental parameters for intermediate pyrolysis is still being developed, and measurements of the product yields and compositions have not yet been standardised. This is a significant problem when comparing the results of various research investigations, hence it is advised that researchers do laboratory scale experiments while modifying the process parameter to reduce this gap.

During pyrolysis, biomass is thermally degraded in the absence of oxygen to produce char, liquids (oil/wax), and gaseous byproducts as shown in the stages listed in equation (1) to (3). Many studies on pyrolysis have been conducted with the aim of producing bio-oil, pyrolysis gas, or bio-char. Despite being a complicated process, the method by which biomass is pyrolyzed in the thermochemical conversion may be summarised into three fundamental reaction stages [18] as in equation (1) to (2).

Pre Pyrolysis:

$$\text{BIOMASS} \longrightarrow H_2O_{(v)} + \text{Unreacted Residue} \quad (1)$$

Fragmentation or primary Pyrolysis:

$$\text{Unreacted Residue} \longrightarrow \text{Volatile} + \text{Gases} + \text{Char} \quad (2)$$

Depolymerization or Secondary pyrolysis:

$$\text{Char} \longrightarrow \text{Volatiles} + \text{Gases} + \text{Char} \quad (3)$$

Fig 2 Pre Pyrolysis: BIOMASS

The predominate chemistry of fast pyrolysis are most common in the vapour phase, the thermal degradation of a sold biomass material results into several pyrolysis products which is promoted by the transfer of heat into the biomass particle in a high temperature environment. As a result of the particle's brief heating, which raises the local temperature, moisture may evaporate quickly in the dehydration stage, and the main pyrolysis process may then see the subsequent development of the product species. The principal volatiles are known as Pyrolysis gases, liquids (Oil/wax), and char which are created by the thermal breakdown of extractives, lignin, hemicelluloses, and cellulose, which are typically the components that make up the biomass material [3]. Condensable pyrolysis products such as bio-oil, bio-crude, etc. are produced by this degradation at various pre- or pyrolysis temperatures, as well as pyrolysis gas mixes of CO, CO_2, H_2, CH_4, C_nH_n, C_2H_4 and H_2O. Comparatively, a temperature of, say, less than 500°C is required for the main pyrolysis process to completely convert, even if cellulose, hemicelluloses, lignin, and extractives degrade quickly at various temperatures. However, when the fuel is heated to an elevated temperature, some of the primary volatiles inside the particle are released, which leads to a series of secondary reactions that yield a variety of pyrolysis products. These secondary processes, which may occur homogeneously or heterogeneously, include cracking, water gas shift behaviours, gasification, polymerization, and others [17][3]. Primary and secondary pyrolysis differ, with secondary pyrolysis occurring inside the particle pores and primary pyrolysis occurring outside. Charring and primary pyrolysis occur at different rates, with charring being slower, and the production of volatiles is dependent on the conditions of the process. Secondary reactions of initial volatiles can also take place, leading to breakdown and depolymerization of the primary volatiles. The physio-chemical mechanisms shown in Fig.2. also control the main shrinkage and fragmentation of the biomass material to yield the required pyrolysis products.

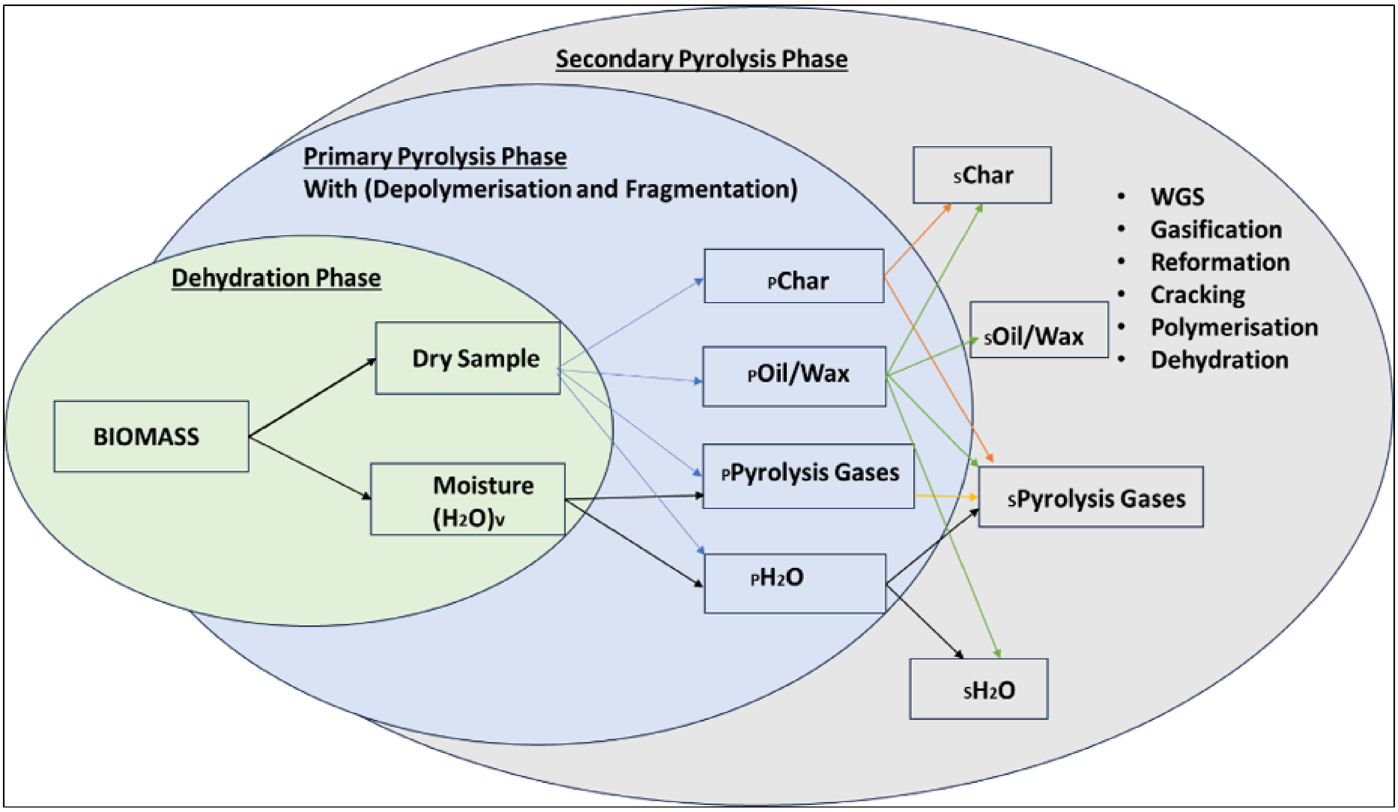

Fig 3 The three Phases in Pyrolysis [Modified from Uddin et al., 2014 [47].]

Pyrolysis process parameters such as temperature, pressure, moisture content, biomass composition, heating rate, and sweeping gas flow rate play a significant role in the desirable yet of pyrolysis products, various biomass even under the same experimental conditions show remarkable difference in pyrolytic gas because of their compositions. Hence, it remains challenging to comprehensively investigate the influences on pyrolytic gas yield and compositions concerning both biomass characteristics and pyrolysis conditions or even their interactions [33].

➢ *Effect of Moisture on Hydrogen Yield*

The distribution and yield of the product, density, change in weight, temperature profile, rate of heat transfer, and other factors are all positively impacted by the moisture content during the pyrolysis process. It's significant to remember that before combustion starts as a distinct process, the moisture content of biomass fuels is projected to be no more than 65% (on a wet basis) [25]. Additionally, it should be mentioned that although the range of 7% moisture content is recommended for the process according to the maximum allowable limit of moisture content [18], there is a negative correlation between the heating value of biomass fuel and the relative quantity of moisture.

It is expected that 7% moisture concentration is ideal throughout the whole pyrolysis process to achieve the optimum results since excess moisture content consumes a significant amount of heat, which results in poor percentage yields [31]. The formation of H_2 gas was, however, enhanced by moisture due to a secondary reaction, demonstrating that, under fast-heating rate and without the use of sweeping gas, in comparison to pyrolysis of pre-dried biomass with a moisture content of 7.9wt%, wet biomass with a moisture content of 47.4wt% produced a greater output of H_2. Additionally, when the rate of water evaporation grew, the rate of hydrogen generation increased as well until its value reached an optimal level. The rate of hydrogen generation, beyond this point dropped because the amount of water vaporised exceeded the reduction bed's conversion capacity and the equivalency ratio fell.

- *Effect of Particle Size on Hydrogen Yield*

Particle size regulates how much the main pyrolysis and drying pathways overlap when the fuel is thermally disintegrating, controls the speeds of both processes, and has a significant impact on the compositions and quality of the end products. Since the internal surface area of particle size is connected to a slow heating rate, secondary reactions might potentially be strong when particle size rose noticeably over time [7]. Such circumstances encourage the development of Hydrogen and other gases substantially more than the generation of liquid. Large fuel particles can be pyrolyzed to provide a poor yield of liquid products [7][34], and as a result, the particle size may affect the secondary reactions of volatiles. For instance, when tested particle size increased from 53-63 mm to 270-500mm, respectively, the greatest tar output could be reduced from 53 to 38% of fuel [34]. The secondary reactions from fuel pyrolysis at 500°C in a fluidized fixed bed can also be affected by a particle size increase of 3 to 12mm [32]. During rapeseed pyrolysis in a fluidized fixed bed reactor, when the particle size was increased from 0.425 to 0.85mm with a heating rate of 40°C/min at 500°C, the gas output rose from 16.77 to 19.10% [36]. The possibility of homogenous tar cracking events occurring at temperatures below 500°C, which boosted the catalytic activity of the char layer, may be the cause of this feature, where the tar conversion may increase as the particle size is increased.

- *Effect of Heating Rate on Hydrogen Yield*

Primary volatiles, such as pyrolytic water and tars, were created during the thermal breakdown (>600°C) of solid fuel particles derived from biomass. While the fluctuation in total gas production cannot be seen at considerable levels, the generation of liquid can grow quickly below 600°C. Above 450–550°C, primary volatiles undergo a secondary conversion (secondary pyrolysis of tars), which can lead to a decrease in the yield of pyrolytic liquid. A variety of interpretations of this data suggest that the output of gaseous products increases at high heating rates and is comparatively extremely low at low heating rates. A significant quantity of pyrolytic gases produced by the thermal cracking of primary tars, which results from fast pyrolysis below pyrolysis temperature of 450–550°C, at higher temperatures [37][35]. Regarding the yields of hydrogen and carbon during cellulose breakdown, heating rate has a significant impact. The yields of CH_4, H_2, and CO rise noticeably at pyrolysis temperatures above (567-607°C) as the heating rate rises [40]. Due to the high heating rate (100°C/sec), secondary phase pyrolysis of cellulose tar/oil to produce CH_4, H_2, and CO is greatly increased before the reactor is evacuated. It is important to emphasise that quickly heating cellulose promotes gas production by enhancing the secondary pyrolysis of volatiles generated by primary pyrolysis (WGS and steam reforming reaction may also happen after rapid heating rate).On the other hand, tar generated by cellulose dissolving at low temperatures quickly escaped from the reactor prior to heating, resulting in secondary pyrolysis of tar releasing CO and H_2 in the gas phase, which is minimal.

- *Effect of Pyrolysis Temperature on Hydrogen Yield*

Similarly, at lower temperatures during the thermal degradation of lignin, weak linkages are broken, but at higher temperatures, stronger connections are severed. In terms of structure, lignin has a large concentration of aromatic rings and $O\text{-}CH_3$ functional groups. At higher temperatures (>500°C), the cracking and rearrangement of the aromatic bonds of C-H and C=C, releases H_2, while CH_4 is produced by the comparatively weak link of the Methoxyl group ($-O\text{-}CH_3$). In addition to lignin breakdown, cellulose decomposition with a high carbonyl concentration yields a lot of CO, whereas hemicellulose decomposition with a high carboxyl content yields a lot of CO_2 [38]. While xylan pyrolysis produces the most gas below this temperature, the production of gas from cellulose pyrolysis increases noticeably with temperature and reaches a maximum yield when the temperature approaches 560°C [45]. In the whole temperature range, lignin is exposed to less gas species production than xylan and cellulose pyrolysis. The subsequent degradation of the bio-oil and the emission of volatile materials may be to blame for this.

Between 500 to 600°C, there was an increase in hydrocarbon product output. However, the yields rose more slowly or stayed constant at higher temperatures, between 750 to 800°C. Up until a temperature of 550°C, the CO production significantly increased before remaining practically constant. Researchers created a mathematical model that takes into consideration heat transport restrictions throughout the heating and cooling stages and found a correlation between the specific rate of lignin degradation and reaction temperature. They then calculated the heat of reaction as 116 kJ/kg lignin. However, the splitting of hydrocarbons into smaller fragments at greater pyrolysis temperatures enhances the generation of pyrolysis gases. The secondary cracking rate is so high at higher pyrolysis temperatures that char formation and total gas formation both rise [43].

- *Effect of Inert Gas on Hydrogen Yield*

The primary function of inert gas in the biomass pyrolysis process is to remove oxygen and volatiles from the pyrolysis environment. Typically, a purge gas is an inert gas such as nitrogen, CO_2, steam, hydrogen, helium, or a combination of these substances. The pyrolysis gas production of birch wood increased from 33 weight percent to 69 weight percent when a steam environment was used, however the hydrogen yield declined from 47 to 43.1vol%. They added that the procedure was far less affected by heating rate in a steam environment than it was in a nitrogen atmosphere [39]. Because a significant portion of the N_2 stream was in the vapour phase, the N_2 purge rate might diminish both the condensation of the pyrolysis volatiles into pyrolysis oil as well as the partial pressure of the volatiles. Such outcomes generate a tremendous amount of heat inside the reactor, which causes the main pyrolysis products to decompose secondarily and encourages the generation of pyrolysis gaseous products [42]. The inert gas, however, removes the volatiles from the pyrolysis environment, therefore secondary processes such as thermal cracking, re-polymerization, and re-condensation should be maximised when the goal is to produce as much pyrolysis gas as possible [44].

Likewise, the amount of gas produced would be greatly increased in an environment that contained both steam and nitrogen. Additionally, it was found that the production of hydrogen, carbon monoxide, and pyrolysis gas all increased when biomass-derived oil was pyrolyzed at a temperature of 800 °C, respectively, from 47 to 49 mol%, 26.6 to 30.2 mol%, and 67 to 81wt% [48]. The production of methane and other hydrocarbons, on the other hand, decreased with steam flow rate because of the extra reaction of methane via steam reformation and partial oxidation processes.

- *Effect of Reactor System on Hydrogen Yield*

Due to their higher heating rates, fluidized bed reactors would be able to create hydrogen from biomass pyrolysis at a higher output rate [46]. But in addition to the fluidized bed reactor, circulating fluidized beds, cyclone reactors, rotating reactors, and transportable bed reactors all have some of the same properties. In addition to these, additional types of reactors exist, such as ablative, screw, and fixed bed reactors [46]. The main reaction of indirect gasification, which produces char, condensable vapours, and permanent gases, is devolatilization of the feedstock. The final gas composition as well as its characteristics may be influenced by secondary pyrolysis gaseous phase reactions, such as the WGS reaction, however this phenomenon is highly reliant on the vapour residence time and reaction medium.

- *Biomass Selection*

Biomass feedstock on pyrolysis plays a significant role in the yield of pyrolysis product, primarily three major biomass building blocks which are namely hemicellulose, cellulose and lignin, this building blocks consist of different functional groups which makes the biomass a heterogeneous polymer consisting of 40-50% of cellulose, 15-30% hemicellulose and 15-30% lignin at a biomass dry weight base [51]. The biomass selection was based on the structural components from elemental, proximate analysis and heating value are applied to the selection of feedstock for various applications, the behaviour when thermally decomposed, products formed can be accessed with the data obtained from the named analysis, agricultural based feedstock are quite higher in volatile matter consisting of 60-90wt% compared to woody biomass [52]. From literature heating value is a key measure of the energy content of the material. For the pyrolysis process, biomass with a high net energy content is preferable since it may provide superior energy products. The biomass properties that were sorted for the biomass selection were, the biomass with moisture content of 7-10%, lignin composition of 15-29% and heating value of 18-27MJ/Kg as shown in Table 1 and Table 2 as the properties that will be suitable for high Hydrogen yield from biomass [14][13].

Table 1 Elemental Analysis of RSS, SCB, EFB, PKS

Biomass	Lignin (%)	Hemicellulose (%)	Cellulose (%)	Holocellulose (%)	Ref
Rubber Seed Shell (RSSK)	7-21	19-25	38-65	57-90	[27]
Sugarcane Bagasse (SCB)	9-29	29	36-69	-	[29]
Empty Fruit Bunch (EFB)	18-25	22-35	37-60	-	[30] [28]
Palm Kernel Shell (PKS)	25	26-46	30-51	-	[26]

Table 2 The Proximate, Ultimate, and Heating Value of PKS, EFB, SCB, RSS

COMPONENTS	FEEDSTOCK SAMPLES			
	PKS	EFB	SCB	RSS
PROXIMATE ANALYSIS				
Moisture (%)	9.7	7.95	8.5	8.59
Volatiles matter (%)	72.8	83.86	82.4	80.98
Fixed Carbon (%)	13.0	10.78	13.4	6.62
Ash (%)	4.5	5.36	4.2	3.81
ULTIMATE ANALYSIS				
Carbon (%)	48.88	32.03	47.3	44.31
Hydrogen (%)	5.71	7.85	5.7	4.38
Nitrogen (%)	1.01	0.78	0.4	0.51
Oxygen (%)	44.39	40.76	46.7	50.67
HEATING VALUE				
HHV(MJ/kg)	18.82	20.20	18.1	23-27.5
REFERENCE	[13]	[13][51]	[15]	[16]

- *Effect of Biomass Composition on Hydrogen Yield*

The chemical makeup of biomass's main constituents, cellulose, hemicellulose, and lignin, determines its pyrolytic properties. Hydrogen is produced from biomass under identical thermal conditions regardless of the type of feed, but under different thermal conditions and reactor types, particularly vapour residence time, hydrogen compositions vary. It is interesting that the degree of thermal severities has a greater influence on hydrogen generation than biomass feedstock does [49]. Different types of volatiles, including CO, CO_2, H_2O, and H_2, as well as various hydrocarbons, including CH_4, C_2H_6, C_2H_4, and C_3H_8, are produced during the thermal breakdown of these components. The characterization of materials, which is based on the elemental analysis of the different biomass, provides information on the nature and composition of the material and aids in deciding on the material's best use. A lingo-cellulose's chemical makeup is determined on the characteristics of the plants. The three main elements of any lingo-cellulosic feedstock are cellulose, lignin, and hemicellulose. The ratio of these components in a fibre is influenced by the fibre's origin, age, and the conditions under which it was extracted. Using conventional methods, the components of the rubber tree's seed shell have been identified as holocellulose, lignin, ash, hemicellulose, and cellulose.

- *Catalyst (Al-MCM-41)*

Scientists at Mobil Oil Corporation first developed MCM-41, a member of the silicate and alumosilicate family with a layered structure. It is composed of a regular arrangement of cylindrical mesopores that have a distinct pore distribution and a large surface area and pore volume [2]. Unlike zeolites, the material does not contain Bronsted acid sites, but instead relies on surfactants as a template. The total number of acid sites, as well as the type and strength of the acid sites, have a major influence on the activity and selectivity of the catalyst. Al-MCM-41 materials contain both Lewis and Bronsted acidity of mild to moderate strength. The type and strength of acidity present in Al-MCM-41 materials are important, as it affects the activity and selectivity of the catalyst. Both Bronsted and Lewis acidity of a mild-to-moderate strength is present in the materials. These acid sites catalyze several reactions, including cracking, isomerization, oligomerization-aromatization, decarboxylation, and dehydration, in catalytic cracking and pyrolysis processes, such as biomass pyrolysis.

- *Effect of Catalyst on Hydrogen Yield*

From several literature cited Al-MCM-41, have shown remarkable performance as a catalyst in the synthesis of hydrogen from biomass. Significant Bronsted acid sites facilitated the breakdown of biomass-derived hydrocarbons into smaller molecular components like H_2 and CO. However, the creation of hydrogen and reformation during the gasification of wood sawdust have both been greatly enhanced by the abundance of Bronsted acid sites on the supports. His Ni/H-[Al]MCM-41 catalyst produced more hydrogen than the other two catalysts combined, by a factor of at least 2 or 3. Due to their unique acidic and porosity characteristics (high surface area, comparatively wide pores of around 3nm pore diameter, and mild-to-moderate acidity), the mesoporous aluminosilicates Al-MCM-41 can be regarded as potential catalysts for biomass pyrolysis [5]. Previous research has demonstrated the high activity of Al-MCM-41 or composite catalysts made of Al-MCM-41 and ZSM-5 in the catalytic cracking of palm oil to produce petrol. Al-MCM-41 samples have recently been investigated as biomass rapid catalytic pyrolysis catalysts, with corresponding variations in the quality of bio-oil. Both Lewis and Bronsted type acid sites may be present in an Al-MCM-41 catalytic material, and both types can participate in the biomass pyrolysis through various processes. While it was noted that Al-MCM-41 greatly improved both gas and hydrogen production of PKS yield compared to other catalyst tested, with a structural collapse at 700°C [41], it was also noted that Al-MCM-41 materials exhibit relatively low hydrothermal stability compared to zeolites [4], inhibiting their use in high-temperature processes in the presence of steam.

II. MATERIAL AND METHODOLOGY

- *Sample Preparation.*

The Biomass sample PKS, EFB, SCB, and RSS were obtained from Petronas Malaysia, after the sample have been washed to remove dirt like sand particles, the samples were dried by oven drying using Solab model SL-100/42 at 105°C to constant mass, PKS and EFB were grinded and sieved into 180μm fine particles using Laboratory Test Sieve produced by Endcotts Ltd, London, England. While RSS and SCB was crushed and chopped with laboratory crusher and scissors respectively into sizeable particle that can be feed into the reactor.

- *Experimental Method*

The experiment starts with weighing and recording the sample of the biomass to be used, for the ex-situ catalytic pyrolysis weigh out the amount of catalyst needed, with the weighing ratio of biomass to catalyst to be 2:1 respectively and the value recorded. The bottom of the reactor is screwed tightly, and the metal rod is placed inside the reactor, to elevate the biomass sample to the centre of the reactor. The reactor layers are setup as shown in Fig.3(A)(C). In that simple order the reactor layer is formed, and the top is screwed tightly to prevent sucking in air and gas linkage, then the rector is weighed and recorded before the pyrolysis.

The fluidized fixed bed reactor is placed in the centre of the furnace to facilitate free and even heat transfer to the biomass sample in the reactor. The Nitrogen supply channel which is used as the reactor flushing gas is connected to the top of the reactor and its tightly screwed to maintain steady gas flow and prevent linkages. The condensing bottle 1, condensing bottle 2, and condensing bottle 3 are weighed initially and their value recorded. The three condensing bottles are connected to the reactor as shown in Fig.3(C) the bottles are connected in series with the condensing bottles 2, and 3 placed within the ice bath, to condense some of the gaseous volatiles condensable in the gaseous phase at a low temperature. The connection from condensing bottle 3 is placed in a beaker filled with water to check if there is gas flow when the gas valve is turned on.

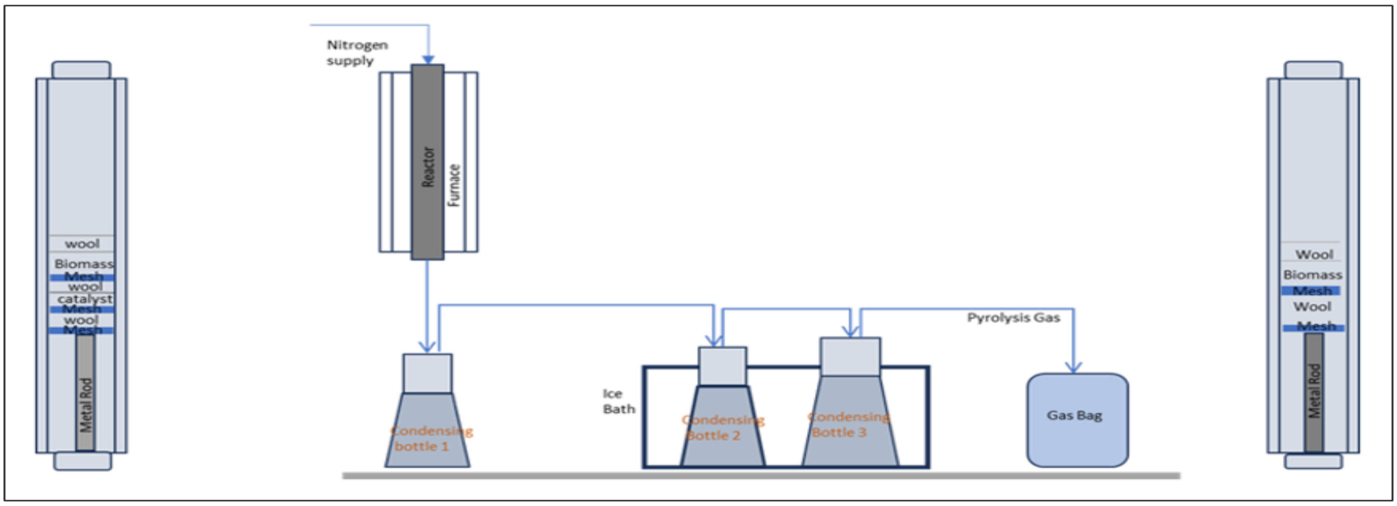

Fig 4 (A) Catalytic reactor layers (B) Full pyrolysis experiment setup (C) Non-catalytic reactor layers.

Once the setup has been properly made as indicated on Fig.3(B) the Nitrogen gas valve is opened to start purging the reactor of oxygen and the gas flowrate is set at 100ml/min using a gas flowmeter, and the furnace is also set to either 700 or 800°C non-isothermal pyrolysis temperature, with a heating rate of 100°C/min at an isothermal residence time of 15mins once the desired pyrolysis temperature is reached, the top and bottom of the furnace is packed with glass fibre to reduce heat lost by convention, and the direct connection from the reactor to the first condensing bottle is lagged with wool and foil to prevent it from melting down, and the furnace is turned on to start the pyrolysis process. when the furnace has been heated up to a temperature of between 300 to 450°C, the gas outlet from condensing bottle 3 is connected to a gas bag as the furnace heats up to the desired pyrolysis temperature of 700 or 800°C the gas is allowed for 15minutes after the required temperature is reached the collected gas is further analysed using Hubei Cubic-Ruiyi Instrument Company limited. Model Infrared Syngas Analyzer, Gasboard-3100 and the furnace is turned off and allowed to cool down before dismantling.

When the setup is cold, the condensing will be removed from the ice bath dried properly, the three condensing bottles are reweighed and records with their connecting tubes for there would be some oil in them to be accounted for, then the Nitrogen supply is disconnected from the reactor and the reactor is reweighed and recorded after the pyrolysis process. After weighing the reactor and bottles some char and oil are collected in separate sample bottle for further analysis, then the empty reactor and condensing bottles are rinsed with acetone, dried in the oven for further use.

III. RESULTS AND DISCUSSION.

➢ *Pyrolysis Gas Production*

As shown in Table 3, the non-catalytic and ex-situ catalytic pyrolysis with Al-MCM-41 as catalyst, at a constant heating rate of 100°C/min, inert gas flowrate of 100ml/min with a varying pyrolysis temperature of 700°C to 800°C and a final holding time of 15mins, the various biomass sample PKS, EFB, SCB, RSSK, and RSS showed different variation in the percentage of pyrolysis gas produced, even under the same thermal decomposition condition.

Table 3 Composition of Pyrolysis Products.

BIOMASS SAMPLE	Pyrolysis Temperature (°C)	Pyrolysis Products (wt%)		
		Oil/wax	Char	Gas
Catalytic	700			
PKS		49.7	12.7	37.6
EFB		53.5	19	27.5
SCB		36.5	12.5	51
RSSK		56.5	13.3	30.2
RSS		55.6	17.1	27.3
	800			
PKS		58.2	14.6	27.2
EFB		62.6	8.4	29
SCB		48.75	4.25	47
RSSK		55.3	10.9	33.8
RSS		62.29	9.7	27.4
Non-catalytic	700			
PKS		41.5	28.1	30.4
EFB		34.1	21.9	44
SCB		31	53.5	15.5
RSSK		36.6	24.47	38.93
RSS		47.13	26.87	26
	800			

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PKS		45.8	27	27
EFB		21.5	22.6	55.9
SCB		38.25	14.75	47
RSSK		44.07	23.13	32.8
RSS		53.87	15.07	31.07

With the ex-situ catalytic pyrolysis with Al-MCM-41 catalyst at 700°C, the trend of the pyrolysis gas produced as compared with the non-catalytic pyrolysis were distinctive, the pyrolysis gas produced in general was enhanced by the Al-MCM-41 as for PKS, SCB and RSS there were notable increase from 30.4wt%, 15.5wt% and 26wt% to 37.6wt%, 51wt%, and 27.3wt%, while the other biomass sample like EFB and RSSK showed a reduction in their general pyrolysis gas production at this this pyrolysis temperature with the enhancement of Al-MCM-41 catalyst as from 44wt% and 38.93wt% to 27.5wt% and 30.2wt% respectively, while there were some variation and notable reduction or slight increase in either oil/wax, and char production as shown in the Table 3 above. When the pyrolysis temperature was elevated to 800°C, with the same pyrolysis operational parameter as for the pyrolytic temperature of 700°C, the general gas production of PKS and RSSK were observed to have a slight increase in the pyrolysis gas formation at 800°C when Al-MCM-41 catalysts was used to enhance the pyrolysis process from 27wt% and 32.8wt% to 27.2wt% and 33.8wt%, comparing the result with that obtained at 700°C with or without catalyst there was a reduction in the general gas production at 800°C when Al-MCM-41 was used as catalyst. While EFB, SCB, and RSS showed a decrease in pyrolysis gas production from 55.9wt%, 47wt%, and 31.07wt% to 47wt%, 33.8wt%, and 27.4wt%, as represented in the Fig. 4 (C)(D) below. The outcome was not in confirmation with what was stated by Caballero et al [50] even with or without the enhancement with a catalyst. when he experimented with almond shell, the gas production increased with increase in temperature, this pyrolytic behaviour is controlled by different biomass elemental composition that makes up its components, i.e., cellulose, hemicellulose, and lignin. Where the decomposition of this component can take place at lower temperature for some biomass, and the pyrolysis gases go into secondary reactions such as re-polymerization at elevated temperatures. And the pyrolytic behaviour when Al-MCM-41 catalyst is attributed to acid sites present in an Al-MCM-41 catalytic material can be of both Bronsted and Lewis type, each of them participating in the biomass pyrolysis via different mechanisms. While it was noted that Al-MCM-41 greatly improved both gas and hydrogen production of PKS yield compared to other catalyst tested, with a structural collapse at 700°C [41], it was also noted that Al-MCM-41 materials exhibit relatively low hydrothermal stability compared to zeolites [4], inhibiting their use in high-temperature processes in the presence of steam.

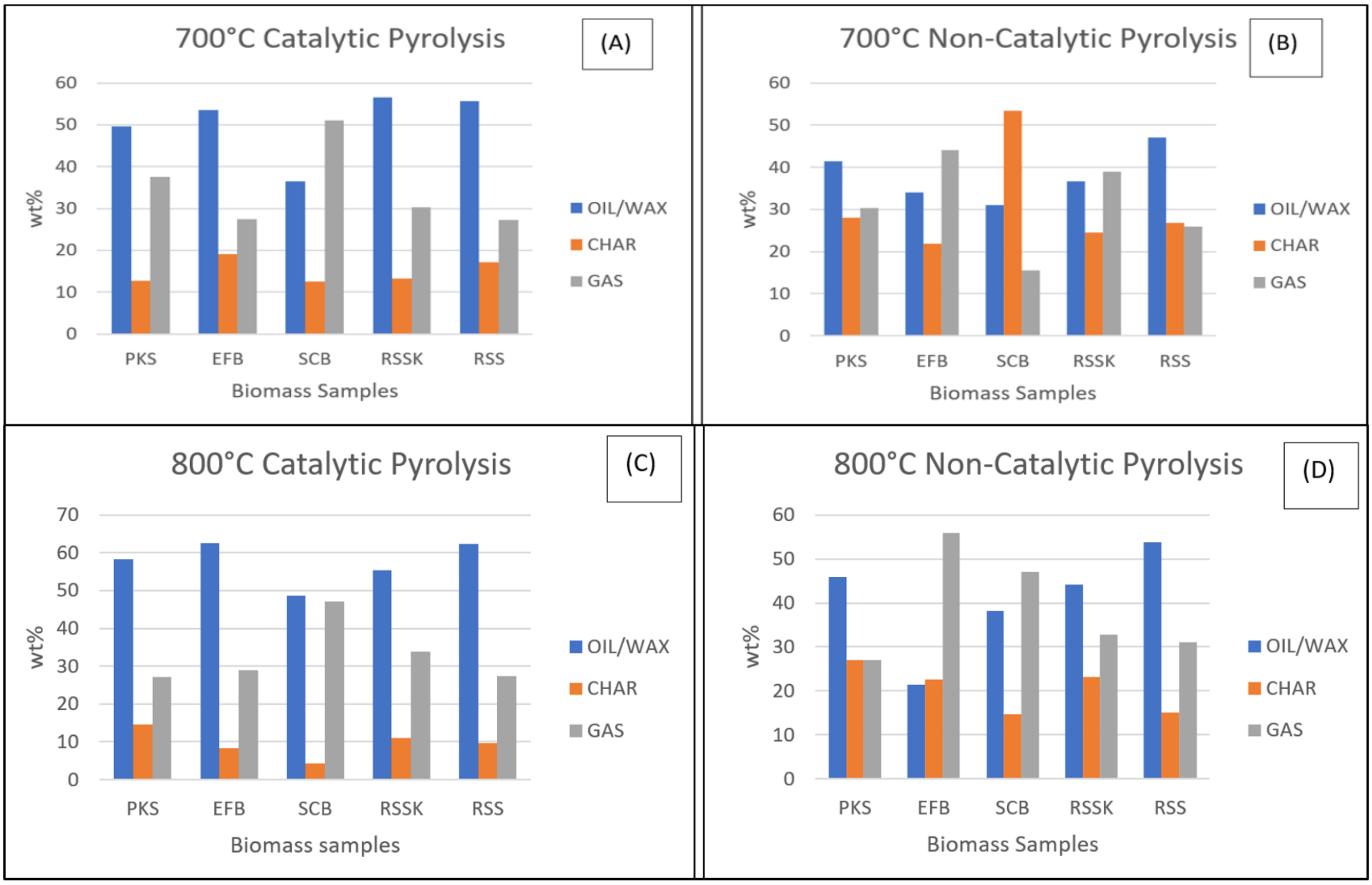

Fig 5 (A) 700°C Catalytic Pyrolysis Results. (B) 700°C Non Catalytic Pyrolysis Results. (C) 800°C Catalytic Pyrolysis Results. (D) 800°C Non Catalytic Pyrolysis Results.

➢ *Pyrolysis Gas Analysis*

pyrolysis gas was analysis to determine the individual gaseous component with CO, CO_2, H_2, CH_4, C_nH_n, and C_2H_4 as major component noted, with its percentage composition in the gaseous pyrolysis product obtained as represented in Table 4, H_2 is our main gaseous component with CO, CO_2, CH_4, C_nH_n, and C_2H_4 as co-component of the pyrolysis Gas.

Table 4 Pyrolysis Gas Analysis Results

Biomass Sample	**Pyrolysis Temp(°C)**	**Gas yield (wt%)**	**Gas Composition in vol%**					
			CO	**CO2**	**H_2**	**CH4**	**CnHn**	**C2H4**
Catalytic	**700**							
PKS		37.6	19.3	25.32	33.07	8.74	1.36	12.38
EFB		27.5	14.53	22.89	41.51	8.01	1.57	11.5
SCB		51	10.41	18.07	50.21	6.64	2.02	12.65
RSSK		30.2	12.19	22.08	32.15	14.25	6.52	12.81
RSS		27.3	23.27	23.88	24.65	15.02	2.52	10.67
	800							
PKS		27.2	25.12	20.69	31.1	12.06	2	9
EFB		29	17.16	19.31	40.55	10.36	1.78	10.83
SCB		47	12.79	15.76	49.84	6.79	1.91	12.9
RSSK		33.8	16.96	22.13	30.23	13.27	4.71	12.71
RSS		27.4	22.7	18.59	31.91	15.4	2.35	9.05
Non-Catalytic	**700**							
PKS		30.4	14.87	22.86	42.51	7.67	0.95	11.13
EFB		44	11.8	27.26	38.61	8.44	3.04	10.85
SCB		15.5	8.21	25.18	46	4.91	1.27	14.44
RSSK		38.93	13.65	20.75	32.24	14.66	5.56	13.14
RSS		26	20.1	20.9	28.33	15.59	2.95	12.13
	800							
PKS		27	21.33	22.31	33.37	10.87	1.51	10.61
EFB		55.9	14.18	19.37	47.17	7.76	1.2	10.31
SCB		47	13.93	18.44	45.84	8.69	1.38	11.72
RSSK		32.8	16.04	15.27	31.59	16.72	4.82	15.56
RSS		26	19.16	18.96	36.47	13.68	2	9.73

The hydrogen content varies across different biomass samples, from Table 4 above, the hydrogen content for PKS for the non-catalytic pyrolysis at 700°C was 42.51vol%, and at 800°C there was a slight drop to 33.37vol%, for the catalytic pyrolysis at 700°C the hydrogen content was 33.07vol% with similar drop in the hydrogen production at 800°C as 31.1vol%. comparing this outcome observed with PKS with EFB when pyrolyzed without the use of Al-MCM-41 as catalyst at 700°C, the content of hydrogen was 38.61vol%, with a slight increase in the hydrogen to 47.17vol% when the pyrolysis temperature was increased to 800°C, when Al-MCM-41 was introduced into the pyrolysis layer as an ex-situ catalyst at pyrolysis temperature of 700°C and 800°C, the hydrogen content was 41.5vol% and 40.55vol% respectively showing a slight fall in the hydrogen yield when the catalyst was introduced and the pyrolysis temperature increased to 800°C. The analysis of SCB pyrolysis gas at 700°C and 800°C without the use of the catalyst and the hydrogen contents were 46vol% and 45.84vol% respectively, showing a fall in the hydrogen content with increase in pyrolysis temperature. RSSK, RSS when pyrolyzed without a catalyst at the pyrolysis temperature of 700°C and 800°C, there was a rise in hydrogen content for RSS from 28.33vol% to 36.47vol% while RSSK had a drop from 32.24vol% to 31.59vol%, when Al-MCM-41 catalyst was used at the same pyrolysis temperature of 700°C and 800°C, RSS still had an increase in the hydrogen content from 24.65vol% to 31.91vol% while RSSK still had a drop from 32.15vol% to 30.23vol%, details discussion will be done in the next section and Fig.5(B)(D) show the gas component distribution of the individual biomass samples for both the catalytic and non-catalytic pyrolysis and the give pyrolysis temperature of 700°C and 800°C.

➢ *Variation in Hydrogen Production from Biomass Feedstock.*

Mettler et al., state that the variation in hydrogen production experienced from different biomass is attributed to the chemical composition of its main component which can be hemi-cellulose, cellulose, and lignin, hydrogen depends on the type of biomass feed stock as show in the Fig. 5 below, at the same thermal conditions. Biomass with high lignin content which contains the aromatic rings and O-CH_3 functional group decomposes to produce hydrogen, in addition to lignin breakdown, the large carbonyl content of cellulose results in a substantial CO yield, and the substantial carboxyl content of hemicellulose results in a sizable quantity of CO_2 production.

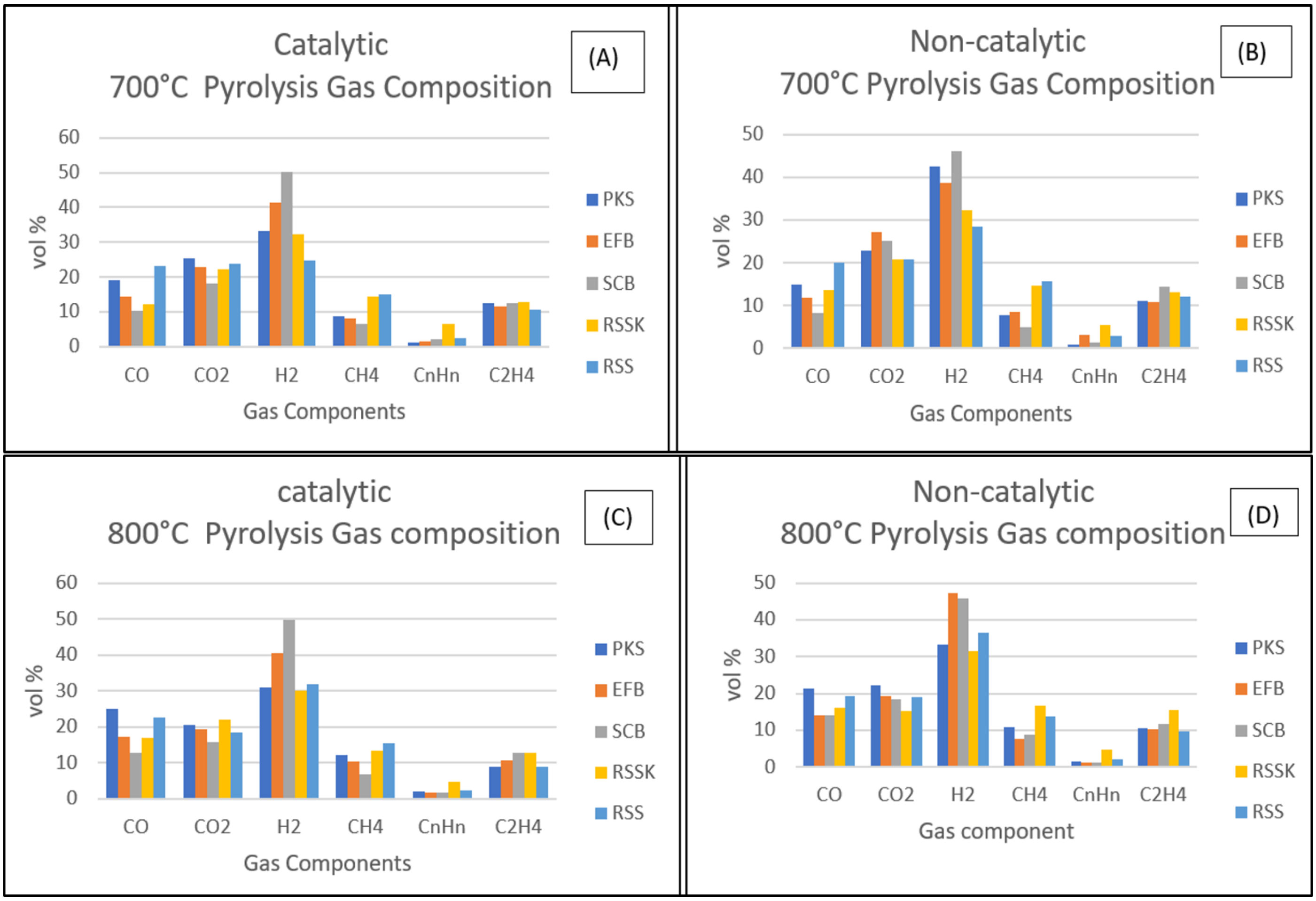

Fig 6 (A) 700°C Catalytic Pyrolysis Gas Results. (B) 700°C Non Catalytic Pyrolysis Gas Results. (C) 800°C Catalytic Pyrolysis Gas Results. (D) 800°C Non Catalytic Pyrolysis Gas Results.

Pyrolysis gas from biomass samples showed a variation in the percentage of hydrogen as SCB showed a higher percentage of 46wt%, PKS 42.3vol%, EFB 38.61vol%, RSSK 32.24vol% and the least RSS 28.33vol%, showing SCB contains more of lignin than cellulose or hemi-cellulose and extractives, than PKS, EFB, RSSK, and RSS as their variation in percentage of hydrogen indicates. Similarly reported by, Ioannidou *et al., biomass with more extractive and lignin produce more of hydrogen gas. This variation can as well be related to the moisture content of the biomass sample as started by wright et al., and Guoxin et al., moisture content of 7% is suitable for pyrolysis process and moisture content enhances secondary reaction of water gas shift (WGS) which further produces more hydrogen.*

- ➢ *Catalyst Effect of Hydrogen Yield.*

From Fig. 5 (A)(C) production of hydrogen from the biomass sample when Al-MCM-41 was used as a catalyst at 700°C showed that the highest hydrogen yield for all the biomass sample studied except for RSS which showed a different trend with a low hydrogen percentage at 700°C compared to 800°C. The increase is related to the activity strength and selectivity nature of the catalyst which depend on acid sites, but also the nature of the bronsted or lewis acid sites for the catalytic cracking, decarbonization, dehydration, isomerization, oligomerization-aromatization reactions taking place in catalytic pyrolysis processes. It can be well said that Al-MCM-41 is not suitable for the pyrolysis of biomass at 800°C, as we can observe the decrease in the percentage of hydrogen in the pyrolysis gas at 800°C, except for RSS which had an increase which can be said to be associated with the thermal decomposition of the lignin at high pyrolysis temperature. From Demirbas et al., [19] the inherent chemical mineral in the biomass feedstock leads to pyrolytic chemical kinetics, the decrease in the hydrogen at 800°C can be attributed to this and as said by Uddin et al, [47] catalyst dose as well can be a major setback which could be a reason for the hydrogen gas percentage decrease.

- ➢ *Effect of Pyrolysis Temperature on Hydrogen Yield.*

It has been reported by a lot of researchers that the rate of gas production increases with increase in the pyrolysis temperature, because of the devolatilization, thermal decomposition of the biomass sample associated with the elevation of pyrolysis temperature. As stated by yang et al., [38] at higher temperatures during the thermolytic degradation of lignin, weaker bonds are broken at lower temperatures. In terms of structure, lignin has a large concentration of aromatic rings and O-CH_3 functional groups at higher temperatures (>500°C), H_2 is released from the breaking and rearrangement of the aromatic bonds of C═C and C-H, while CH_4 is produced by the comparatively weak link of the Methoxyl group (O-CH_3) [38]. In addition to lignin breakdown, the enormous carbonyl content of cellulose results in a substantial CO yield, and the substantial carboxyl content of hemicellulose results in a sizable quantity of CO_2 production. There was a clear variation in the hydrogen production as shown in Fig. 5 (B)(D), there was an increase in hydrogen for EFB from 38.61vol% to 47.17vol% as the pyrolysis temperature was increased as stated by Yang et al.,[38] RSS show similar trend when the pyrolysis temperature is increased from 700°C to 800°C the hydrogen production increased from 28.33vol% to 36.47vol% which is because of the thermal decomposition of the biomass lignin at high temperature which contains the aromatic rings, and O-CH_3 group. Meanwhile PKS, SCB, and RSSK showed a different trend from this which is related to secondary pyrolysis reactions from the pyrolysis gas formed. PKS at pyrolysis temperature of 700°C produced 14.87vol% CO, 22.86vol% CO_2.42.51vol% H_2, 7.67vol% CH_4, 0.95vol% C_nH_n, 11.13vol% C_2H_4, at 800°C there was a drop in H_2 to 33.37vol% as a result of re-polymerisation and reverse WGS leading to the increase in CO to 21.33vol%, slight fall in CO_2 and an increase in CH_4 and C_nH_n as shown in Fig. 5 (C)(D) similar trend was observed for SCB and RSSK which is indicative to be secondary pyrolysis reactions such as reverse water gas shift and re-polymerisation.

IV. CONCLUSION

From the non-catalytic and ex-situ catalytic non-isothermal pyrolytic investigation of the hydrogen potential of the following biomass samples PKS, EFB, SCB, RSSK, and RSS the following conclusion were drawn, there was no general trend pattern in the general pyrolysis hydrogen production with respect to pyrolysis temperature or catalyst, the general hydrogen production from the various biomass is dependent on the biomass which is pyrolyzed, as the biomass samples, showed different variation in there percentage volume of produced, with respect to either increasing pyrolysis temperature from 700-800°C, or with the enhancement of Al-MCM-41 as catalyst, but generally hydrogen production is more suitable at 700°C, as it is observed that all biomass percentage volume of the gas at this temperature are encouraging. The structural collapse of the catalyst had a negative effect on the hydrogen production at 800°C due to its hydrothermal instability at high temperatures. From the biomass samples experimented on SCB and EFB showed to be promising feedstock with their Hydrogen yield at all the process conditions remarkably above all other samples on the value of 47.17vol% for EFB at 800°C non catalytic pyrolysis, and 50.21vol% for SCB at 700°C catalytic pyrolysis.

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