

Production of Hydrogen and Methane Rich Gas by Stepped Pyrolysis of Biomass and Its Utilization in I.C. Engines.

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Abstract

Automobile industries are majorly based on petroleum-based fuels like petrol and diesel that create environmental hazards, a high carbon footprint, and creating serious health issues. To reduce the problem associated with fossil fuel utilization, the world is focusing on CNG-based energy solutions and developing the infrastructures for CNG. There is a need to transfer towards hydrogen fuel-based infrastructure in near future. The current focus to introduce a fraction of hydrogen with CNG in the existing fuel system is initiated here. Therefore, the utilization of biomass is taken into account for the production of high hydrogen-containing fuel to cut down the carbon footprint and environmental issues. Biomass residues such as Sun hemp, Pigeon pea, Mustard stem, Wheat straw, Dhaincha, and Vantulsi were slow pyrolyzed in a stepped manner to produce a hydrogen-rich clean fuel. Product gas (hydrogen-rich CNG i.e., H-CNG) obtain by this pyrolysis process contains almost 40%-55% hydrogen and 10%-25% methane balanced with oxides of carbon depending on different biomass feedstocks. This study is also focused on the performance of 2kva HONDA Genset in terms of its running duration when obtained Bio-HCNG gas is used as fuel and a correlation is also developed between H_2 , CH_4 , ΔH (Change in Hydrogen wt. % during the process) and D (Duration for which Genset will run in minutes) i.e., $D = -6.25 + 0.996\Delta H + 0.3889CG$ for model 1 & $D = -9.20 + 0.090\Delta H + 0.6099H_2 + 0.1893CH_4$ for model 2.

1. Introduction

Energy is the lifeblood of human society; imagining the world without a continuous supply of energy is impossible; currently, the major portion of energy demand fulfills by fossil fuels. However, the continuous supply of fossil fuels is becoming a challenge in recent years resulting in a continuous price rise (Edwards et al. 2007; Pawar et al. 2013). Further, the exhausts resulting from the combustion of these fossil fuels are very dangerous, for human beings and the environment leaving a huge carbon footprint behind (Reşitoğlu et al. 2015). The inter-related problems of energy and the environment are one of the biggest challenges the world is facing today. Energy sustainability and the decreasing carbon footprint is the biggest challenge, that must be attained and rectified in an accelerated way. The thermochemical conversion route is a good solution to use biomass energy in the technical application (Chen et al. 2003) and to overcome the environmental pollution due to exhaust of internal combustion (IC) engines and industries, the world is moving towards CNG and HCNG (a mixture of Hydrogen and CNG) (Lang et al. 2011; Jiang et al. 2012; Abuadala and Dincer 2012).

Hydrogen has many positive characteristics while using in internal combustion engines like better flammability, improve the performance of engines due to these reasons HCNG has more advantages over CNG. (Moreno et al. 2012). Emission (Exhaust) of the hydrogen fuel system is water vapor which does not have any adverse environmental effect, so it can be adopted as a future fuel because of its different characteristics like rapid burning speed, no emissions of greenhouse gases, higher energy density, low minimum ignition energy, and a very high octane number (Ingersoll 1996; Mu et al. 2006; Balat and Kirtay 2010; Luque et al. 2011).

The immediate replacement of fossil fuel systems with a pure hydrogen system is a gigantic task and must be attained in a stepwise manner in the near future. One of the alternatives is to replace a proportion of hydrogen with methane in a stepwise manner so that smooth transfer from petroleum-based technology to hydrogen-based technology can be done (Nanthagopal et al. 2011). Many conventional and established ways are there to obtain H₂ and CH₄ mixture, but they can only be environment friendly if extracted from renewable energy sources like biomass other than fossil fuels. Hydrogen can be obtained from syngas, methane reforming, and dark fermentation processes whose main gaseous component is hydrogen. However, methane can be obtained from the anaerobic digestion process (Liu et al. 2018).

Agricultural or forestry wastes can be considered as a potential source of renewable energy. The estimation of Bio-waste produced each year is about 120 billion tons, the energy capacity of which is five times the total current energy consumption in the world, is formed each year using photosynthesis, only 1% of the total energy capacity has been used as energy, which can supply 14% of total energy consumption in the world, however, most of the biomass waste goes under bacterial decomposition or combustion which results in GHG emissions into the atmosphere (Wengjie Wang).

In the literature (Luo et al. 2011), (David et al. 2019) it is reported that researchers follow a two-stage anaerobic digestion process to get Bio-HCNG in different proportions. Sometimes hydrogen and methane are produced separately, and to get HCNG different appropriate proportion of hydrogen and methane is mixed. The main routes to produce hydrogen from agricultural and forestry residues are namely thermo-chemical and biochemical processes. Thermo-chemical routes can be adopted for continuous and rapid utilization of biomass. Thermo-chemical routes are gasification (Chang et al. 2011), pyrolysis of bio-oil (Xu et al. 2010), steam reforming of biomass-derived higher alkanes and alcohols (Seyedeyn-Azad et al. 2011), and aqueous phase reforming of oxygenated hydrocarbons (Chang et al.) The main route of getting methane from biowastes is anaerobic digestion.

Gasification is a process where hydrocarbons undergo partial combustion and the main product is synthesis gas. Slow pyrolysis is a process in which bio-organic materials undergo thermal degradation in a completely oxygen-free atmosphere. At the end of biomass pyrolysis one can get solid (biochar), liquid (bio-oil), and bio-gas [a mixture of H₂, CO, CH₄, CO₂, and lower hydrocarbon of (C₁ – C₃)] (Karagöz 2009). Biomass structures also define the proportion of different pyrolytic products and the composition of the gaseous product. The heating rate also changes the composition of different pyrolytic products (Debdoubi et al. 2006). As lignin is responsible for high H₂ and CH₄ formation, hemicellulose is responsible for the high CO₂ emission, and cellulose is responsible for high CO production (Hlavsová et al. 2014). The content of hydrogen (H₂) is dependent on the temperature of pyrolysis and increases as the latter increases, (Li et al. 2004; Domínguez et al. 2007; Dufour et al. 2009; Neves et al. 2011). The conversion of raw biomass to the gaseous product during the pyrolysis process is high (Zhao et al. 2001). Unfortunately, the pyrolysis process has been adopted to produce liquid fuel from biomass, not a gaseous fuel. The gas yield from conventional pyrolysis process is very low, generally, less than 40 by

wt.% and besides corrosion is a serious issue to downstream equipment, like a gas turbine/engine, caused by the high content of higher hydrocarbons vapor (Tar) contained in the gas phase, these are the reasons which supports the above approach (Buhre and Andries, 2000). However, pyrolysis gas is more advantageous, has a higher heating value in compared with conventional gasification gas, and therefore can be applied well to the downstream gas turbine/combustion engines to generate power or used for other civil purposes (Chen et al. 2003). This work indicates the potentiality and utilization of obtained pyrolytic gases for different purposes from different biomasses.

The final goal of the present work is to compare the composition, the process, and yield of gaseous products w.r.t. temperature during the stepped pyrolysis of different agricultural residues in a fixed bed reactor. It also emphasizes the potential utilization in downstream equipment of gases evolved during the pyrolysis process in a 2kva HONDA petrol Genset. This paper explores the method to produce high yield hydrogen and methane or HCNG in a single process from different agricultural waste.

2. Material And Methods

2.1 Sample collection and Preparation

The raw material used for this present study were agricultural waste like Pigeon pea, sun hemp, mustard stem, wheat straw, dhaincha (*sesbania bispinosas*), and forestry waste like vantulsi (*Ocimum Gratissimum*) were used as biomass feed. These samples are abbreviated as PP, SH, MS, WS, DH, and VT respectively. These samples were collected from the village area of Varanasi and the forestry area of the Mirzapur district of Uttar Pradesh, India. The biomass samples were first dried in a normal atmosphere for 5-10 days and then chopped and milled in the size range of <2 inches. Then the sample was oven-dried at 105°C for 24 hours. The biomass samples were prepared in the size range of -18#+72# and utilized for different analyses.

2.2 Reactor Setup and testing: Reactor design/set-up and attached testing facility layout are given below Figure 1. shows the flow chart of the test reactor.

The biomass conversion was performed under anaerobic conditions in our designed pyrolysis reactor. The reactor set up consists of a quartz reactor, a tripod sample holder is there which holds the sample inside the heating zone, and a furnace with a PID controller, in addition to this there is a toggle valve at the bottom of the reactor which facilitates the flow of nitrogen inside the reactor to maintain the oxygen-free environment. Setup is also provided with an electric resistance furnace for indirect heating the charge and a pressure regulator are there to show and control the pressure inside the reactor. A condenser is also attached at the outlet of the reactor to separate condensable (Bio-oil + water) from non-condensable gas. Non-condensable gas is collected in a gas collector, and intermediate gas sampling is carried out to get the composition of product gas with temperature.

2.3 Experimental Procedure

Pyrolysis is the process in which biomass decomposes into valuable cleaner fuel under anaerobic conditions at elevated temperatures in a vertical reactor. In this process, the biomass samples of <2 inches size are fed into the reactor. The test sample was kept in the reactor and N₂ gas was purged inside the reactor to maintain an inert environment. Product gases were analyzed by gas chromatography (G.C.) (MM TECH, M 2012) equipped with a molecular sieve pack column and thermal conductivity detector (TCD). The analysis was carried out using (N 2000) software attached with the instrument. Once the inert atmosphere is achieved in the reactor, nitrogen purging is stopped and heating of the reactor starts till the temperature of the reactor reaches up to 150°C @ 15°C/minute. Once the pressure inside the reactor reached up to 1.1bar at 150°C, the valve is opened to remove the exhaust that mostly contains moisture. Valve closed and again further N₂ is purged in the reactor to maintain an inert atmosphere. Heating the reactor resumed from 150°C to 800°C @ 25°C/minute. At approximately, 400°C when the pressure reaches 1.2 bar, the valve was opened for sampling to examined the gas mixture through G.C. A very high CO₂ was detected at this point. The valve was opened to release the exhaust and maintain the atmospheric pressure of the reactor. The valve was closed again. When the temperature reaches 600°C and the pressure was 1.2 bar, the valve was opened again to examine gas content. The formation of H₂, CH₄, and CO₂ wherever very little of CO was detected at this moment. After that, samples were taken at 700°C, 800°C, and at 5 minutes after reaching 800°C at a pressure close to 1.3 bar. The concentration of H₂, CH₄ was found to increase with temperature. Thus, during the pyrolysis process, the biomass was converted into valuable H₂ and CH₄ (the major component). During the study, the product exhaust gas mixture was passed through condensers to make the gas-liquid or tar free.

3. Results And Discussion

3.1 Proximate analysis of biomass samples

Proximate analysis of the biomass samples was carried out as per ASTM standard E871-82, E1755-01, and E872-82 (Suman and Gautam 2017), biomass char was also prepared following ASTM standards D1762-84 (Suman and Gautam 2017), the result of proximate analysis is given in Table 1.

Table 1: Proximate analysis and GCV of biomass and char (*db).

Sample Name	Volatile Matter Wt.%		Fixed Carbon Wt.%		Ash Content Wt.%		Gross Calorific Value (cal./gm)	
	Raw	Char	Raw	Char	Raw	Char	Raw	Char
SH	78.46	9.57	10.4	80.88	11.13	9.54	4143	6431
PP	71.65	7.8	15.73	79.51	12.61	12.68	4454	6264
MS	78.37	16.96	12.60	64.50	9.02	18.52	4264	5994
WS	70.48	8.12	15.92	64.62	13.58	27.25	4081	5456
VT	77.69	15.64	17.5	72.13	4.81	12.22	3941	6081
DH	77.61	11.05	17.47	83.26	4.9	5.67	4184	6899

* dry basis

The above Table 1. contains a dry basis proximate analysis of different biomass and their respective chars. All biomass samples having high volatile matters; sun hemp, mustard stem, vantulsi, and dhaincha are having about 78% volatile matter. In char, we can see the extent of the evolution of volatile matter @ 800°C (VM) into valuable gases. The highest evolution of VM is taken place in sun hemp (nearly 68%), followed by wheat straw (nearly 62%) and dhaicha (nearly 66%). High VM is desired in the present study. After stepped pyrolysis (a series of devolatilization reactions) that progressively leave behind an increasingly condensed carbonaceous matrix, which is nothing but fixed carbon and ash, higher fixed carbon in bio-char indicates higher energy value for the respective char (Ronsse et al. 2013). Dhaicha, Sun hemp, and Pigeon pea chars having about 83%-79% of fixed carbon. Lower the ash content better will be the fuel quality and at the same time lesser problematic in operations. The mustard stem char contains 18.5% of ash and the wheat straw char has 27.25 % ash content, which is higher among all the above samples.

Higher the fixed carbon in biomass higher will the bio-char yield while higher volatile matter and ash content in biomass results in lesser bio-char yield (Leonel JR Nunes, Joao Carlos De Oliveira Matias). Therefore, it can be concluded that greater volatile content leads to higher gas production rather than the solid phase (Nunes et al. 2018).

3.2 Elemental analysis

The elemental (C, H, N, S, and O) analysis of these biomass materials was analyzed by Vario elemental analyzer (IIT (ISM) Dhanbad) using standard ASTM E777, 778, and 775 (Hernandez-Mena et al. 2014). This gives the information only about (C, H, N, and S). The below C, H, N, S, and O are calculated on ash and moisture-free basis. The result of elemental analysis is shown in Table 2.

Table 2: Elemental analysis (wt.%, dry basis).

S. NO.	Sample name	C (%)		H (%)		N (%)		S (%)		O (%)	
		Raw	Char	Raw	Char	Raw	Char	Raw	Char	Raw	Char
1.	SH	53.40	93.48	7.59	1.84	2.62	0.86	0.48	0.17	35.91	3.65
2.	PP	56.13	95.42	7.77	1.62	3.19	1.03	0.43	0.09	32.48	1.84
3.	MS	52.93	90.24	7.56	2.47	1.00	1.04	0.20	0.35	38.31	5.90
4.	WS	47.01	92.44	6.93	2.11	1.13	1.15	0.31	0.50	44.60	3.80
5.	VT	48.24	93.15	6.93	2.24	0.68	0.70	0.15	0.17	44.00	3.56
6.	DH	50.99	89.31	7.10	2.49	1.07	0.83	0.23	0.17	40.61	7.19

3.2.1 Carbon & Hydrogen Content:

From Table 2, it is observed that the carbon content in raw biomass samples lies between (47%-56.13%) and in char (89.31% - 95.42%). When a solid fuel (coal, biomass, etc.) is combusted the carbon comes out in the form of CO₂ and as hydrocarbons. CO₂ can be produced from the organic compounds but, if there is carbonate (e.g., calcite–CaCO₃) minerals are present in the sample then it can be liberated from there also ([CSL STYLE ERROR: reference with no printed form.]). This means that the total carbon measurement may include both mineral carbon fraction as well as organic carbon fraction. After pyrolysis processing, the carbon content was increased due to the removal of aromatic hydrocarbons, short and long-chain hydrocarbons, and sulfur (VM) (Muthu Dinesh Kumar and Anand 2019) which is well represented in Table 2.

The hydrogen content in studied raw samples lies in the range of (6.93%-7.77%) and char (1.62% - 2.49%). Hydrogen is the most important element in this investigation that will be responsible for hydrogen production and methane production. Higher the hydrogen content, the better the fuel is. Hydrogen is mainly generated from the condensation of aromatics or alkyl aromatization reaction during pyrolysis at a temperature beyond 400 °C (Liu et al. 2020). Thus, these plants can act as a good source of hydrogen. The difference of hydrogen in raw and in char after pyrolysis processing shows the extent of hydrogen evolution mainly in the form of hydrogen and methane, which is highest in SH and PP. Thus, the high hydrogen-rich fuel can be produced using SH and PP as bio-waste. The C & H content of the sample plays an important role in the combustibility of any biomass (Loison R., Foch P. 1989).

3.2.2 Nitrogen and Sulfur Content:

From table 2, it can be observed that nitrogen content in raw biomass samples lies in the range of (0.68% - 3.19%) and their char lies in the range of (0.70% - 1.15%). The nitrogen content in SH and PP is a little high which is because they are nitrogenous crops. The amount of sulfur present in raw samples of SH, PP, MS, WS, VT, and DH lies in the range of (0.15% - 0.48%) and their char in the range of (0.09% - 0.50%). High sulfur-containing fuel is not suitable for internal combustion engines as well for power production.

The low S & N containing biomass consider as a good fuel because there will be a low formation of sulfur and nitrogen oxides during the thermochemical conversion process (Enweremadu and Ojediran 2004). That is an indication that the biomass samples used in this study will not pollute the atmosphere. The sulfur-containing fuel affects adversely on the metal quality due to its corrosive nature towards metal, because of this reason sulfur-containing fuels are not fit for I.C. engines (Loison R., Foch P. 1989). Therefore, the biomass used in this work can reduce the corrosion severity impact on the equipment use and can reduce the cost for maintenance.

3.2.3 Oxygen Content:

From Table 2, the amount of oxygen present in raw samples is in the range of (32.48% - 44.60%) and their char in the range of (1.84% - 7.19%). Higher oxygen content was found in WS, VT, followed by DH whereas SH and PP have a relatively lower percentage. The thermal decomposition of the oxygen functionality is responsible for the formation of Carbon dioxide and carbon monoxide, which is present in the molecular structure of biomass (Nunes et al. 2018). Thus, for better applicability as a suitable fuel source, the oxygen content and conversion should be less. In the case of SH and PP having lesser oxygen conversion took place, thus making them a better alternative as bio-waste to produce high hydrogen-containing fuel.

3.3 Calorific values:

The combustion of a substance gives energy in the form of heat which can be used for different purposes (the blast furnace, power production, small furnaces, etc.). Biomass consist of volatile matter and fixed carbon as the main source are responsible for high calorific values. Calorific values of different biomass samples were tested in bomb calorimeter [IIT (ISM) Dhanbad] according to (ASTM D4809-00) standard test method (Suman et al. 2017).

The calorific value of raw samples lies in the range of (3941 kcal/kg – 4454 kcal/kg) and their GCV in the range of (5456 kcal/kg – 6899 kcal/gm). well-represented in Table 1. Calorific value is the result of the different combustible elements present in the studied samples like (hydrogen & carbon) majorly. The calorific value also can be calculated by using the below equation developed by Sheng and Azevedo

$$CV \text{ (MJ/kg)} = -1.3675 + 0.3137 \cdot C + 0.7009 \cdot H + 0.0318 \cdot O \dots\dots\dots \text{eq. (1) (Sheng and Azevedo 2005).}$$

From this equation, it is seen that hydrogen is more responsible for calorific value than carbon. so high hydrogen is desirable in a fuel. Raw PP has the highest hydrogen content nearly 8% that eventually visualized in its overall highest calorific value. On the other hand, the calorific values of chars are the result of carbon combustion. The higher the carbon content, the higher will be the calorific values of char. DH char is having a high calorific value of about 6900 kcal/kg, this is the result of a high fixed carbon presence in DH.

3.4 Thermogravimetric analysis:

The ASTM E1131-03 standard method was being followed for TGA by using a computerized NETZSCH SAT 449F3 TG analyzer [IIT (ISM) Dhanbad]. The temperature program used for the TGA shown in [Figure 2](#), starts at room temperature to 105°C and is further allowed to go up to 800°C with an increment rate of 25°C/min in a nitrogenous environment.

The main components of all biomass are lignin, hemicelluloses, cellulose, and extractives. Their concentrations vary in different biomass samples depending on their growth conditions as well as from species to species. These components decompose during pyrolysis and produce different condensable (bio-oil and tar) and non-condensable (gases) parts.

From the [Table 3](#), the whole TGA is divided into 5 zones which interpret the decomposition of each component as below.

Table 3: Volatiles released (wt. %) during biomass pyrolysis in TGA

SAMPLE NAME	MOISTURE ZONE-I <100	Volatiles released (%)				
		Temperature range (°C)				
		ZONE-II 100 – 300	ZONE-III 300-400	ZONE-IV 400-600	ZONE-V >600	TOTAL
SH	15	9	51	5	3	83
PP	12	19	27	11	7	76
MS	10	13	42	9	3	77
WS	11	11	30	10	5	67
DH	10.5	10.5	33	10	9	73
VT	15	26	20	8	6	75

Zone I: <100°C mainly moisture evolution takes place in this zone.

Zone II: 100°C-300°C extractives start decomposing.

Zone III: 300°C-400°C predominantly hemicelluloses decomposition.

Zone IV: 400°C-600°C mainly cellulose and lignin decomposition.

Zone V: >600°C mainly lignin decomposition ([Raveendran et al. 1996](#)).

Oxygen concentration is higher in the case of hemicelluloses and cellulose as compare to lignin, and from the above table, it is evident that at lower temperature hemicelluloses and cellulose decomposed and lignin decomposed at the higher temperature.

3.5 Gas Chromatographic Analysis:

Analysis of the produced gas was done through Gas Chromatography (GC), results of GC for each of the selected biomass samples are shown below. [Tables 4,5,6,7,8, and 9].

*Overall sampling indicates the sample is taken from the gas storage balloon at the end of the process at room temperature.

^{R5}Sample was collected at 800°C after 5 minutes of residence time

Table 4: Volumetric Composition of produced gas during the slow pyrolysis process of Sun Hemp.

Temperature	Volume %			
	H ₂	CH ₄	CO	CO ₂
600°C	7.89	35.03	33.23	23.83
700°C	58.8	24.6	9.8	6.8
800°C	81.34	12.07	6.35	0.22
^{R5} 800°C	71.41	12.21	7.08	9.27
*Overall	57.22	20.09	10.26	12.43

From the Table 4, it is seen that in sun hemp, hydrogen starts coming out about 600°C, the evolution of carbon mono-oxide and carbon- dioxide is higher at lower temperatures. Hydrogen content is increasing as the temperature increases on the other hand carbon monoxide and carbon-dioxide decrease. Methane is higher at starting and it started decreasing at 800°C. The total composition of product gas contains nearly 57% of hydrogen, 20% of methane, 10.26% of carbon monoxide, and 12.43% of carbon dioxide.

Table 5: Volumetric Composition of produced gas during the slow pyrolysis process of Pigeon Pea.

Temperature	Volume %			
	H ₂	CH ₄	CO	CO ₂
600°C	12.8	54.2	16.8	16.2
700°C	50.8	32.2	11.4	5.6
800°C	47.08	30.5	10.3	12.12
R ⁵ 800°C	52.49	31.3	7.14	9.07
*Overall	52.45	18.82	11.50	15.85

As evident from Table 5, at 600°C, the hydrogen is 12.8%, methane is 54.2%, carbon mono-oxide 16.8% and CO₂ is 16.2%. At 700°C, hydrogen increases, and the CH₄ also decreases but not much, on the other hand, the concentration of CO and CO₂ decreases significantly. Gas composition evolving at further temperatures like at 800°C and 5 minutes after reaching 800°C are almost the same as previously. The overall composition obtained from the product gas of pigeon pea was found close to 52.45 % H₂, 18.82% CH₄, 11.50% CO and approximately 16% CO₂ and it is better than coal gas. H₂ composition increases from top to bottom w.r.t the increase in temperature. This may be because of the decomposition of lignin at higher temperatures which restricts the decomposition of bonds at lower temperatures.

Table 6: Volumetric Composition of produced gas during the slow pyrolysis process of Mustard Stem

Temperature	Volume %			
	H ₂	CH ₄	CO	CO ₂
600°C	23.6	5.4	35.9	35.1
700°C	29.05	23.39	23.33	18.21
800°C	51.3	23.03	12.62	13.05
R ⁵ 800°C	55.08	30.02	8.88	6.02
*Overall	52.53	25.65	4.03	17.39

From the Table 6, it is seen that the evolution of H₂ is significant at 600°C its concentration is about 23.6%, methane concentration is very less like about 5%, CO, and CO₂ are high in concentration. At higher temperatures concentration of H₂ increases and CH₄ also increases but CO and CO₂ decrease. The final composition of H₂ is about 52 %, CH₄ nearly 25%, CO is about 4% and CO₂ is about 17%.

Table 7: Volumetric Composition of produced gas during the slow pyrolysis process of Wheat Straw

Temperature	Volume %			
	H ₂	CH ₄	CO	CO ₂
600°C	27.9	43.6	12.8	14.9
700°C	67.03	16.4	2.49	13.98
800°C	77.91	13.3	2.16	6.55
R ⁵ 800°C	76.3	18.5	1.8	3.26
*Overall	51.29	19.9	9.98	19.83

From the [Table 7](#), we can see that the production of H₂ and CH₄ starts at a relatively lower temperature. The concentration of H₂ is 27%, CH₄ is 43%, CO is 12% and CO₂ is 15% at 600°C. At higher temperatures like at 700°C, the concentration of hydrogen increases significantly and the concentration of methane, carbon mono-oxide, and carbon dioxide are decreasing. At further temperatures, the concentration of evolving gas is almost the same as at 700°C. The final gas composition of gas produced during the pyrolysis of wheat straw is H₂ 51%, CH₄ is about 20%, CO is about 10% and 19% CO₂.

Table 8: Volumetric Composition of produced gas during the slow pyrolysis process of Dhaicha

Temperature	Volume %			
	H ₂	CH ₄	CO	CO ₂
600°C	29.39	27.27	12.39	20.07
700°C	53.57	27.07	2.38	14.41
800°C	60.08	25.59	3.85	9.99
R ⁵ 800°C	67.2	19.5	4.15	9.15
*Overall	49.95	20.56	9.1	20.39

[Table 8](#), shows that the concentration of H₂ and CH₄ at 600°C is in a significant amount, and CO, CO₂ are relatively low. At higher temperatures, H₂ concentration is increasing from 29% to 67 % but in the case of methane, it is almost the same at a higher temperature to about 25%. The concentration of CO and CO₂ is decreasing to 9%. The overall composition of H₂ is 49%, CH₄ is 20%, CO is 9% and CO₂ is 20%.

Table 9: Volumetric Composition of produced gas during the slow pyrolysis process of Vantulasi

Temperature	Volume %			
	H ₂	CH ₄	CO	CO ₂
600°C	34.6	7.6	1.33	55.97
700°C	52.8	19.5	9.2	28.5
800°C	58.6	19.7	9.2	12.12
R ⁵ 800°C	60.34	22.83	3.98	12.35
*Overall	38.12	8.46	1.25	51.8

From the Table 9, we can see that hydrogen content is 34.6%, methane is 7%, carbon mono-oxide is very less than 1.33% and CO₂ is 55% which is high in concentration at 600°C. At higher temperatures yielding of hydrogen, methane, carbon monoxide, and carbon-dioxide is increasing but carbon dioxide decreases. The overall volumetric concentration of the gaseous sample is H₂ 38%, methane 8%, carbon mono-oxide 1.25%, and very high carbon dioxide 51.8%.

4. Application of BIO-HCNG in a 2kva petrol Genset for power production

As we can see in Figure 3, that the color of the flame is very light blue which indicates the gaseous mixture is rich in hydrogen and methane which is highly suitable for the internal combustion engines for the transportation sector. ([CSL STYLE ERROR: reference with no printed form.]

A 2kva HONDA petrol Genset is modified for gaseous fuel to utilize the available hydrogen-rich mixture of gaseous fuel from the process. Genset was functioning from the non-condensable gases of the pyrolysis process. As the mixture was hydrogen-rich the Genset creates lesser sound and shows smooth functioning as compared to gasoline fuel. The generator was subjected to full load (1 exhaust of 1kva, 1 cooler of 0.2kva, 1 pump of 0.7kva) at a time.

Table 10, shows the duration of electricity produced using different biomass samples as input (2.5kg biomass) to the reactor and using hydrogen-rich mixture gas as fuel to the generator.

Table 10: Running duration of Genset (in minutes) using produced H₂ rich mixture of gases from different biomass samples.

Sample Name	SH	PP	MS	WS	DH	VT
Duration (minute)	30	27	28	26	26	16

5. Mathematical Analysis

Mathematical analysis is done to obtain correlations MODEL-1, between running time of Genset to net hydrogen (from raw to char composition) as well as the cumulative percentage of Hydrogen percent and

Methane percent, and MODEL-2 between running time of Genset to net Hydrogen (from raw to char composition) as well as hydrogen percent, and Methane percent of product gas. The derived model is shown in Table 11.

Data from Table 2, Tables 4 to 9, and Table 10 are used to develop a correlation for estimating the running duration of 2 kva Genset. The correlation was developed using the least square regression analysis in MINITAB 19.2020 software. Some assumptions like constant heating rate and were made to obtain the relation.

Table 11: Derived MODEL-1 and MODEL-2 based on different parameters (ΔH , CG, H₂, and CH₄).

SOURCE	MODEL-1			MODEL-2		
	P-VALUE	V.I.F.	Regression Eq.	P-VALUE	V.I.F.	Regression Eq.
Regression	0.002	-		0.004	-	
ΔH	0.186	1.32		0.851	2.62	D = -9.20 + 0.090 ΔH + 0.6099H ₂ + 0.1893CH ₄
CG	0.001	1.32	D = -6.25 + 0.996 ΔH + 0.3889CG	-	-	
H ₂	-	-		0.015	7.72	
CH ₄	-	-		0.107	4.92	

i.e.,

ΔH = Change in hydrogen wt.% during the pyrolysis process.

CG = Cumulative volumetric gas % of (H₂ & CH₄) obtained from Gas Chromatography.

H₂ = Volumetric gas % of hydrogen reported in Gas Chromatography.

CH₄ = Volumetric gas % of methane reported in Gas Chromatography.

5.1 Model Summary

From the regression analysis, I get R-square value = 0.985 for model-1 and R-square = 0.997 for Model-2. As the value of R-square is greater than 0.95 then it shows a good correlation between dependent and independent variables (Gautam 2017).

5.2 Analysis of variance.

If the value of P indicates the effect of the independent variable on the dependent variable, the lower the p-value higher the impact on the dependent variable. From the below table 10, we can see in model-1 that the P-value for both independent variables is very close to zero, which means both independent variables

contribute significantly in the regression eq.1 obtained from the model-1. But in the case of model-2, the value of ΔH having a lesser effect on model-2 as compare to H_2 and CH_4 .

When we are looking for VIF (variance inflation factor) it should be closer to 1. Higher the value indicates the multicollinearity, in the case of MODEL-1 it is 1.32 for both the variable which is very close to 1 (desirable) but in the case of MODEL-2, it is 2.62, 7.72, and 4.92 for different variables which are very high (undesirable).

5.2 Residual plots for Duration

From the below **Figure 4(a)** it is seen that the data are very close to the fitted line, and the line represents the equation of regression. From **Figure 4(b)**, the histogram shows the data are normally distributed which means the regression equation holds for the value beyond the table. In the case of **Figure 4(aç)** the data shows relatively more deviation from fitted line, and from **Figure 4(bç)** it is seen that the data is not distributed normally.

4. Conclusion

The biomass like the stem of sun hemp, pigeon pea, mustard stem, wheat straw, vantulsi, and dhaincha was categorized as high hydrogen content crops and results in hydrogen-rich product gas during stepped pyrolysis. Whereas hydrogen and methane production was directly proportional to temperature; however, higher temperature ranges contributed more towards hydrogen and methane production. Typically, non-condensable Bio-gases contained 40%-55% hydrogen, 8%-25% methane along with 1%-12% carbon monoxide and carbon dioxide depending on different biomass samples. As the samples were pyrolyzed in a stepped (temperature-wise) manner, the oxygen functionality evolved in the initial stages which reduces the concentration of CO and CO₂ in the product gas. Eventually, increase in the concentration of Hydrogen and Methane in the product gases. Gas chromatography of product gas, it was seen that sun hemp having the highest (57.22%) hydrogen, and mustard stem having the highest (25.65%) methane among all 6 biomass samples. High hydrogen and methane-containing fuel can be considered as a good gaseous fuel. The potential utilization of pyrolytic gas as hydrogen-rich fuel in I.C. engine, among all the samples Sun hemp product gas performed highest 12 minutes/kg in 2kva HONDA petrol Genset. A mathematical correlation between net hydrogen (wt. %), hydrogen gas (vol. %) and methane gas (vol. %) is developed and found that the MODEL-1 ($D = -6.25 + 0.996\Delta H + 0.3889CG$) is well-fitted over MODEL-2 ($D = -9.20 + 0.090\Delta H + 0.6099H_2 + 0.1893CH_4$).

Declarations

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Figures

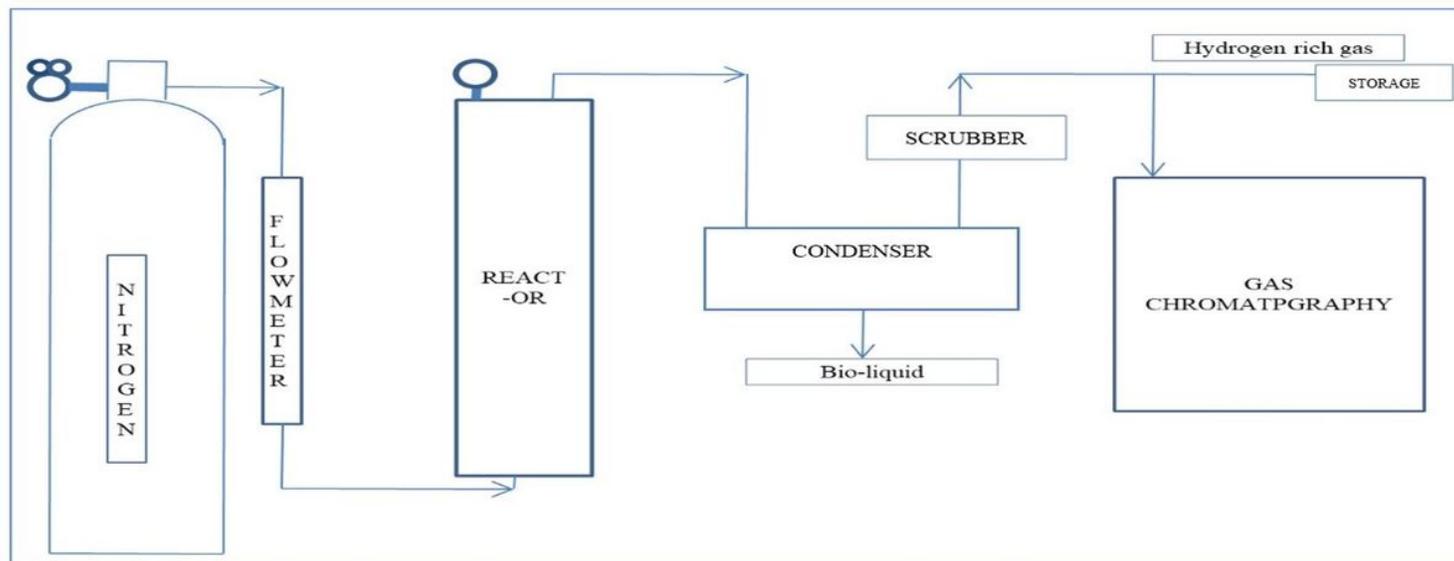


Figure 1

Flow chart of the pyrolysis process.

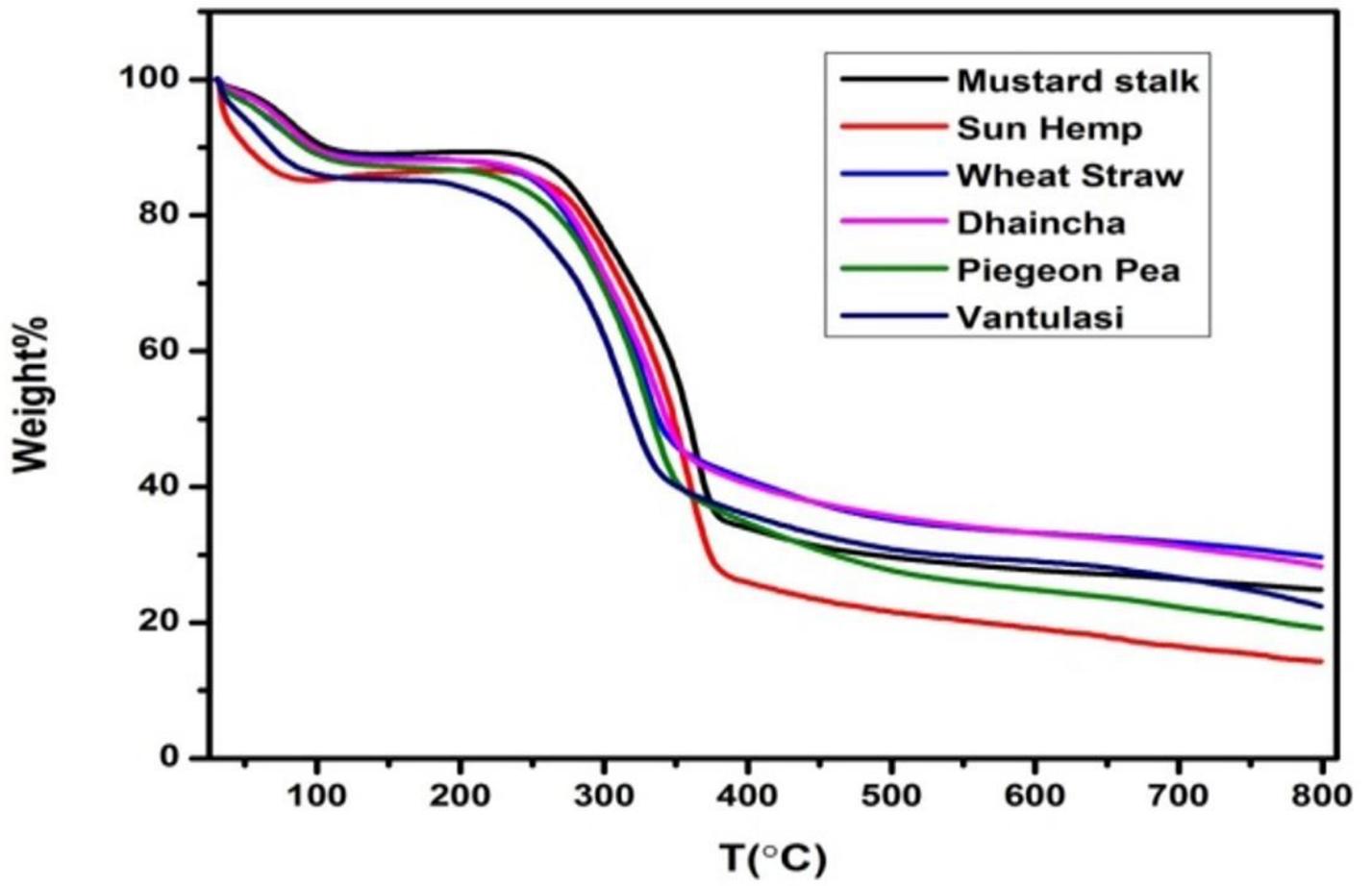


Figure 2

TGA of MS, SH, WS, DH, PP, and VT Samples



Figure 3

Flame of hydrogen and methane-rich produced gas from the stepped pyrolysis of biomass.

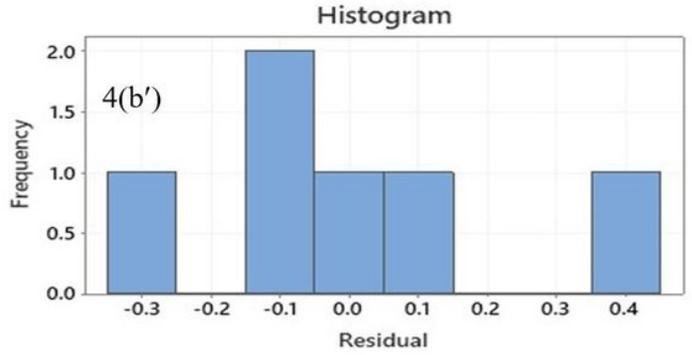
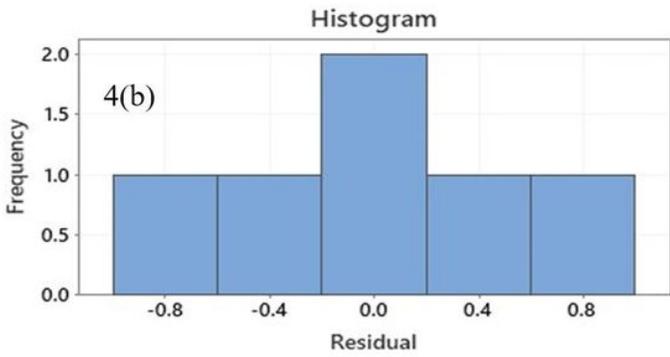
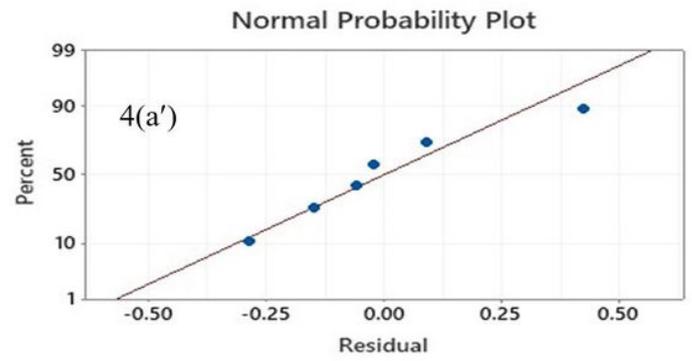
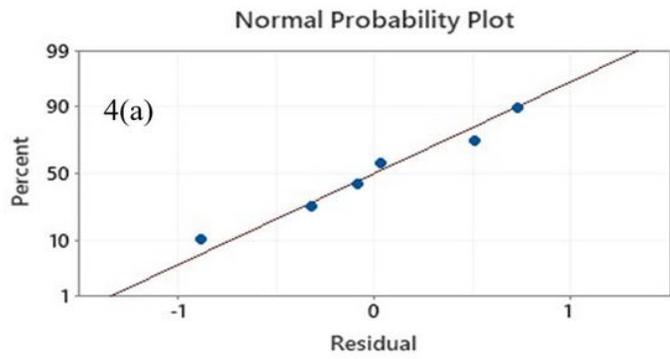


Figure 4

This figure consists of the normal probability plot and histogram for MODEL-1, denoted by (4a, 4b) and for MODEL-2 denoted by (4a', 4b')