

Hydrogen-rich Syngas by Steam-gasification of Waste Lignocellulosic Biomass

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ABSTRACT

The depleting petroleum reserve, as well as increasing demand for crude oil, has attracted the research interest for alternative sources of energy. The surplus lignocellulosic biomass such as forest residues, crop residues, and weeds may be a potential source to derive biofuel by the thermochemical route. Gasification is an established technology for the utilization of biomass to obtain producer gas containing mainly H₂ and CO as combustibles. The air-blown biomass gasifiers are widely installed where the resulting producer gas contains 55-60 per cent nitrogen and a lower percentage of H₂ and CO with an H₂/CO ratio of less than one. Gasification of lignocellulosic biomass using steam as an oxidant produces syn-gas with a lower amount of nitrogen, a higher percentage of hydrogen, and H₂/CO > 2.1. Steam as an oxidant favors water gas shift reaction with the formation of hydrogen and enhances the H₂/CO ratio. The ratio of steam to biomass was 1.20-1.25 so the water gas shift reaction and steam reforming of methane occur. The percentage of hydrogen in the syngas obtained by gasification of pine needles, camelina straw and Lantana biomass was 56.8, 68.7, and 72.8 per cent respectively. The present article describes the steam gasification of pine needle biomass, crop residue from *Camelina sativa*, and biomass from weed i.e. *Lantana camara* to produce syngas with a higher H₂/CO ratio along with a high calorific value compared to the one with air-blown gasification.

Keywords: Gasification; Lignocellulose; Syngas; Pine needles; Lantana; *Camelina sativa*

NOMENCLATURE

FY	Financial Year
FT	Fischer-Tropsch
BTL	Biomass to Liquid
DIBER	Defence Institute of Bio-Energy Research
GC	Gas Chromatograph
TCD	Thermal Conductivity Detector
HHV	High Heating Value
CGE	Cold Gas Efficiency

1. INTRODUCTION

In the present global scenario, there is a need for energy sources to support industrial development, presently crude oil is serving as the major source. The majority of the energy requirement is met by conventional petroleum-based fuels; the liquid fuels are universally preferred by the transportation sector for their ease of storage, transportation, and usage unlike tidal, geothermal, and solar or wind energies. Indian imports about 80 per cent of the crude oil from the Middle East to meet the domestic demand. The import of crude petroleum for the last five year are 213.93 million tonnes (FY 2017); 220.43 (FY 2018); 226.5 (FY 2019); 214.13 (FY 2020);

212.2 million tonnes (FY 2021).^{1,2} The major consumers of petroleum fuel are Indian Railway, Defence, and industries. The Indian Defence sector including Air Force and Navy is one of the biggest consumers. New and alternative sources of energy are being explored to ensure the energy security of the nation and to meet the demand at the time of global crisis or emergency. Biofuels such as biodiesel from vegetable oils and bio-ethanol from starchy and sugar crops are the liquid fuels alternative to conventional diesel and gasoline respectively. The technologies are well developed whereas the poor availability of the feedstock has been the constrained for commercial production and their use on a large scale. The feedstock for first-generation biofuels competes with the food crops for land and water creating a situation of food vs. fuel. The waste lignocellulose biomass is another potential feedstock for deriving advanced fuels and has been the focus of the present time^{3,4}. There is an imminent need to develop technologies for conversion to second-generation liquid fuel with high efficiencies. It has been estimated that India produces about 686 million tonnes of crop residues of which 34 per cent (234 million tonnes) are estimated to be available to derive bio-energy.³ Sugarcane and rice are the top most crop that produces a higher amount of surplus biomass in the country. The selected biomass for the present study includes Pine needles, *Camelina sativa* straw, and *Lantana camara*. Pine needles are abundantly

available in the Northern part of India with a potential of 2.7 million tonnes of lignocellulosic biomass per annum⁵, the accumulation of pine needle in the forest land cause fire hazards. *Camelina sativa* is an oilseed crop of the temperate zone, which is being adopted for cultivation in the winter season in India due to its high oil content, short duration crop, and requires less agricultural inputs. The straw of *Camelina* is the crop residue that may be suitable biomass feedstock for gasification. *Lantana camara* is a widely grown plant generally used for perimeter fencing and is a thicket-forming shrub, which has been considered an invasive species in India. The plant is found throughout India as a weed and may serve as lignocellulosic biomass for gasification. The air-blown gasification of lignocellulosic biomass results in syngas with low calorific value, low hydrogen content, and an H_2/CO ratio of nearly one which is quite low for the Fischer-Tropsch (FT) process to synthesize to liquid fuel⁶⁻⁹. The composition of syngas, the ratio of H_2/CO , and heating values of producer gas from air-blown biomass gasification are listed in Table 1. To synthesize liquid fuel by FT process, the H_2/CO ratio in syngas should be ≥ 2.1 which is achieved in the case of gasification of coal and natural gases. The use of oxygen and steam as gasifying agents had been studied for the gasification of wet wood chips to enhance the hydrogen yield. The syngas contained 48.1 per cent hydrogen with an H_2/CO ratio of 3.9 when dry biomass was gasifier with superheated steam¹⁰. The steam gasification of biomass has been reported in the literature, the experiment conducted in fluidized bed reactors and also on an industrial scale for the production of syngas and hydrogen¹¹⁻¹⁵. The catalytic gasification has been reported in the literature where magnesite has been used for biomass gasification in circulating fluidized bed gasifier with steam and oxygen as gasifying agent¹⁶. The hydrogen concentration increased from 21.9 per cent to 36.2 per cent vol using magnesite as the bed material during gasification. The decrease of carbon monoxide in the product gas along with enrichment of the hydrogen and improvement of the H_2/CO ratio to 2.3 was observed. The use of CaO as a catalyst for steam gasification of pine needles in a bubbled fluidized bed reactor at a temperature up to 850°C has also been reported in the literature¹⁷. The gasification of the available lignocellulosic biomass is one of the viable thermochemical routes to convert the biomass to synthetic gas or syngas and thereafter Fischer-Tropsch (FT) synthesis to liquid fuels in an integrated approach of biomass to liquid fuel (BTL) process.

The occurrence of water gas shift reaction along with biomass gasification improves the hydrogen percentage and the H_2/CO ratio in the syngas. The present article describes the production of hydrogen-rich syngas by an alternate and efficient method

of gasification of lignocellulosic biomass using steam as an oxidant.

2. METHODOLOGY

Lignocellulosic biomass feedstock in the present study includes pine needles as forest residue, biomass from *Camelina sativa* as crop residue, and *Lantana camara* as a weed. The pine needles were collected from various locations in the Nainital district in Uttarakhand. Biomass from *Camelina sativa* was collected from DIBER Project Site, Secunderabad (Telangana, India) where it was intercropped with *Jatropha* plantation to harvest oilseed, the straw was taken in the study. Biomass from *Lantana* was collected where it has been grown widely in the *Jatropha* plantation site at DIBER Project Site, Secunderabad. The biomass was further dried by keeping in a hot air oven at 50°C overnight. The dried biomass was crushed by a mixture grinder until the powdered biomass was passed through a sieve of 600 μ m. The finely powdered biomass was used for gasification.

The setup of the laboratory scale biomass gasifier is shown in Figure 1, which was fabricated locally at Secunderabad. The tubular furnace of the vertical design was made with a height of 500 mm and an inner diameter of 70 mm, with a power consumption of 2000 watts that can be heated up to 1100°C. The temperature of the tubular furnace was controlled by a temperature controller and indicator.

The fixed bed reactor of SS-316 material was fabricated with a length of 800 mm, and an inner diameter of 18 mm, and provision was made to fix a metallic sieve at a height of 150 from the bottom of the reactor. The biomass was packed in such a way that an inert phase of glass beads (4-5mm diameter) is kept for 200 mm above the metallic sieve, followed by the powdered biomass and then glass bean till the top of the reactor. Provision was made to create steam and to introduce it to the reactor containing biomass. 200ml of water was taken into the

Table 1. Composition of syngas obtained by air-blown biomass gasification

S. No.	Biomass	Syngas composition (% vol)					H_2/CO ratio	Heating value (MJ/Nm ³)
		H ₂	CO	N ₂	CO ₂	CH ₄		
1.	Pine needles (present study)	11.7	13.4	56.9	15.5	2.5	0.87	4.18
2.	Pine needles ⁸	10.59	14.0	59.03	14.0	2.38	0.76	3.87
3.	Mixed wood saw dust ⁹	11.81	9.12	62.72	11.29	3.90	1.29	4.91
4.	Olive husk ¹⁰	14.1	13.9	55.9	13.2	2.9	1.01	4.1
5.	Almond biomass ¹¹	15.1	16.5	48.3	16.7	3.4	0.92	-

vessel and heating arrangements were made so that the steam can be introduced into the reactor when the reactor is attaining 350°C. To calculate the steam to biomass ratio, the weight of the vessel (up to 0.1g accuracy) with water was noted. Once the gasification is complete, the condensate water in the pipeline connecting the reactor was collected back to the vessel and the weight of the vessel along with the remaining water was noted. The difference in the weight is the amount of water used as steam for gasification. The outlet of the reactor was fitted with a condenser to liquefy the condensable product of biomass gasification and separate the non-condensable gaseous product to be sent to a glass column to collect synthetic gas (syngas) as shown in Figure 1.

The gasification was conducted by heating the reactor up to 600°C at the rate of 15-17°C, with allowable overheating up to 10°C above the set temperature of 600°C. After completion of gasification, the syngas was collected and analyzed for H₂, CO, CO₂ and CH₄ content

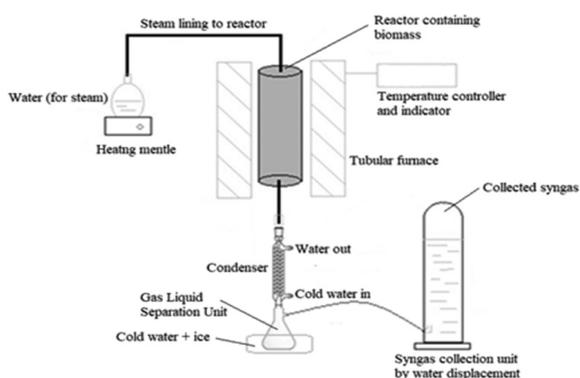


Figure 1. Laboratory scale set up for steam gasification of lignocellulosic biomass.

by a gas chromatograph with thermal conductivity detector using Nucon 5700 Gas Chromatograph with Porapak (80-100 mesh) column, injector temperature 110°C, column oven 110°C, detector 150°C calibrated with reference gas mixture containing H₂, CO, CO₂, CH₄, and N₂ obtained from Centurion Scientific Limited, New Delhi.

The calorific value (high heating value or HHV) of the syngas has been calculated¹⁸ by equation (1).

$$HV_{SG} = 12.76 \times V_{H_2} + 12.63 \times V_{CO} + 39.76 \times V_{CH_4} \dots (1)$$

Where V_{H₂}, V_{CO}, and V_{CH₄} are the respective volume fractions of hydrogen, carbon monoxide and methane in the produced syngas and HV_{SG} is the calculated heating value of syngas.

The cold gas efficiency (CGE) is calculated by equation (2) considering the heating value of biomass 15.89 MJ (or 3800 kCal/kg).

$$CGE(\%) = \frac{HV_{SG} \times V_{SG}}{HV_B \times W_B} \times 100 \dots (2)$$

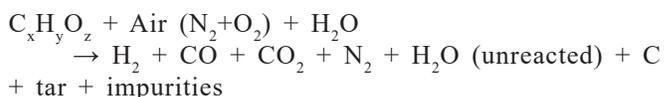
Where HV_B is the heating value of biomass, W_B is the weight of biomass used for gasification and V_{SG} is the volume of syngas produced.

3. RESULT AND DISCUSSION

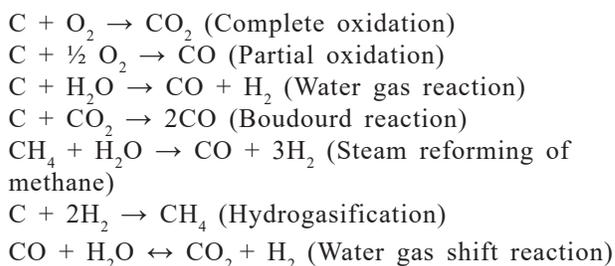
The lignocellulosic biomass in the present study was characterized by the tapped density, moisture content, and lignin; the results are shown in Table 2. Pine needle is having the highest tap density of 0.38 g/cm³, with high lignin content compared to biomass from Lantana and Camelina. The moisture content was higher in pine needles compared to other biomass.

Gasification experiments were conducted with 15g biomass packed in the fixed bed reactor kept in between the inert phase, started the thermochemical reaction by heating the reactor at the rate of 15-17°C/min from ambient to 600°C. The formation of the gaseous product was observed at the temperature of 230-250°C where volatile gases escape from the biomass. The steam is passed to the reactor when the temperature of the reactor reached 350°C, and thereafter the continuous formation of the gaseous product was observed after 440-450°C, the gaseous product being collected by the water displacement method.

The produced gas is mainly composed of hydrogen, carbon monoxide, carbon dioxide, and methane. The overall chemical reaction of biomass gasification is generally represented as below considering the biomass is composed of carbon, hydrogen, and oxygen.



The following chemical reactions occur simultaneously during the steam gasification of lignocellulosic biomass.



In the case of air-blown biomass gasification, the complete as well as partial oxidation of carbon occurs, followed by related reactions and to a lesser extent the water gas shift reaction and hydrogasification. In the case of steam as an oxidant, the ratio of steam to biomass was 1.20-1.25, so there was the water-gas shift reaction as well as steam reforming of methane. It has been observed that the use of steam as an oxidant results in syngas with a little amount of nitrogen unlike the producer gas from air-blown gasification due to the presence of air in the vessel to create steam and also in the gas-liquid separation vessel as depicted in Figure 1. The volume of syngas produced from 15 g

pine needles was 4850 ml, compared to 5600-5650 ml from the same weight of Lantana and Camelina biomass.

The GC-TCD chromatogram of syngas from pine needles, Lantana, and Camelina are shown in Figures 2, 3, and 4 respectively. The hydrogen content in the syngas was 56.8 per cent in the case of syngas from pine needles as shown in Table 3 along with the H_2/CO ratio and heating value of syngas. The hydrogen content in the case of syngas from Lantana and Camelina was 67.8 and 72.8 per cent respectively. The higher yield of syngas, as well as hydrogen in the case of biomass from Camelina and Lantana as compared to that of pine needles, is due to lower lignin content, the thermochemical degradation of lignin may require a temperature higher than 600° C. The liquid product (bio-oil) formed in the case of pine needle was 2.9g whereas it is less than 1g in the cases of Camelina and Lantana biomass. The presence of 15.5 per cent of methane in the syngas reveals that steam reforming of methane is incomplete. The comparatively lesser density of Camelina straw as compared to that of Lantana is likely to have a better distribution of steam and heat, resulting in higher hydrogen in the syngas. In all the cases, the ratio of H_2/CO ranges from 6.5 to 14.2 which is quite higher than the required ratio of 2.1. The syngas with such a high H_2/CO ratio may be utilized for the Fischer-Tropsch process for the synthesis of hydrocarbons, dimethyl ether, and alcohols, where there is the requirement for a cleaning step to remove impurities i.e. compounds of nitrogen, sulfur, higher hydrocarbons, etc.

The calorific value of the product of air-blown biomass gasification varied from 3.87-4.91 MJ/Nm³ as shown in Table 1, the low calorific value is due to the dilution of combustible gases in nitrogen. The products of biomass gasification using steam as oxidant have heating values as calculated by the equation using the heating values of pure hydrogen, carbon monoxide, and methane, the values are in the range of 13.49-14.50 MJ/Nm³. The presence of a higher percentage of methane in the syngas in the case of pine needles is having higher heating value as compared to that of Camelina and Lantana biomass as shown in Table 3. It has been observed that there has been a three times increase in the heating value of syngas when shifting the oxidant from air to steam. The cold gas efficiency has been calculated to be 28 per

Table 2. Characterization of lignocellulosic biomass

S. No.	Biomass	Characteristics		
		Density (g/cm ³)	Moisture (wt. %)	Lignin (wt. %)
1.	Pine needles (Forest residue)	0.38	10.7	32
2.	Lantana biomass (Weed)	0.26	7.4	18
3.	Camelina straw (crop residue)	0.21	5.2	14.7

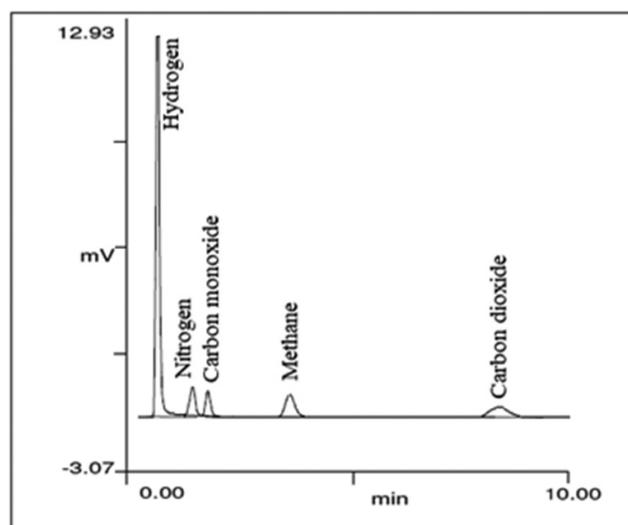


Figure 2. GC-TCD chromatogram of syngas from steam gasification of pine needles.

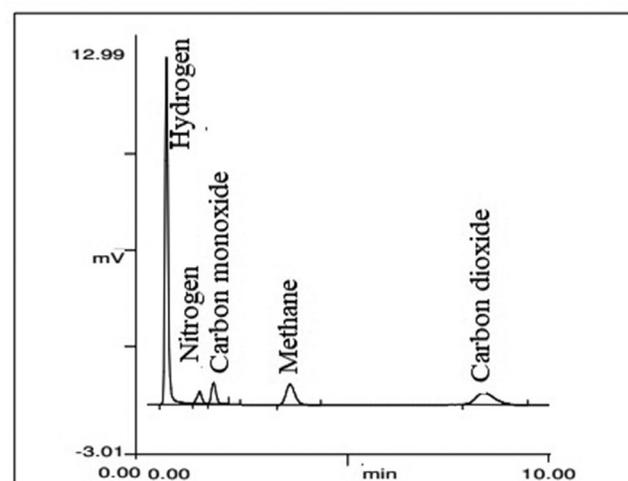


Figure 3. GC-TCD chromatogram of syngas from steam gasification of Camelina biomass.

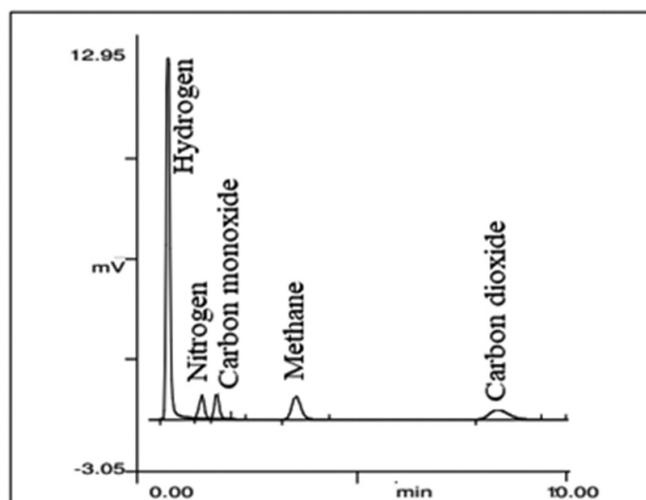


Figure 4. GC-TCD chromatogram of syngas from steam gasification of Lantana biomass.

Table 3. Composition of syngas from gasification of lignocellulosic biomass

S. No.	Biomass	Gas obtained (ml) from 15g biomass	Syngas composition (% vol)					H ₂ /CO ratio	Bio-oil collected (g)	Heating value (MJ/Nm ³)
			H ₂	CO	N ₂	CO ₂	CH ₄			
1.	Pine needles (Forest residue)	4850±150	56.8	8.7	5.6	13.4	15.5	6.5	2.9	14.50
2.	Lantana biomass (Weed)	5600±160	67.8	5.6	3.2	12.9	10.4	12.1	<1	13.49
3.	Camelina biomass (Crop residue)	5650±120	72.8	5.1	4.2	8.4	9.4	14.2	<1	13.67

cent in the case of gasification of pine needles and 32 per cent in the case of gasification of both Lantana and Camelina biomass, which may be improved by conducting the gasification at higher temperature.¹⁹ Syngas with comparatively high heating value may be utilised in gas Genset for power generation in off-grid locations.

4. CONCLUSION

The product of air-blown biomass gasification is lean in energy for use as fuel for power generation. Biomass gasification using steam as an oxidant has the benefit that the syngas contains a lesser percentage of nitrogen. The heating value of syngas in the case of steam as an oxidant is three times more than that of the syngas produced by air blown biomass gasification. The hydrogen content in the product of steam gasification is significantly high compared to air-blown biomass gasification. The hydrogen content in the syngas from pine needles may be further increased by gasification at a temperature higher than 600° C. The alternate method is the two-stage gasification to further enhance the hydrogen content in the syngas. The H₂/CO ratio is ≥ 2.1 so that the syngas after purification may be utilized for the synthesis of liquid fuels such as hydrocarbons by the Fischer-Tropsch process. Further research and development are required to scale up the process in continuous mode as well as syngas purification in a pilot-scale setup to remove the impurities which are expected to affect the downstream processing.

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Mr Milan Bora has done B. Tech. in Chemical Engineering and presently working as Senior Research Fellow at Defence Institute of Bio-Energy Research (DRDO), Haldwani. He has conducted laboratory experiments for the gasification of lignocellulosic biomass mentioned in the manuscript.

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Dr Madhu Bala, (Ph.D., FABMS, FISRB) was former Director of DIBER, DRDO, Haldwani. Her research interests are in the field of radiation sciences, development of medical radiation countermeasures, bio-energy, plant bioresource, and microbiological studies. In the current study, she has contributed to the critical revision and editing of the manuscript.