


CHAPTER 3



MATERIALS AND METHODS

CHAPTER 3

3. MATERIALS AND METHODS

3.1. Raw material and feedstock preparation

Unripe coconut coir was collected from the Vishwanath temple and local market nearby the campus of Indian Institute of Technology (Banaras Hindu University) Varanasi, India. It was chopped in small pieces and sun dried for one week. After that, it was kept in air oven at 105 °C for 48 h to dry it completely. Then it was ground and sieved for separating the materials in the average size of 0.25, 0.72, 2 and 3 mm and named as unripe coconut husk (UCH). The UCH was further impregnated with waste water of pulp and paper industry which was named as impregnated coconut husk (ICH). Impregnation of constituents present in waste water of pulp and paper industry was made in three different temperatures by mixing UCH and water in the ratio of 1:10 (gm:mL). After mixing it was kept at 25, 65 and 105 °C in airtight bottles for 8 h. It was named as ICH25, ICH65 and ICH105. Pulp and paper industry wastewater for impregnation on UCH was collected from the outlet of the primary settler of paper and pulp industry which is situated in Uttarakhand, India. The UCH and ICH were used as feedstock for gasification process.

3.2. Analytical instruments details

Chemical compositions of UCH were investigated by determining neutral detergent fiber (NDF) and acid detergent fiber (ADF) (Soest and Wine, 1968). Proximate analysis of feedstock was performed in accordance to American Society for Testing and

Materials (ASTM) standard (ASTM D3173-75) for moisture, ash and volatile matter content in the sample. Whereas, the fixed carbon was evaluated by the difference from 100 to the sum of percentages by weight of moisture, ash and volatile matter content. The ultimate analysis was performed (EURO-EA, Euro Vector instruments, Italy) for C, H, N and S content in the UCH and ICH25 then O content was calculated by difference. The HHV of UCH and ICH at impregnation temperature of 25 °C (ICH25) and 105 °C (ICH105) were calculated by bomb calorimeter (Rajdhani Scientific, NSTTS Co., New Delhi, India). Elemental analysis of UCH and ICH25 samples was also performed by Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (SEM-EDX) (ZEISS SUPRA 40). The humidity of inlet air was measured by humidity meter (RS-232, HT-315) made in Taiwan. The quantitative analysis of fuel gas produced after gasification was done by gas-chromatography (GC) Nucon 5765 with thermal conductivity detectors (TCD) and flame-ionisation detector (FID) fitted with Porapak-Q. The qualitative and quantitative analysis of fuel gas produced after gasification were also investigated by NDIR based syngas gas analyser (RS232, model: gasboard-3100PLUS) made by Wuhan Cubic Optoelectronics Cooperation Limited, China. Following are the list of equipment used during the research.

Table 3.1 List of instruments and equipment used during current research work

Name of instruments and equipments	Make, model, country	Characteristics studied
Bomb Calorimeter	(Rajdhani Scientific, NSTTS Co., New Delhi) India	Calorific value of biomass
CHNS analyser	(EURO-EA, EUROVECTOR instruments) Italy	Ultimate analysis of

		biomass
Air oven		Drying
Muffle furnace	(Narang scientific works, New Delhi) India	Proximate analysis
Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray analysis (SEM-EDX)	(ZEISS SUPRA 40)	Surface morphology and elemental analysis
Energy Dispersive X-Ray Fluorescence (ED-XRF)	Epsilon5 PANalytical	Elemental analysis
Brunauer-Emmett-Teller (BET)	Micro-meritics Gemini 2375	Surface area
Split tube furnace	(Narang scientific works, New Delhi) India	Gasification
Humidity meter	(RS-232, HT-315) made in Taiwan	Humidity of entering gas media
Gas chromatography	(Nucon 5765)	Fuel gas composition analysis
Syn gas analyser	(RS232, model no: gasboard-3100PLUS) made by Wuhan Cubic Optoelectronics Cooperation Limited, China.	Fuel gas composition and HHV analysis
Gas-chromatography mass spectroscopy (GC-MS)	Shimadzu -17A (Kyoto, Japan), QP-5000 (Quadrapole)	Fuel-oil analysis
Fourier-transform infrared spectroscopy (FTIR)	ALPHA BRUKER Eco-ATR	Functional group analysis

3.3. Experimental set up and procedure

3.3.1. Fixed bed gasification

The schematic diagram of experimental set up of fixed bed gasification column has been illustrated in Figure 3.1. The gasification column was made of 1Cr18Ni9Ti stainless steel pipe with outer and inner diameter 52 and 44 mm, respectively. The total height of the gasification column was 520 mm out of which 130 mm length of column from the bottom was subjected to heating zone. At the both ends, 10 mm thick of same material was welded to make the thread groves airtight. There was a stainless steel air distributor of diameter 34 mm. Total 114 openings were used in the air distributor for uniform distribution of gasifying medium inside the gasification column. This distributor also acted as support of the bed for the UCH and ICH materials.

The experimental setup comprised of three sections as shown by dashed boxes in Figure 3.1. The first part was used for simulating the gasifying medium which had the provision to feed air, humidified air, and CO₂ gas as and when required. It consisted of an air compressor (model XLBM24), temperature controlled water bath (Rajendra Electric Motor Industries, REMI) to heat the water bubbler for humidified air, a CO₂ cylinder (50 % pure) and gas rotameters (Five Stars, Mumbai). The second section contained an electrically heated single zone split tube furnace (Model-NSW-104, Narang scientific works private limited, India) fitted with PID temperature controller and gasification column. The gasification column with above specifications was fixed in this split tube furnace as shown in Figure 3.2 and it was used for the gasification purpose. There was a provision of gas distributor as shown in Figure 3.3 made up of stainless steel (no-2), which was also served as a support for gasification bed. The upper part of the column was made long and exposed at room temperature so that the higher aromatic compounds (tar) could easily liquefy and returned into the gasification (Li and

Suzuki, 2009) for further cracking and reformation to get the higher yield of fuel gas. This section was regarded as the heart of the process at which uniform size of UCH, ICH25, ICH75 and ICH105 were subjected to the CO₂ and humidified air stream as per need for gasification. The third section was gas cleaning as shown in Figure 3.4 and then analysis of fuel gas was conducted. The condensable higher hydrocarbons were removed by chilling the upstream gases, whereas non-condensable tar was removed by treating with dichloromethane. There was also a provision for collection of tar in this section as shown in Figure 3.1.

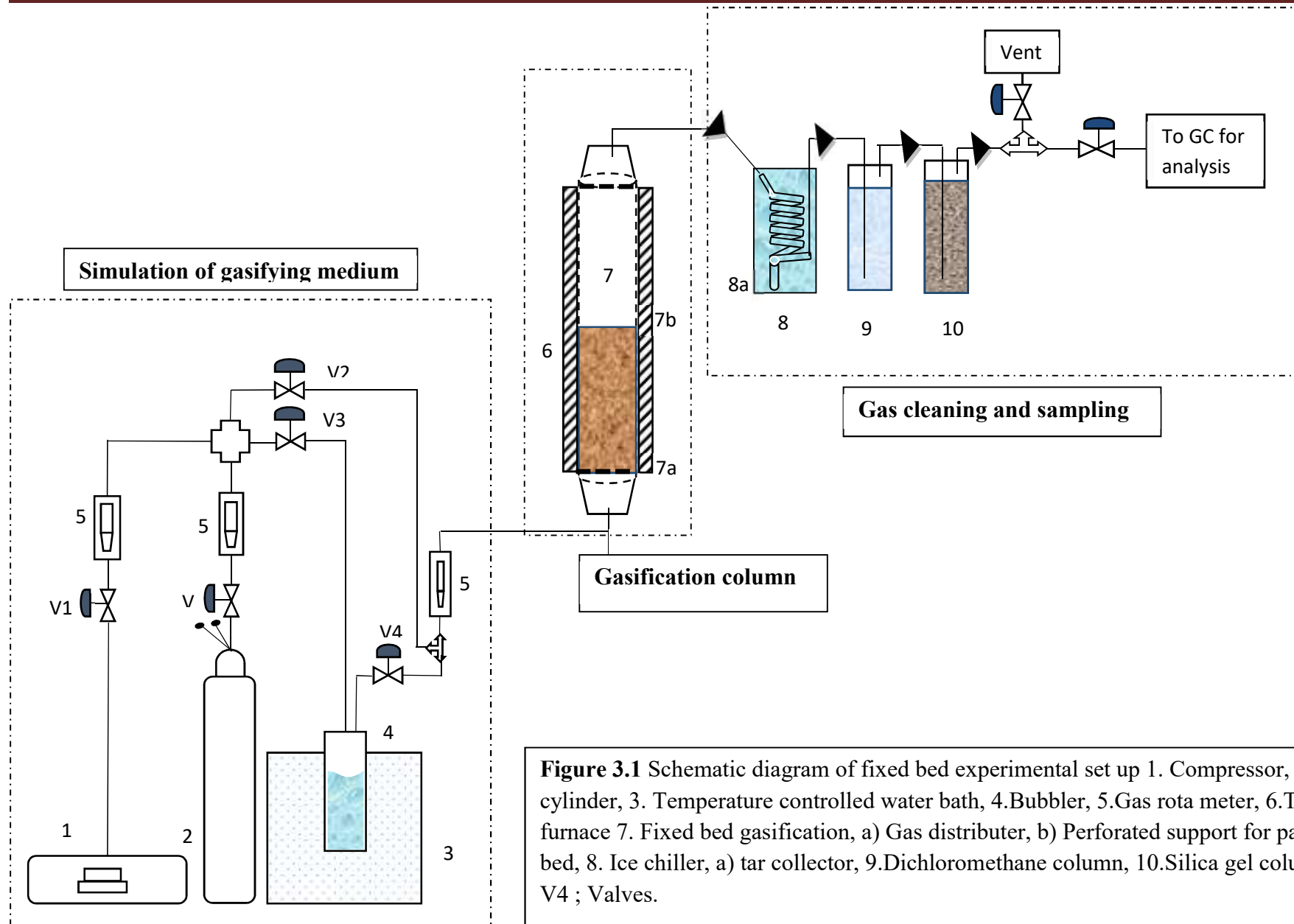




Figure 3.2 Single zone split tube furnace fitted with gasification column



Figure 3.3 Inlet gas distributor cum support of bed inside gasification column

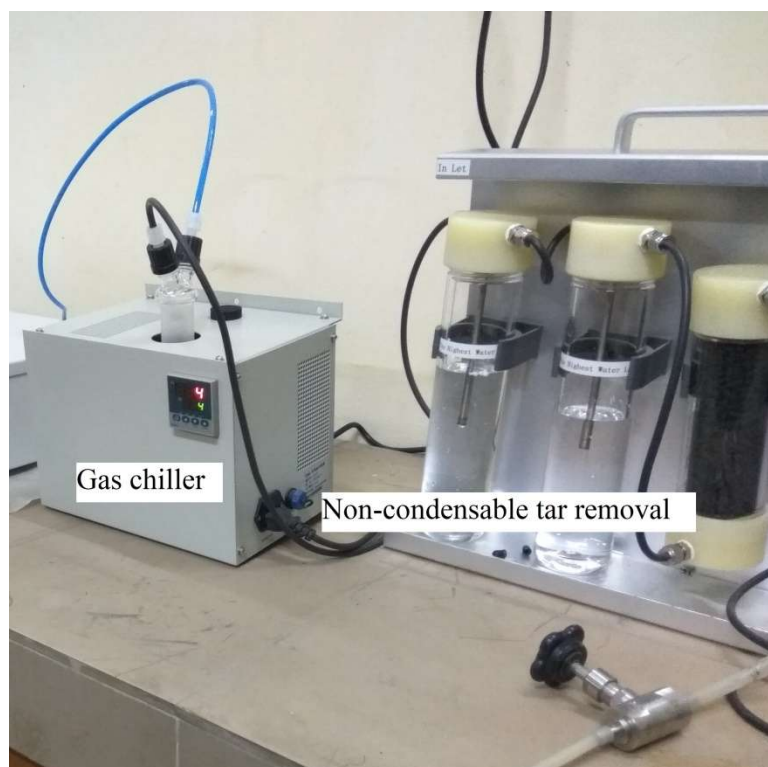


Figure 3.4 System setup for upstream gas cleaning

3.3.2. Fluidized bed gasification

The same experimental setup with a slight modification as shown in Figure 3.5 was used for fluidized bed gasification. A U-tube manometer was attached between inlet and outlet of the gasification column to ensure the fluidization of bed inside the gasification column. The gasification column also contains one distributor which has openings of 2 mm diameter each arranged in triangular pitch arrangement. The experimental setup also has fuel gas cleaning systems consisting of series of chilliers and scrubbers. After cleaning of fuel gas, it has proper arrangement to pass required amount of gas in the syn gas analyser for the qualitative analysis.

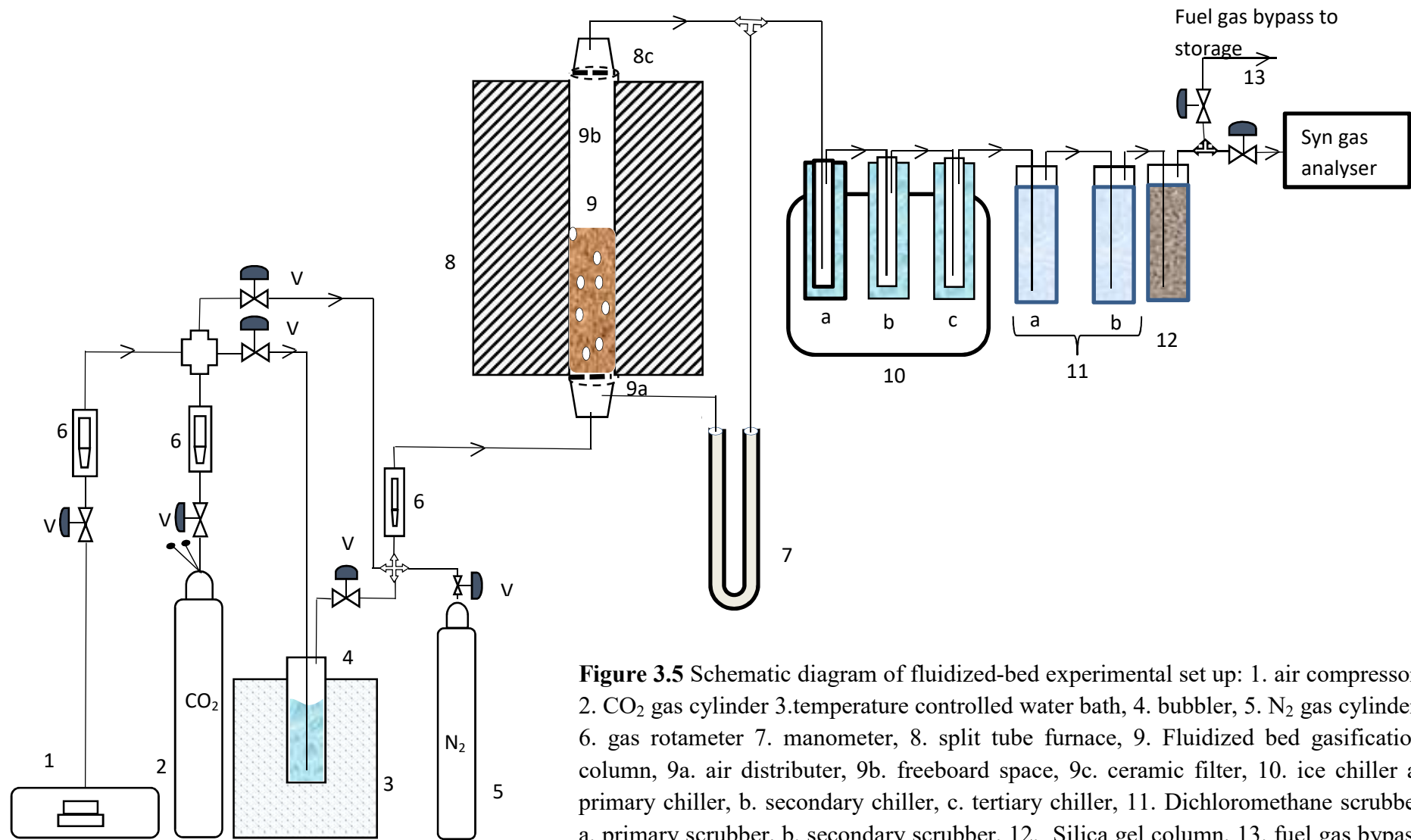


Figure 3.5 Schematic diagram of fluidized-bed experimental set up: 1. air compressor, 2. CO₂ gas cylinder 3. temperature controlled water bath, 4. bubbler, 5. N₂ gas cylinder, 6. gas rotameter 7. manometer, 8. split tube furnace, 9. Fluidized bed gasification column, 9a. air distributor, 9b. freeboard space, 9c. ceramic filter, 10. ice chiller a. primary chiller, b. secondary chiller, c. tertiary chiller, 11. Dichloromethane scrubber a. primary scrubber, b. secondary scrubber, 12. Silica gel column, 13. fuel gas bypass for storage, V; Valves

3.4. Experimental procedure

3.4.1. Fixed bed study

The experiments were performed to see the gas yield using UCH as raw material. Further, UCH was impregnated with metal constituents present in pulp and paper wastewater at different impregnation temperatures, and gasification was performed with impregnated coconut husk. 60 gm of UCH sample was taken inside the gasification column, and the gasification column was then placed inside in a split tube furnace. As shown in Figure 3.1, the experiments for fixed bed gasification were initiated with air alone at flow rates ranging from 0.8 to 3 L/min for ER 0.1 to 0.4 as gasifying medium by opening the valves V1 and V2 and simultaneously closing the valves V3 and V4. Thus air was passed through gasification column without humidity. For the experiments regarding humidified air, the gas stream was introduced inside the gasification column by opening the valves V3 and V4, while the valve V2 was kept closed. After opening valve V3 and V4, the air was allowed to pass through a bubbler containing water at a fixed temperature maintained by using temperature controlled water bath to get humidified air. Relative humidity of the air was continuously measured by humidity meter having resolution of 0.01%RH (model: HT-315, Taiwan). It was varied by controlling the water bath temperature. The gasification column was heated up to required temperature in the presence of N₂ atmosphere, and after achieving the desired temperature, air/humidified air was passed through it as per requirement. The each experiment run was performed for 30 min. The gas coming out from the gasification column was chilled successively in primary, secondary and tertiary chillers connected in series to remove condensable vapors and gases. After tertiary chiller, it was passed through bubblers containing dichloromethane for last-minute removal of tar followed by the wet gas flow meter. The gas sample was collected after removal of moisture via

silica gel column in tedler glass gas sampler at a regular interval of 5 min. Gas sample was analyzed by using gas chromatography (Nucon 5765) with TCD (temperature: injector 120 °C; oven 110 °C) and FID (temperature: injector 80 °C; oven 60 °C) detectors having porapak-q column of length 2 m. The TCD and FID were calibrated with standard gas mixture at periodic intervals. The same procedure was followed using ICH25, ICH65 and ICH105 as feedstocks for fixed bed gasification.

3.4.2. Fluidized bed study

After getting optimized condition for fixed bed gasification, perforated support was removed from it and a manometer was installed between inlet and outlet of the gasification column. Moreover, a chamber with the same dimension as gasification column was made of Perspex and fluidization hydrodynamics was studied in cold condition. In cold condition initially, the fluidization studies were performed in this chamber with 20% (10 gm) biomass of average particle size 0.72 mm mixed with 80% (40 gm) sand of average particle diameter of 0.5 mm to get necessary pressure difference for proper fluidization inside the column. The same pressure difference was maintained in hot condition to ensure fluidization of solid particles with gasifying medium in the column. The desired amount of biomass sample was mixed with sand in the pre-specified ratio as that of cold condition and kept inside the column. Then the gasification column was fitted into the tube furnace as shown in the Figure 3.5. Initially nitrogen gas was purged for 5 min to maintain inert atmosphere inside the column. Furthermore, the furnace was switched on and desired temperature was set inside the column. After reaching the pre-set temperature, the required gasifying medium was passed through the column and the exit gas was first chilled for converting condensable components of gas into liquid in three consecutive chilliers. Then non-condensable gas along with tar vapour was scrubbed with dichloromethane in the scrubbers. Then it was

passed through silica gel column followed by syngas analyser. The produced fuel gas composition was analysed using syngas analyser. There was a provision to bypass the fuel gas before analyser to maintain the fixed flow rate of fuel gas needed by the analyser for analysis. Syngas analyser was calibrated by using 30% CO, 25% CO₂, 30% CH₄, and all balanced with N₂ and 100% H₂ (all GC grade) prior to the analysis of gas. Furthermore, concentrations of H₂, CO, CH₄, CO₂ in the fuel gas and HHV of the gas were measured by using syngas analyser.

Each experimental run was performed for 30 min and arithmetic mean on N₂ free basis have been reported for various components present in the fuel gas. To see the repeatability each experimental run was performed in triplicates and the standard deviation was found less than 2 %. The solid residue left (char) after gasification was analyzed for surface area and its morphological characteristics. The Brunauer, Emmett and Teller (BET, Micro-meritics Gemini 2375) surface area analyzer was used to find its surface area and pore volume. In order to inspect the morphological changes before and after gasification process, coconut husk and its solid residue were characterized by scanning electron microscopy and ED-XRF. Liquid condensed in 1st chiller is collected after each experiment and preceded for the analysis whenever required. The following equations from 3.1 to 3.4 have been used for the calculations (Xiao et al., 2006).

Gas yield (*GY*), in Nm³/kg biomass was calculated by

$$GY = \frac{Q_a * 79 * t}{W_c N_2} \quad (3.1)$$

Where, Q_a is the volumetric flow rate of air (Nm³/h), W_c is weight of biomass fed to the column (kg) for time t (h) and N_2 is fuel gas as vol %.

The carbon conversion, η_c (%) was found by equation (3.2):

$$\eta_c = \frac{Y(\text{CO} + \text{CO}_2 + \text{CH}_4) * 12}{22.4 * C\%} * 100 \quad (3.2)$$

Where, CO, CO₂, CH₄ are in mole percent in fuel gas yield and C is carbon percentage in the ultimate analysis.

Cold gas efficiency, η (%) was obtained by:

$$\eta = \frac{H_g * GY}{H_c} \quad (3.3)$$

Where, H_g and H_c are the higher heating values of cold fuel gas (kJ/Nm³) and biomass in (kJ/kg) respectively.

The higher heating value (HHV) of the dry gas was determined by the following equation:

$$HHV = (3052 * H_2\% + 3018 * CO\% + 9500 * CH_4) * 0.01 * 4.1868 \text{ (kJ/Nm}^3\text{)} \quad (3.4)$$

Where, % indicates the molar composition of specified component present in dry flue gas.

And, potential energy recovery (PER) was calculated from equation (3.5):

$$PER = \frac{HHV \text{ of fuel gas} \times \text{gas yield}}{HHV \text{ of biomass} \times \text{amount of biomass fed in reactor}} \times 100 \quad (3.5)$$