

Chapter-3

Material and methods

3. Introduction

Samples of agricultural waste biomass were gathered from local sources and processed for further examination. The proximate and ultimate analyses of biomass samples, as well as the assessment of calorific value and the percentages of cellulose, hemicellulose, and lignin, were performed using the basic protocols. All samples were analyzed for TG and DTG using a TGA/DTGA instrument. The resulting data were evaluated using both model-free and model-fitting based approaches. A temperature-controlled fixed bed tubular reactor was also used for batch pyrolysis of the selected biomasses. The generated bio-char and bio-oil were collected and evaluated. This section describes the experimental and analytical procedures utilized for the aforementioned aim.

3.1 Collection and preparation of biomass

Lagerstroemia speciosa seed hull (LS) was collected from the premises of IIT (BHU) Varanasi, whereas Mustard stalk (MS) and *Sesbania bispinosa* (SB) were collected from the villages of Azamgarh (26.0739 °N, 83.1859 °E) district of Uttar Pradesh, India. Initially, it was cleaned with tap water after that with distilled water to eradicate the surface dirt and then dried in an air oven at 105 °C for 24 h. The dried biomass was ground in the disintegrator (Wiley Mill Model 2, Philadelphia, USA) and sieved to the desired particle size of 0.21 to 0.25 mm (60 to 70 mesh). Further, the grounded biomass is stored in an airtight glass container to prevent absorbing the humidity. Fig. 3.1 shows the photograph of the powdered samples of all of the chosen biomass.



Lagerstroemia speciosa seed hull Mustard straw

Sesbania bispinosa

Fig. 3.1: Photographs of selected biomasses

3.2 Physicochemical characterization and thermal degradation studies

The fundamental step before pyrolysis is the feasibility analysis of any feedstock. The physicochemical analysis includes a proximate study (moisture content, volatile matter, ash, and fixed carbon content), ultimate analysis (carbon, hydrogen, nitrogen, and sulfur), calorific value, bulk density, fiber analysis (cellulose, hemicellulose, and lignin) were carried out using the standard protocols, whereas thermal degradation analysis was carried out using a thermogravimetric analyzer.

3.2.1 Proximate study

Proximate analysis is the first step in the characterization process. It is used to determine the moisture content (MC), ash content (AC), volatile matter (VM) content, and fixed carbon (FC) content of a biomass sample.

3.2.1.1 Moisture content

In the estimation of moisture content of biomass, 5 g of sun-dried biomass was taken in a glass petri dish. The biomass with a petri dish is placed in a laboratory oven for a duration of 3 h at 105 °C. The moisture content was calculated using the following formula:

$$MC (\%) = \left(\frac{A - B}{A} \times 100 \right) \quad (3.1)$$

where MC is the moisture content, A is the weight of biomass on a received basis, and B is the weight of biomass on a dry basis.

3.2.1.2 Volatile matter

In a crucible, 1.0 g of oven-dried biomass sample was placed, covered with a lid, and held in a muffle furnace for 7.0 minutes at the prescribed temperature of 925 ± 10 °C. When the requisite temperature was reached, the crucible was removed and put in a desiccator to cool. The amount of volatile matter is determined by the biomass sample's weight difference.

$$VM (\%) = \left[\left(\frac{A - B}{A} \times 100 \right) - MC(\%) \right] \quad (3.2)$$

where A and B are the weight of biomass before and after heating

3.2.1.3 Ash content

In a crucible, 1.0 g of oven-dried sample was taken and put for 3.0 hours in the muffle furnace at 575 ± 10 °C. When the temperature reached the desired level, the crucible was removed and placed in a desiccator to cool. The weight disparities between the original and final masses indicated the ash content (AC).

3.2.1.4 Fixed carbon

The difference approach was used to calculate the fixed carbon content (FC) of the biomass as mentioned below.

$$FC (\%) = 100 - (\% MC + \% AC + \% VM) \quad (3.3)$$

3.2.2 Ultimate analysis

C, H, N, and S (elemental analysis) of the biomass sample were determined using an elemental analyzer (Euro, EA 3000 Italy); however, the oxygen content was calculated on a difference basis.

3.2.3 Calorific value

The calorific value of biomass is critical in determining the viability of biomass for value-added goods. A bomb calorimeter (Rajdhani Scientific Instrument, New Delhi, India) was used to determine the higher heating value (HHV). The calorific value (MJ/kg) was determined by pelletizing and burning 1.0g of biomass sample in an automated adiabatic bomb calorimeter. The calorific value was calculated using the equation below.

$$CV = \frac{W * \Delta t - (CV_t + CV_w)}{m} \quad (3.4)$$

where W represents the water equivalent, Δt represents the rise in temperature, CV_t represents the calorific value of thread, CV_w represents the calorific value of wire, and m represents the weight of the sample.

3.2.4 Bulk density

The bulk density of biomass was defined as the ratio of the mass of biomass to total biomass particle volume, including pore space volume between and within biomass particles. The bulk density of biomass is determined by particle size and shape, particle density, moisture content, surface properties, and degree of fill tightness. The bulk density of biomass is an essential physical feature in transport infrastructure and logistic network operations. The density of biomass influences material size, fuel storage needs, material handling, and, most critically, biomass behavior during thermochemical or biological processes. Obernberger and Thek's [85] approach was used to analyze and estimate it. A basic laboratory balance was used to determine the weight of biomass. A graduated cylinder was used to calculate the volume of biomass. The experiment was performed thrice to ensure the repeatability of correct data, and the average data was given in this study.

3.2.5 Van-Krevelen diagram

The Van-Krevelen plot was created by comparing the atomic ratios of hydrogen (H) and carbon (C) to oxygen (O) and carbon (C). This graph depicts the amount of carbon-hydrogen and oxygen composition of any biomass material as well as its relative location in relation to coal. Biomass having low atomic ratios have better fuel characteristics due to reduction in smoke, energy loss, and water vapor during combustion.

3.2.6 Biofuel reactivity

Biofuel reactivity is an essential metric for the consideration of lignocellulosic biomass for thermochemical conversion. It provides information on the reactivity of any biomass resource for optimal use. The proximate and ultimate analysis data were used to evaluate biofuel reactivity. The atomic ratios of oxygen to carbon (O/C) and hydrogen (H/C), as well as volatile matter to fixed carbon (VM/FC), were used to calculate reactivity.

3.2.7 Fiber analysis

3.2.7.1 Lignin content

In a flask, two grams of sample were taken, and 15 ml of 72% sulfuric acid was added. The mixture was agitated regularly for two and a half hours at 25 °C, and then 200 ml of distilled water was added. The mixture was then boiled for 2 hours and cooled. After 24 hours, the lignin was moved to the crucible and continuously cleaned with hot water until it was acid-free. The collected lignin was dried at 105 °C, cooled in a desiccator, and weighed. The drying and weighing processes were repeated until a consistent weight was achieved.

3.2.7.2 Hollocellulose content

Three grams of air-dried samples were weighed and inserted in an Erlenmeyer flask, followed by the addition of 160 ml of distilled water, 0.5 ml of glacial acetic acid, and 1.5 g of sodium chloride. The flask was put in a water bath and heated to 75 °C for an hour before adding a further 0.5 ml of glacial acetic acid and 1.5 g of sodium chloride. The acetic acid and sodium

chloride additions were carried out twice an hour. The flask was put in an ice bath and chilled to below 10 °C. The holocellulose was filtered and washed with acetone, ethanol, and water, then dried in an oven at 105 °C before being weighed.

3.2.7.3 α – cellulose content

In a beaker, two grams of holocellulose were added, and 10 ml of sodium hydroxide solution (17.5%) was injected. The fibers were aggressively soaked in sodium hydroxide solution after being mixed up by a glass rod. The combination was then treated with a sodium hydroxide solution that was added to it on a regular basis (every 5 minutes) for half an hour while the temperature was held at 20 °C. In the beaker, 33 ml of distilled water was added and left for an hour. The holocellulose residue was filtered and transported to the crucible. It was washed again with 100 ml of sodium hydroxide (8.3%), 200 ml of distilled water, 15 ml of acetic acid (10%), and water. The α -cellulose crucible was dried and weighed.

Hemicellulose contents

Hemicellulose = Holocellulose - α – cellulose

3.3 FTIR analysis

The functional groups attached to the raw biomass and pyrolysis products were analyzed using Fourier transform infrared spectroscopy (FTIR, iS5 Nicolet) in the wavelength range of 400 – 4000 cm^{-1} . The FTIR analysis of the raw biomass was mixed with KBr and passed into a translucent pelletized disc to form pellets, whereas ATR (attenuated total reflection) mode was used for the FTIR analysis of bio-oil at a rate of 40 with a step size of 4 cm^{-1} .

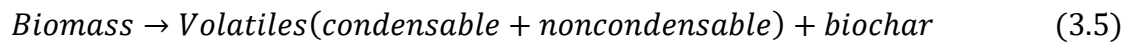
3.4 Thermogravimetric analysis

Thermogravimetric analyzer (Shimadzu Asia Pacific Pvt. Ltd., Singapore) was employed for the thermal degradation behavior of the biomass at a heating rate of 10 °C/min and a steady flow of nitrogen (100 ml/min) to understand the mass loss pattern against the time or temperature throughout the experiment. Furthermore, a desired amount of sample was taken

and pyrolyzed in the same TGA for at least three different heating rates. The experiment was repeated thrice for the accuracy of data, and the acquired data from the TGA was utilized for further investigation.

3.5 Kinetic parameters estimation

During the pyrolysis of solid biomass, major biomass constituents (cellulose, hemicellulose, and lignin) decomposes, thus forming recombines to give valuable products. Several chemical reactions take place in parallel and series throughout the process, which are difficult to study individually. Hence, the process of thermal degradation of biomass is described by the following global reaction.



Various researchers have used this global reaction who adopted the model-free kinetic approach in computing activation energy values (E_a) and pre-exponential factor (A) from the thermogravimetric data generated under non-isothermal conditions. They all expressed the rate of conversion $\frac{d\alpha}{dt}$ of biomass as the function of the temperature as:

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (3.6)$$

where $f(\alpha)$ is the differential form of the reaction model that describes the dependency of the reaction rate on the amount of conversion (α), t is the time, $K(T)$ is the temperature-based rate constant, and α is the conversion of feedstock that is expressed as:

$$\alpha = \frac{m_i - m}{m_i - m_\infty} \quad (3.7)$$

where m_i denotes the initial weight, m is the instantaneous weight, and m_∞ is the biomass final weight, respectively. From the Arrhenius equation, rate constant $K(T)$ can be defined as:

$$K(T) = A \exp\left(\frac{-E_a}{RT}\right) \quad (3.8)$$

where A (min^{-1}), T (K), E_α (kJ/mol), and R (kJ/mol.K) denote frequency factor, temperature, activation energy, and gas constant, respectively. On combining equations (3.6) and (3.8)

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_\alpha}{RT}\right) f(\alpha) \quad (3.9)$$

The heating rate β ($^\circ\text{C}/\text{min}$) is introduced in Eq. (3.9)

$$\frac{d\alpha}{dt} = \frac{A}{\beta} \exp\left(\frac{-E_\alpha}{RT}\right) f(\alpha) \quad (3.10)$$

where, $\beta = \frac{dT}{dt} = \frac{dT}{d\alpha} \frac{d\alpha}{dt}$

After integration of Eq. (3.10) and put the limit for α and T gives

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^T \frac{A}{\beta} \exp\left(\frac{-E_\alpha}{RT}\right) dT = \frac{AE_\alpha}{\beta R} Q(x) \quad (3.11)$$

In Eq. (3.11), the term $Q(x)$ has no analytical solution; hence different numerical techniques were adopted for calculating the activation energy and frequency factor.

3.5.1 Isoconversional model-free methods

3.5.1.1 Ozawa Flynn Wall (OFW) Method

It is an isoconversional model-free method and uses Doyle's approximation for temperature integral, which resulted in the equation:

$$\ln\beta = \ln\left(\frac{AE_\alpha}{Rg(\alpha)}\right) - 5.331 - 1.052 \frac{E_\alpha}{RT} \quad (3.12)$$

On plotting $\ln\beta$ vs. $(1/T)$ at a specific conversion, the individual heating rate imparts a straight line, and its slope will give E_α .

3.5.1.2 Kissinger Akahira Sunose (KAS) Method

This method is based on a linear integral approach that permits the evaluation of E_α values more accurately through the use of equation:

$$\ln \frac{\beta}{T^2} = \ln \left(\frac{AE_\alpha}{Rg(\alpha)} \right) - \left(\frac{E_\alpha}{RT} \right) \quad (3.13)$$

On plotting $\ln \left(\frac{\beta}{T^2} \right)$ vs. $(1/T)$ at specific conversion (extent of reaction), and individual heating rate imparts a straight line, and its slope will give E_α .

3.5.1.3 Tang Method (TM)

In this method, the apparent value of activation energy is evaluated from the isoconversional plot of $\ln \left(\frac{\beta}{T^{1.894661}} \right)$ vs. $(1/T)$ within the specific conversion range based on utilizing the following equation:

$$\ln \frac{\beta}{T^{1.894661}} = C_1 - 1.001450 \frac{E_\alpha}{RT} \quad (3.14)$$

3.5.1.4 Starink Method (ST)

It is the combination of both Kissinger Akahira Sunose (KAS) and Ozawa Flynn Wall (OFW) methods, and the equation is represented as:

$$\ln \frac{\beta}{T^{1.92}} = C_2 - 1.0008 \frac{E_\alpha}{RT} \quad (3.15)$$

On plotting $\ln \left(\frac{\beta}{T^{1.92}} \right)$ and $1/T$ at specific conversion and individual heating rate imparts a straight line, and its slope will give E_α

3.5.1.5 Vyazovkin Method (VZK)

Vyazovkin method was developed to enhance the accuracy of analysis by computing the temperature integral as a part of the evaluation of activation energy E_α at a particular point of conversion by minimizing the following function:

$$\varphi = \sum_i^n \sum_{j \neq i}^n \frac{I(E_\alpha, T_{\alpha,i})\beta_j}{I(E_\alpha, T_{\alpha,j})\beta_i} = \text{minimum} \quad (3.16)$$

$$\text{where } I(E_\alpha, T_\alpha) = \int_0^{T_\alpha} \exp \left(\frac{-E}{RT} \right) dT \quad (3.17)$$

The experimental values pertaining to temperature (T) and heating rate (β) are substituted in Eq. (3.16) and E_α is varied till the minimum value of the function φ in Eq. (3.16) is achieved. The values for $I(E_\alpha, T_\alpha)$ were calculated by the Senum-Yang approximation. The procedure is related to the repetition of minimization of function φ for every single conversion value (α) to get the value of activation energy as the absolute function of the conversion.

3.5.2 Model fitting method

3.5.2.1 Coats Redfern method

The model fitting method was proposed by Coats and Redfern (1964) for solving Eq. (3.11) for various values of (a) to interpret the reaction mechanism and obtain the values of E_a , and A. Eq. (3.11) can be written as

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^T \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) dT \quad (3.18)$$

$$g(\alpha) = \frac{ART^2}{\beta E_a} \left(1 - \frac{2RT}{E_a}\right) \cdot \exp\left(\frac{-E_a}{RT}\right) \quad (3.19)$$

Taking log both side of Eq. (3.19)

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E_a}\right) \left(1 - \frac{2RT}{E_a}\right) - \frac{E_a}{RT} \quad (3.20)$$

If in Eq. (3.19), the value of E_a is large, then the term $2RT/E_a \ll 1$ and Eq. (3.20) can be written as:

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E_a}\right) - \frac{E_a}{RT} \quad (3.21)$$

The slope of the plot between $\ln\left(\frac{g(\alpha)}{T^2}\right)$ vs. $\frac{1}{T}$ gives the value of activation energy (E_a), and its intercept gives the pre-exponential factor.

3.6 Reaction Mechanism and $z(\alpha)$ Master Plots

The rate of reaction expressed as the rate of change of conversion ($d\alpha/dt$) for a solid-state system corresponding to the process temperature T and to the conversion α was given by Criado et al., (1989).

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_\alpha}{RT}\right) f(\alpha)$$

where, $f(\alpha)$ governs algebraic function based on the reaction mechanism of the pyrolytic process, heating rate $\beta = dT/dt$, and if the temperature of the process rises at a constant value of heating rate (β) and on the integration of above equation yield:

$$g(\alpha) = \frac{AE_\alpha}{\beta R} \exp\left(\frac{-E_\alpha}{RT}\right) \left[\frac{Y(E_\alpha/RT)}{E_\alpha/RT} \right] \quad (3.22)$$

Where $Y(E_\alpha/RT)$ is a guesstimate pertaining to temperature integral that is not described in analytical form. In the present work, the fourth rational equation given by Senum and Yang was used because it gives minor errors.

$$\gamma\left(\frac{E_\alpha}{RT}\right) = \frac{x^3 + 18x^2 + 86x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (3.23)$$

On merging integral as well as differential form, the $z(\alpha)$ plot are derived

$$z(\alpha) = f(\alpha) \times g(\alpha) \quad (3.24)$$

therefore,

$$z(\alpha) = \frac{d\alpha}{dt} \exp\left(\frac{E_\alpha}{RT}\right) \int_0^T \exp\left(\frac{-E_\alpha}{RT}\right) \quad (3.25)$$

where $z(\alpha)$ in Eq. (3.24) was used to obtain the theoretical master plot and $z(\alpha)$ in Eq. (3.25) was used to produce the experimental master plot. The used algebraic equation are listed in Table 3.1. Both the plots were compared to find the exact reaction mechanism, and the one which fitted closely with the experimental curve gives the required mechanism.

Table 3.1: Algebraic expressions for $f(\alpha)$ and $g(\alpha)$ for the most frequently used mechanisms of solid-state processes

Reaction model	Code	Integral form $g(\alpha)$	Differential form $f(\alpha)$
Nucleation and growth (Avrami Eq.1)	A2	$[-\ln(1 - \alpha)]^{1/2}$	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$
Nucleation and growth (Avrami Eq. 2)	A3	$[-\ln(1 - \alpha)]^{1/3}$	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$
Nucleation and growth (Avrami Eq. 3)	A4	$[-\ln(1 - \alpha)]^{1/4}$	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$
Phase boundary-controlled reaction (one-dimensional movement)	R1	α	1
Phase boundary-controlled reaction (contracting area)	R2	$[1 - (1 - \alpha)]^{1/2}$	$2(1 - \alpha)^{1/2}$
Phase boundary-controlled reaction (contracting volume)	R3	$[1 - (1 - \alpha)]^{1/3}$	$3(1 - \alpha)^{2/3}$
One-dimensional diffusion	D1	α^2	$(1/2)\alpha$
Two-dimensional diffusion (Valensi model)	D2	$(1 - \alpha)\ln(1 - \alpha) + \alpha$ $[1 - (1 - \alpha)^{1/3}]^2$	$[-\ln(1 - \alpha)]^{-1}$
Three-dimensional diffusion (Jander model)	D3		$3/2(1 - \alpha)^{2/3}[1 - (1 - \alpha)^{1/3}]^{-1}$
Three-dimensional diffusion (Ginstlinge-Brounshtein model)	D4	$[1-(2/3) \alpha] -(1-\alpha)^{2/3}$	$(3/2) [1-(1-\alpha)^{1/3}]^{-1}$
Random nucleation with one nucleus on the individual particle	F1	$-\ln(1 - \alpha)$	$(1 - \alpha)$
Random nucleation with two nuclei on the individual particle	F2	$1/(1 - \alpha)$	$(1 - \alpha)^2$
Random nucleation with three nuclei on the individual particle	F3	$1/(1 - \alpha)^2$	$(1/2)(1 - \alpha)^3$

3.7 Thermodynamic analysis

The pre-exponential factor and reaction mechanism specified by various isoconversional processes are not appropriate [87]. The activation energy (E_a) plays an important role in the estimation of the reactivity of fuel. The reactivity of fuel plays an important role in pyrolysis processes. For assessing the fuel potential of biomass, thermodynamic parameters is also crucial for assessing the energy potential of biomass. The change in enthalpy (ΔH) indicates the absolute energy required by the biomass during pyrolysis. The change in Gibbs free energy (ΔG) uncovers the overall increment in the system's energy in the approachability of the biomass and product formation. So for calculating the pre-exponential factor and thermodynamic parameters (ΔH , ΔG and ΔS), the following equations have been used.

$$A = \beta \cdot E_a \cdot \exp\left(\frac{E_a}{RT_m}\right) \quad (3.26)$$

$$\Delta H = E_a - RT_m \quad (3.27)$$

$$\Delta G = E_a + R \cdot T_m \cdot \ln\left(\frac{K_b \cdot T_m}{h \cdot A}\right) \quad (3.28)$$

$$\Delta S = \left(\frac{\Delta H - \Delta G}{T_m}\right) \quad (3.29)$$

where h governs Plank's constant (6.626×10^{-34} Js), K_b is the value for Boltzmann constant (1.381×10^{-23} J/K), and T_m is the peak temperature obtained by inspecting the DTG thermograph.

3.8 Experimental setup

A stainless-steel fixed tubular bed reactor (Fig. 3.2) was employed for thermal pyrolysis of biomass. The height of the reactor was 42 cm, and its inner diameter was 4.5 cm. The reactor was fitted with a cylindrical-shaped electrical furnace, and it was governed by a controller (PID). For each run, the desired amount of biomass sample was kept in the reactor. An inert

atmosphere was created by passing N₂ gas to evacuate oxygen and other impurities. The purging of N₂ gas was started half an hour earlier and was maintained constant throughout the pyrolysis process. The reactor is placed inside the furnace in a way that the heat is distributed uniformly across the reactor. The condenser was attached at the lower end to condense the volatiles released from the reactor. After the pyrolysis experiment, the system was led to cool, and the obtained product was collected for further characterization. The below-mentioned equation was utilized to calculate solid, liquid, and non-condensable gas yield.

$$\% \text{solid yield} = \frac{\text{solid fuel}}{\text{weight of total sample}} \times 100 \quad (3.30)$$

$$\% \text{liquid yield} = \frac{\text{liquid fuel}}{\text{weight of total sample}} \times 100 \quad (3.31)$$

$$\% \text{gas yield} = 100 - (\% \text{liquid yield} + \% \text{solid yield}) \quad (3.32)$$

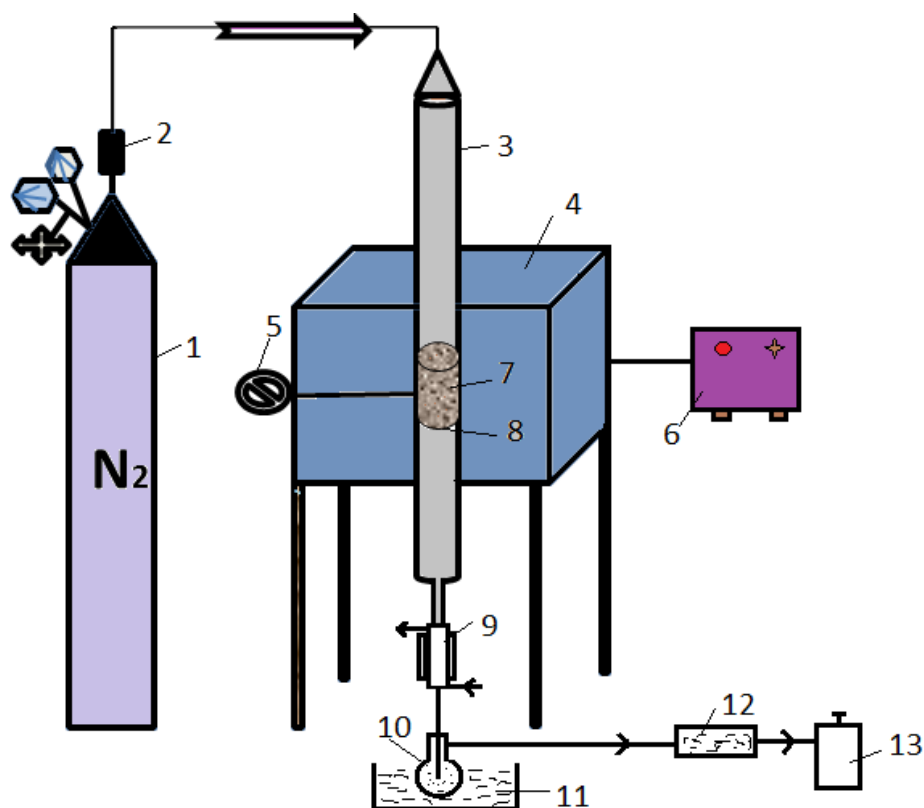


Fig. 3.2: Schematic diagram of pyrolysis experimental setup: 1- N₂ cylinder, 2-Mass flow meter, 3-Stainless steel reactor, 4-Electric furnace, 5-Thermocouple, 6- Furnace controller, 7- Biomass, 8-Biomass holder, 9-Condenser, 10-Bio-oil collector, 11-Ice, 12- Cotton filter, 13- Gas collector