Process Model for Carbon Nanomaterials Production from Plastic Waste Using Agro/Animal Waste

A Project Report submitted by

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B22CH005

In partial fulfillment of the requirements for the award of the degree of B.Tech.

Indian Institute of Technology Jodhpur

Chemical Department

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I hereby declare that the work presented in this Project Report titled **PROCESS MODEL FOR CARBON NANOMATERIALS FROM PLASTIC WASTE USING AGRO/ ANIMAL WASTE IN ASPEN V14** submitted to the Indian Institute of Technology Jodhpur in partial fulfilment of the requirements for the award of the degree of B.Tech. is a Bonafide record of the research work carried out under the supervision of **Professor Manoj Kumar Jena** .The contents of this Project Report in full or in parts, have not been submitted to, and will not be submitted by me to, any other Institute or University in India or abroad for the award of any degree .

Signature

Name of the Student :   Ayushi Singh

Roll Number : B22CH005

Certificate

This is to certify that the Project **PROCESS MODEL FOR CARBON NANOMATERIALS FROM PLASTIC WASTE USING AGRO/ ANIMAL WASTE IN ASPEN V14** submitted by **Ayushi Singh Roll no B22CH005** to the Indian Institute of Technology Jodhpur for the award of the degree of B.Tech is a bonafide record of the research work done by him under my supervision. To the best of my knowledge, the contents of this report, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Signature :

Dr. Manoj kumar Jena

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ABSTRACT

This project offers a complete process model for the eco-friendly creation of carbon nanomaterials (CNMs) from plastic waste, utilizing biochar sourced from agro/animal waste as a catalyst. The holistic method merges plastic waste pyrolysis to create bio-oil with biomass pyrolysis to yield biochar, and then employs catalytic chemical vapor deposition (CVD) to produce valuable carbon nanomaterials such as carbon nanotubes (CNTs) and carbon nanospheres (CNSs). The complete procedure has been modeled with Aspen Plus V14, integrating thermodynamic equilibrium assessments, reaction kinetics, and considerations for equipment design. The dual-feed system tackles two essential waste management issues while generating valuable outputs: hydrogen-rich syngas, high-quality bio-oil with lower polycyclic aromatic hydrocarbons (PAHs), and carbon nanomaterials. Simulation results show that the system can reach methane conversion rates of 40-70% based on operational conditions, while carbon deposition rates vary between 9.4 and 15.6 $mg \cdot h^{-1} \cdot g^{-1}$ catalyst. The biochar catalyst shows enhanced stability during prolonged reaction times because of the creation of crystalline carbon deposits. This effort supports circular economy principles by converting waste materials into valuable products, simultaneously capturing carbon and lowering greenhouse gas emissions

INTRODUCTION

1.1 Background and Motivation

Worldwide plastic production has surpassed 360 million tons each year, with roughly 55% sent to landfills, 25% burned, and merely 20% recycled. This ineffective waste management system creates serious environmental problems, such as microplastic pollution, greenhouse gas emissions from burning waste, and reduction of landfill space. At the same time, the production of agricultural and animal waste is rising, frequently being incinerated or discarded incorrectly, resulting in air contamination and the loss of resources.

The idea of a circular economy requires creative methods that can convert these waste flows into useful products. Carbon nanomaterials, especially carbon nanotubes (CNTs) and carbon nanospheres (CNSs), are valuable materials utilized in fields such as electronics, energy storage, catalysis, biomedical devices, composite materials, and environmental cleanup. The worldwide CNM market is expected to hit USD 9.8 billion by 2028, fueled by rising demand in sophisticated technological uses.

Conventional CNM production techniques depend on costly metal catalysts (Ni, Co, Fe) anchored on metal oxides, carbon precursors from fossil fuels such as methane or acetylene, and processes that require significant energy. These traditional methods encounter various drawbacks such as quick catalyst deactivation, challenging separation of CNMs from metal impurities, expensive catalyst regeneration, and considerable carbon dioxide emissions.

This Project tackles these issues by creating a cohesive method that:

• Employs plastic waste as a carbon source via pyrolysis.

• Utilizes biochar obtained from biomass as an affordable, eco-friendly catalyst

• Generates several beneficial products: CNMs, hydrogen-rich gas, and enhanced bio-oil.

• Captures carbon in stable forms

• Lowers reliance on fossil fuels and costly metal catalysts.

2: LITERATURE REVIEW

This section provides an overview of existing research and knowledge on the conversion of plastic waste and biomass into valuable carbon-rich products such as bio-oil, biochar, and carbon nanomaterials (CNMs). The review is divided into three major parts: plastic waste management and pyrolysis, biochar production from biomass, and the synthesis of carbon nanomaterials.

2.1 Plastic Waste: Challenges and Opportunities

2.1.1 Global Plastic Waste Scenario

Plastic materials, mainly polymers derived from petroleum, have become essential in contemporary society because of their adaptability, resilience, and affordability. Yet, these identical characteristics lead to significant environmental issues. From 1950 to 2015, merely 9% of the total plastic waste produced worldwide was recycled, underscoring the shortcomings of existing waste management systems.

The mechanical recycling of plastics encounters fundamental constraints—recycled plastics frequently have diminished properties, rendering them inappropriate for their initial uses. This results in downcycling, where materials are utilized for lesser-value purposes. Additionally, the presence of additives, polymer degradation, and contamination hinder recycling efforts.

Burning waste, although it retrieves some energy, emits greenhouse gases and may release harmful substances. Landfills deplete precious land resources and pose a risk of leaching additives into the soil and groundwater. As a result, there is an urgent need for alternative methods to transform plastic waste into higher-value products.

2.1.2 Pyrolysis of Plastic Waste

Pyrolysis offers an attractive pathway for plastic waste valorization through thermal decomposition in oxygen-depleted atmospheres. Operating typically between 300°C and 900°C, pyrolysis breaks long polymer chains into shorter hydrocarbon molecules, yielding three distinct product fractions:

1. **Gaseous products:** C_1-C_4 light hydrocarbons, hydrogen, carbon monoxide, carbon dioxide

2. **Liquid bio-oil:** C_5-C_{20} hydrocarbons including aromatics, aliphatics, and waxes

3. **Solid residue:** Carbonaceous char and inorganic components

Common plastics including polypropylene (PP), polyethylene (PE), and polystyrene (PS) have received extensive research attention due to their high hydrocarbon content and abundance in municipal waste streams. Polypropylene copolymer pyrolysis at 500°C typically yields approximately 75% gaseous products and 25% liquid fraction. The gas phase contains substantial methane, ethylene, propylene, and other light hydrocarbons, while the liquid phase comprises aromatic compounds, aliphatic hydrocarbons, and polycyclic aromatic hydrocarbons (PAHs).

Feedstock polymer type: Different polymers exhibit distinct thermal degradation pathways and product distributions

Operating temperature: Higher temperatures favor gas formation and promote cracking of heavier molecules 700C

Heating rate: Slow heating (5-15°C/min) enhances char formation; rapid heating (>100°C/min) maximizes liquid yields

2.2 Biochar Production and Characterization

2.2.1 Biomass Sources and Properties

Agricultural residues (crop stalks, fruit peels, nut shells, bagasse) and animal wastes (manure, poultry litter) constitute abundant, low-cost feedstocks for biochar production. These materials typically contain 30-50% carbon, 4-6% hydrogen, 30-40% oxygen, with minor amounts of nitrogen and sulfur on a dry basis.

Biosolids—treated sewage sludge from municipal wastewater treatment facilities—represent another promising feedstock. Biosolids typically contain approximately 31% carbon, 4.2% hydrogen, 4.6% nitrogen, and 31% oxygen, with ash content around 27%. They contain various metals including iron (11,000 mg/kg), calcium (24,000 mg/kg), zinc (970 mg/kg), and copper (490 mg/kg), which can function as catalytic sites in subsequent reactions.

2.2.2 Pyrolysis Process for Biochar Production

Biochar is produced through slow pyrolysis of biomass at temperatures between 500-700C in an oxygen-limited environment.. During pyrolysis, volatile components are driven off, leaving behind a carbon-rich solid with enhanced porosity and surface area.

The yield and properties of biochar depend critically on:

- **Pyrolysis temperature**: Higher temperatures (>600°C) reduce volatile matter and increase fixed carbon content

- **Feedstock composition**: Lignocellulosic materials (high lignin content) yield more biochar than materials rich in cellulose or hemicellulose

- **Particle size**: Smaller particles enhance heat and mass transfer

- **Atmosphere**: Inert atmospheres (N_2, Ar) prevent oxidation

Biochar exhibits several advantageous properties for catalytic applications:

1. **High surface area** (100-500 m²/g) providing abundant active sites

2. **Porous structure** facilitating reactant access and product release

3. **Thermal stability** enabling operation at elevated temperatures

4. **Inherent metal content** potentially providing catalytic activity

5. **Low cost** compared to conventional catalyst supports

2.3 Carbon Nanomaterials: Synthesis and Applications

2.3.1 Types and Properties of Carbon Nanomaterials

Carbon nanomaterials include a group of carbon-based structures that have at least one dimension within the nanometer range (1-100 nm). The primary categories consist of:

Carbon Nanotubes (CNTs): Tube-like formations created by curling graphene layers. Single-walled CNTs (SWCNTs) are made from one graphene layer, whereas multi-walled CNTs (MWCNTs) have several concentric layers. CNTs display remarkable characteristics:

• Tensile strength: 50-200 GPa (50-100 times more robust than steel)

• Electrical conductivity: 10^6 to 10^7 S/m

• Heat transfer capability: 3000-6000 W/m·K

• Young's modulus: 1 TPa

• Elevated aspect ratio (length/diameter): 1000-10000

Carbon Nanofibers (CNFs): Cylindrical formations featuring graphene layers arranged at different angles relative to the fiber axis. They have diameters ranging from 10 to 100 nm and lengths of multiple micrometers. CNFs have lower crystallinity compared to CNTs but are simpler and more cost-effective to manufacture.

Carbon Nanospheres (CNSs): Spherical carbon formations with diameters between 20-500 nm. They are made up of concentric graphitic layers and demonstrate high surface areas, rendering them ideal for adsorption uses and as supports for catalysts.

Bamboo-Type Carbon Nanotubes (BCNTs): Structures with multiple walls containing periodic sections divided by horizontal graphene layers, similar to bamboo stalks. These structures merge characteristics of CNTs and CNFs.

2.3.2 Synthesis Methods

Chemical Vapor Deposition (CVD): The most widely employed method for CNM synthesis. Hydrocarbon precursors (methane, ethylene, acetylene) decompose on catalyst surfaces at elevated temperatures (600-1000°C), depositing carbon atoms that assemble into nanostructures. CVD offers excellent control over product morphology and can operate at relatively moderate temperatures compared to other methods.

2.3.2 Connection to the Present Study

In this project, bio-oil obtained from plastic pyrolysis functions as a carbon source, whereas biochar produced from biomass pyrolysis serves as a solid template and catalytic foundation for CNM synthesis. Their combination facilitates the conversion of two waste types—plastic waste and biomass waste—into valuable nanocarbon materials, supporting sustainability and circular economy concepts.

2.3.3 Market Opportunity

- Carbon nanomaterials market projected to reach $9.8 billion by 2028

- Traditional CNM production relies on fossil fuels and expensive metal catalysts

- High energy consumption and significant CO_2 emissions

OUR SOLUTION

Transform waste into wealth by creating a circular economy pathway that simultaneously solves waste management problems and produces high-value advanced materials.

3. PROBLEM DEFINITION AND RESEARCH OBJECTIVES

3.1 Problem Statement

The convergence of escalating waste management challenges and growing demand for advanced materials creates an opportunity for innovative technological solutions. However, several critical barriers prevent effective waste-to-nanomaterial conversion:
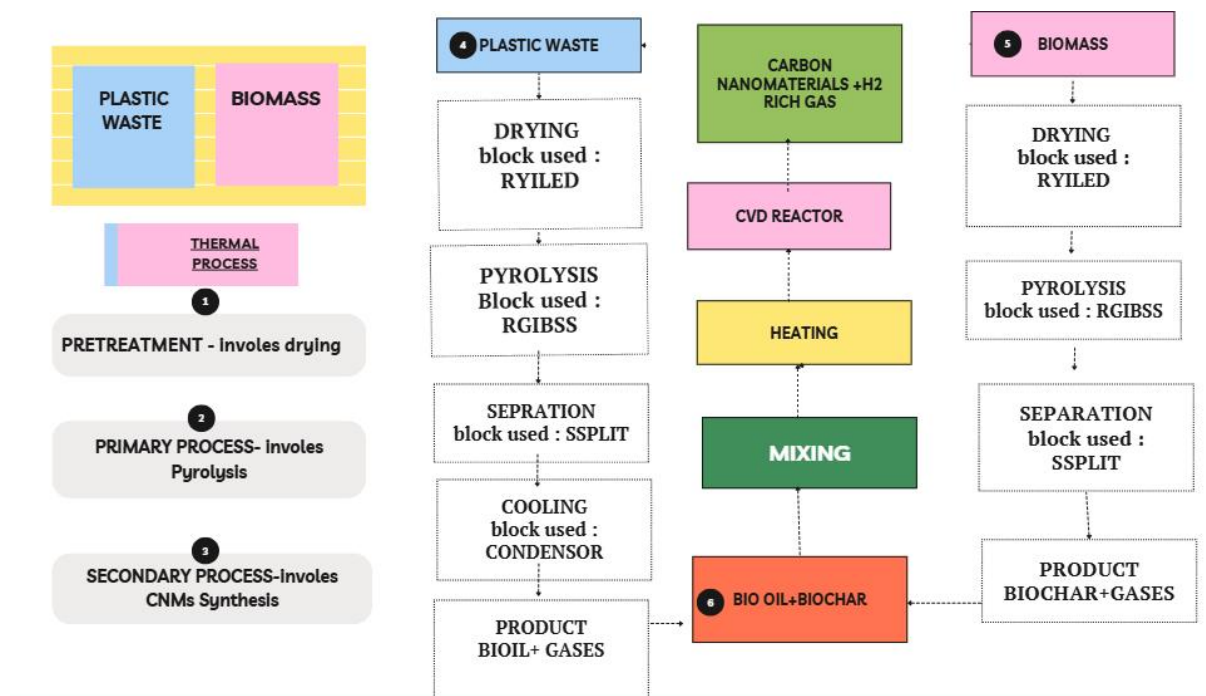
3.2 Primary Objectives

Develop Integrated Process Model

The primary objectives of this project are:

1. To develop a comprehensive process model for converting plastic waste and biomass into carbon nanomaterials

2. To simulate the integrated process using Aspen Plus, incorporating thermodynamic and kinetic considerations

3. To design and select appropriate reactors based on process requirements

4. To evaluate the technical feasibility, product yields, and conversion efficiencies

5. To assess the environmental benefits and economic viability of the proposed process

OVERALL WORK FLOW

3: METHODOLOGY AND OVERALL PROJECT APPROACH

The primary objective of this project is to develop a thermochemical process model for converting plastic waste and agro/animal waste biomass into carbon nanomaterials (CNMs) using Aspen Plus simulation software.

Strategic Framework:

1. **Feedstock Selection and Characterization:** Identify available waste streams and characterize their composition

2. **Process Selection:** Choose appropriate conversion technologies based on feedstock properties and desired products

3. **Flowsheet Development:** Design integrated process configuration with optimal unit operation sequence

4. **Thermodynamic Foundation:** Select property methods ensuring accurate phase equilibria and enthalpy calculations

5. **Simulation Implementation:** Build and validate computational model in Aspen Plus

6. **Parametric Analysis:** Systematically vary key parameters to understand process sensitivities

7. **Results Interpretation:** Analyze outputs to draw conclusions about technical feasibility

3.1 Feedstock Availability and Selection

- Begin by specifying the feedstock (biomass, plastic, etc.) in Aspen Plus, entering compositional data either as nonconventional material (using ultimate/proximate analysis for solids, or molecular breakdown for polymers).

- This step ensures the simulation accurately represents the physical and chemical makeup of the raw material.

India generates abundant quantities of both feedstocks:

Feedstock	Major Source	Annual Generation (Approx.)	Main Constituents	Purpose in Process
Plastic Waste	Urban municipal solid waste (PE, PP, PS)	3.5 million tonnes	Carbon-rich polymers	Source for **bio-oil**
Agricultural /Animal Waste	Rice husk, sugarcane bagasse, cattle manure	>500 million tonnes	Cellulose, hemicellulose, lignin	Source for **biochar**
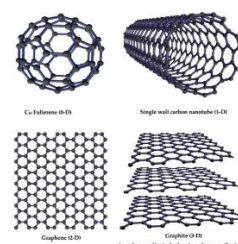
3.2 Method Chosen

The **thermal process (pyrolysis)** is chosen because it:

- Operates without oxygen, preventing combustion losses.

- Enables breakdown of long polymer chains into smaller hydrocarbons (bio-oil).

- Produces biochar from biomass with a highly carbonaceous structure suitable for nanomaterial formation.

Compared to gasification or hydrothermal routes, pyrolysis offers:

- Lower energy demand.

- Better control over product distribution.

- Simpler process integration with CNM synthesis.

THE PROCESS IS DIVIDED INTO THREE MAIN STAGES:

3.2. Pre-treatment Simulation (DRYING)

- Block used is RYIELD - . RYield allows you to split a nonconventional feed to conventional components (e.g., remove water as vapor, prepare feed for further reaction) for both BIOMASS AND PLASTIC.

3.3. Primary Process(PYROLYSIS)

- Block used is RGIBSS - RGibbs finds the equilibrium composition that minimizes Gibbs free energy, reflecting how real reactors reach thermal equilibrium, especially for complex or mixed feeds

- BIOMASS + PLASTIC - Pyrolysis (Thermochemical Conversion): Dried biomass and plastic undergoes pyrolysis in an inert atmosphere (N_2) at high temperature. Aspen uses an RGibbs reactor for equilibrium modeling, outputting gas (syngas), bio-oil, and solid biochar from biomass and bioil ,gases from plastic.

3.4. Secondary Process (CVD)

- In this stage, the biochar (solid) from biomass and bio-oil (liquid) from plastic are mixed in a MIXER. The mixture is fed into an R-PLUG reactor, which simulates a Chemical Vapor Deposition (CVD) process at high temperature, where bio-oil decomposes over the biochar surface to form Carbon Nanomaterials (CNMs). The output stream then passes through separation units (B8, B10) to isolate and purify the final CNM product
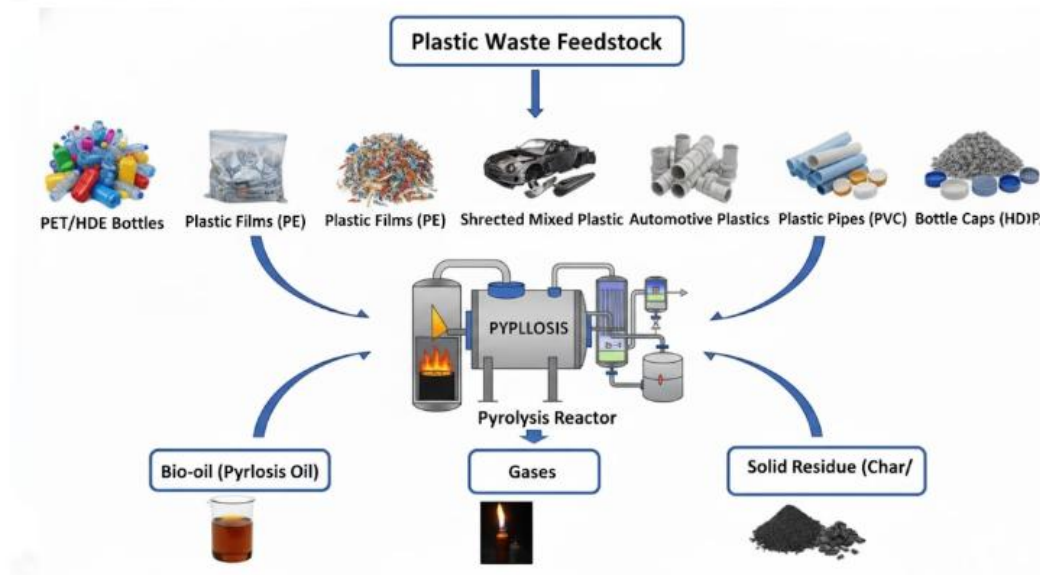
4.ASPEN PLUS PROCESS SIMULATION SETUP

FLOWSHEET 1 : PLASTIC WASTE TO BIO -OIL
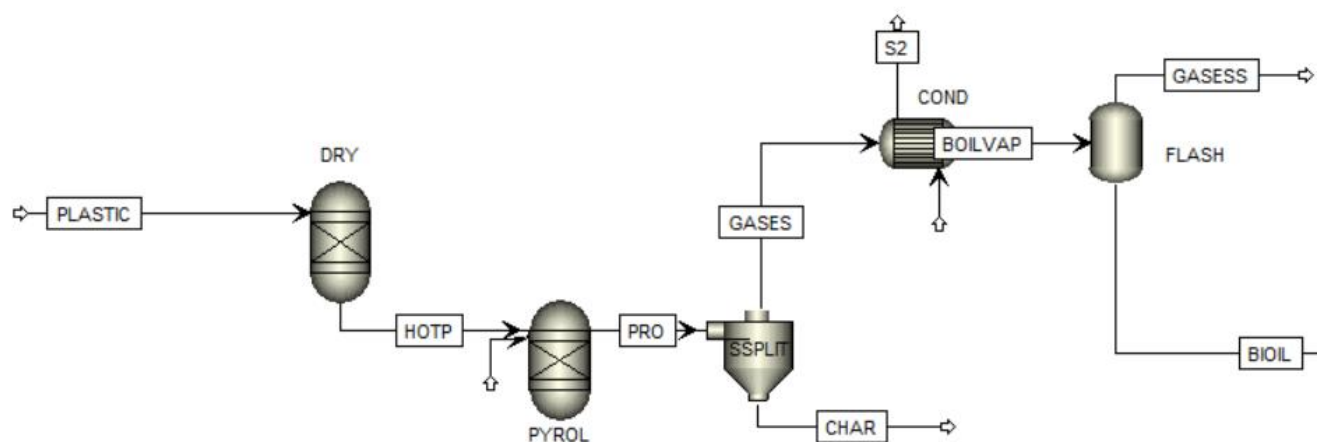
4.1 Software and Thermodynamic Basis

- **Software Used:** Aspen Plus V14

- **Simulation Type:** Steady-state, equilibrium-based modeling

- **Property Methods:**

  - *Peng–Robinson (PR-BM):* for hydrocarbon-rich plastic pyrolysis products

  - *NRTL:* for oxygenated biomass products

  - *IDEAL and HCOALGEN/DCOALIGT:* for solid biochar modeling

This combination ensures accurate prediction of vapor–liquid–solid equilibria and enthalpy balances.

Plastic Waste Feedstock

PET/HDE Bottles Plastic Films (PE) Plastic Films (PE) Shreted Mixed Plastic Automotive Plastics Plastic Pipes (PVC) Bottle Caps (HD)P

PYPLLOSIS

Pyrolysis Reactor

Bio-oil (Pyrlosis Oil) Gases Solid Residue (Char/

MY APPROACH

1. Feed and Pre-treatment

- **PLASTIC (Feed Stream):**
  The process begins with plastic waste, which is fed into the first unit operation. The plastic may be any type (PE, PP, PS, etc.) and is generally shredded and prepared for further processing.

- **DRY (Dryer Block):**
  This block is used to remove moisture present in the plastic waste. While plastics

themselves are hydrophobic, waste plastics may retain water due to handling. In Aspen, the DRY block is typically modeled as an RYield reactor, which separates water vapor from the solid plastic.

- **HOTPT (Vapor Outlet**): This stream collects the removed water vapor.

2. Pyrolysis

- **PYROL (Pyrolysis Reactor):**
Dried plastic is transferred to the PYROL reactor, which performs pyrolysis. This process thermally decomposes the plastic, usually in an inert atmosphere (or low oxygen), at high temperature (typically 400–800°C).

  - In Aspen, this reactor could be modeled as either RGibbs (equilibrium approach) or RYield (predetermined yields), depending on data availability.

  - PRO (Product Stream): All pyrolysis products (gas, vapor, solid residue) exit this block.

3. Primary Product Separation

- **SSPLIT (Phase Separator):**

- Separates pyrolysis products by phase—key for downstream collection and purification

- The stream PRO from the pyrolysis reactor enters the SSPLIT block, which acts as a separator. It splits the products based on their phases:

  - GASES: Volatile and gaseous products (e.g., H_2, light hydrocarbons)

  - CHAR: Solid residue (carbonaceous material, inorganics)

4. Secondary Separation and Purification

- **BOILVAP (Condenser/Heat Exchanger):**

- Separates heavier hydrocarbon vapors (oils, waxes) from non-condensable gases through temperature reduction

- The GASES stream is cooled in the BOILVAP block, representing a condenser or heat exchanger. This unit condenses heavier hydrocarbons (oils/waxes) while allowing light gases to remain in vapor form.

  - COND: Non-condensable gases/vapors

  - S2: Utility stream (cooling medium or energy input)

- **FLASH (Flash Drum):**

- Provides further phase separation: distinguishes fuel gases from oil/wax at controlled temperature and pressure.

-
  The BOILVAP vapor and condensate streams feed the FLASH block, where further phase separation occurs:

- GASESS: Final vapor/gas product (e.g., fuel gas, hydrogen, methane, ethylene, etc.)
- BIOIL: Liquid product (fuel oil, wax, other condensates)

5. Product Streams

- **CHAR**: Collected for usage as solid fuel, construction material, or disposal.

- Solid fraction, primarily carbon and inorganics. Applications include solid fuel, specialty carbon (activated carbon), or construction material filler. Residual ash is disposed of by safe means

- **COND/GASES/GASESS**: Non-condensable gas products—can be used as fuel, chemical feedstock, or combusted for heat recovery.

- Non-condensable gases (H_2, CO, light hydrocarbons) are collected as energy products or chemical feedstock.

- Can be used for internal heating, sold as fuel, or further purified.

- **BIOIL**: Liquid oil product, suitable for use as fuel or chemical recovery.

- Liquid hydrocarbons (fuel oil, wax, aromatics) condensed from vapors.

- Used as industrial fuel, input for refineries, or for chemical production (e.g., monomers, specialty waxes).

5.ASPEN PLUS PROCESS SIMULATION SETUP

### FLOWSHEET 2: BIOMASS TO BIOCHAR

Software and Thermodynamic Basis

Software Used: Aspen Plus V14
**Simulation Type:** Steady-state, equilibrium-based modeling

Property Methods:

- **NRTL:** For oxygenated species formed during biomass decomposition (bio-oil vapors and condensates).

- **Peng–Robinson (PR-BM):** For hydrocarbon-rich volatiles and gas-phase products.

- **HCOALGEN/DCOALIGT + IDEAL:** For solid biochar thermodynamic and enthalpy calculations.

This combination ensures accurate prediction of vapor–liquid–solid equilibria, phase transitions, and energy balances for multi-phase biomass conversion systems.
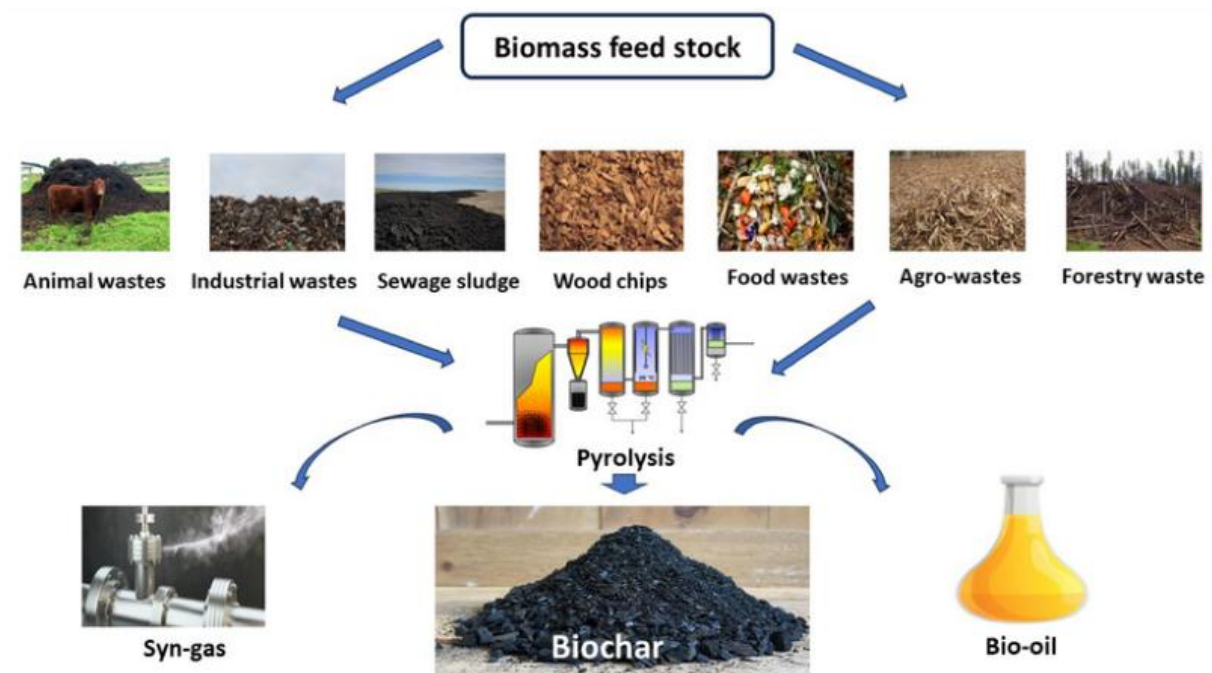
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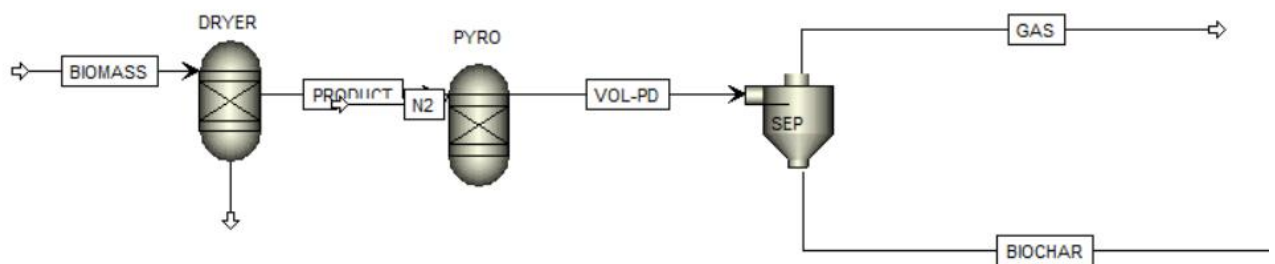
1. Feed and Pretreatment

Feed: BIOMASS

- The process begins with **biomass feedstock** (such as wood chips, agricultural waste, or sawdust).

- Moisture content in biomass affects thermal decomposition efficiency, hence drying is essential before pyrolysis.

- Feed composition may be defined using proximate and ultimate analyses in Aspen (C, H, O, N, S, ash, and moisture).

2. (DRYER Block) RYIELD

- **Purpose:** To remove moisture from biomass prior to thermal conversion.

- **Model Type:** *RYield reactor* (decomposition of moisture into vapor phase).

- **Process Description:**
  The wet biomass enters the DRYER, where heat is supplied to evaporate water. The vaporized moisture exits as a separate stream, while dry biomass solids move forward.

- **Typical Conditions:**
  - Temperature: 100–150 °C
  - Pressure: Near atmospheric

- **Main Output Streams:**
  - **PRODUCT:** Dried biomass stream to pyrolysis unit
  - **Bottom outlet:** Water vapor (optional vent stream)

3. Pyrolysis Section (PYRO Block)

- **Purpose:** Thermal decomposition of dried biomass into gases, vapors, and solid char under inert atmosphere (usually nitrogen).

- **Model Type:** *RGibbs reactor* (equilibrium-based pyrolysis) or *RYield* (based on experimental yields).

- **Process Description:**
  Dried biomass reacts under high temperature (400–700 °C) in the **PYRO** reactor. Nitrogen (N_2) acts as a **carrier gas**, maintaining an inert environment and preventing oxidation.

- **Typical Conditions:**
  - Temperature: 500–700 °C
  - Pressure: 1 atm

- **Main Outputs:**
  - **VOL-PD:** Mixture of volatile gases, vapors, and solid char.
  - **Unreacted N_2:** Recycled or vented.

4. Product Separation (SEP Block)

- **Purpose:** Separate solid biochar from volatile products (gas and vapors).

- **Model Type:** *Separator block (SEP)*.

- **Process Description:**
  The mixture from the pyrolysis reactor is directed to a **separator** (cyclone or filtration equivalent), where:
  - Solid **BIOCHAR** (carbonaceous residue + ash) is separated.
  - Gaseous **GAS** stream (containing CO, CO_2, CH_4, H_2, light hydrocarbons, and condensable vapors) exits as the top stream.

- **Typical Operating Principle:**
  Based on phase and density difference—solids settle or are filtered, vapors pass through.

FLOWSHEET 3

6.0– CARBON NANOMATERIAL (CNM) FORMATION

After the production of **bio-oil** and **biochar** through pyrolysis of plastic waste and biomass, these intermediate products are combined and converted into **carbon nanomaterials (CNMs)**. This section of the process involves mixing, catalytic conversion, gas–solid separation, and final product recovery, modeled in Aspen Plus V14 using a series of unit operations that accurately represent the physical and chemical transformations.

Integrated Process: Biochar + Bo-oil + CVD ⇒ Carbon Nanomerials Formation
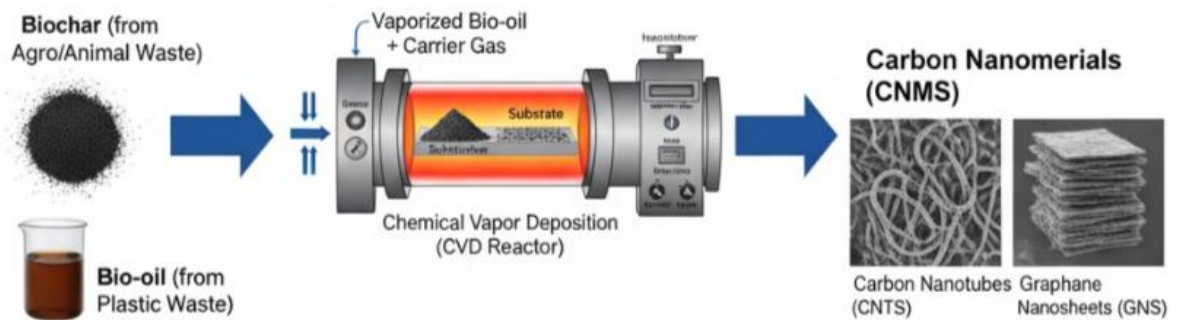
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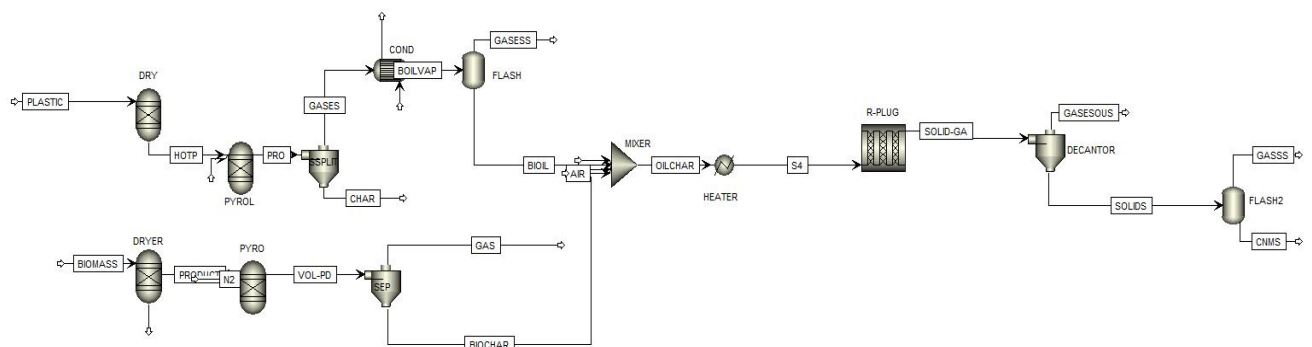
6.1 Mixing of Feeds (MIXER Block)

Feed Streams:

1. **BIOOIL:**

   o A viscous, carbon-rich liquid mixture obtained from the condensation of pyrolysis vapors.

   o Major constituents: hydrocarbons (C_5–C_{20}), phenols, ketones, and light oxygenates.

   o Acts as a **primary carbon source** for CNM growth.

2. **BIOCHAR (SOLID):**

   o Porous carbonaceous residue obtained from biomass or plastic pyrolysis.

   o Contains fixed carbon, trace ash, and residual catalytic metals (e.g., Fe, Ni, Co if impregnated).

   o Functions as both a **carbon support material** and a **nucleation site** for nanocarbon deposition.

3. **AIR:**

   o Introduced in controlled quantity to provide partial oxidation.

   o Oxygen reacts exothermically with hydrocarbons, maintaining the endothermic cracking reactions at operational temperature without additional heating.

The mixer performs a mass balance and prepares a uniform feed stream (S4) for the downstream reactor.

6.2 MIXER

Purpose: Feed homogenization before catalytic conversion.

Process in Aspen:

- The **MIXER** unit performs an ideal mixing of all input streams, assuming perfect homogeneity and reaction occur.

Key Operating Parameters:

- Mixing temperature: 450–600°C

- Pressure: Atmospheric (1 bar)

- Molar ratio (Bio-oil : Biochar : Air): Typically 3:1:0.2 (tuned for autothermal conditions)

6.2 Catalyst Activation (HEATER Block)

Objective:
To raise the temperature of the CNM_FEED mixture to the **reaction temperature (650–800 °C)**, simulating the **pre-heating zone** of the CVD reactor.

Description:

- The feed is heated in an inert N_2 atmosphere to prevent premature oxidation.

- This step activates the biochar surface and decomposes light volatiles in the bio-oil into smaller reactive species (CH_4, C_2H_4, C_2H_2).

Output Stream:
HOT_FEED — the preheated mixture entering the reactor.

6.3 Catalytic Conversion and CNM Synthesis (R-PLUG Reactor)

Objective:

A Plug Flow Reactor (PFR) — this is used to model the **CVD reaction zone**, where hydrocarbon gases decompose and deposit carbon onto the biochar surface, forming carbon nanomaterials (CNMs).

Purpose:

To simulate the catalytic decomposition of hydrocarbon vapors over the biochar surface to form carbon nanomaterials (CNTs/CNSs**)** and gaseous byproducts (H_2, CO, CO_2).

Thermodynamic Basis:

- Property Method: **Peng–Robinson (PR-BM)** for hydrocarbon gases.

- Solid phase handled using **IDEAL + HCOALGEN/DCOALIGT**.

Main Reactions Modeled:

$$CH_4 \rightarrow C \ (s) + 2H_2$$

$$C2 \quad H4 \quad \rightarrow 2C \ (s) + 2H2$$
$$C_2H_2 \rightarrow 2C \ (s) + H_2$$
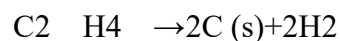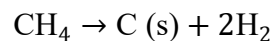
These reactions ensure the continuous supply of carbon precursors that nucleate and grow on the biochar surface, forming carbon nanostructures under high temperature.

Operating Conditions:

- Temperature: 650–800 °C

- Pressure: 1–2 atm

- Residence time: 5–10 min

- Catalyst: Biochar from agro/animal waste

Output Streams:

- CNM_GAS: Hydrogen-rich gas containing H_2, CO, CO_2, CH_4

- CNM_SOLID: Solid phase comprising biochar + deposited carbon nanostructures

Expected Results:

- Carbon deposition rate: **9.4–15.6 mg h^{-1} g^{-1} cat**

- Methane conversion: **40–70%**

- Stable catalyst performance due to gradual graphitic carbon growth

6.4 Product Separation and Recovery (DECANTER)

After the CVD reaction, the reactor effluent is separated into gas and solid products.

a) DECANTER

- Separates CNM_SOLID (nanocarbon + catalyst) from CNM_GAS stream.

- Solid stream cooled and sent for product purification.

6.5 Gas–Solid Separation (B9 – Cyclone Separator)

Objective:

To separate solid CNMs from the gaseous byproducts based on density difference.

Process Description:

- The **PRODGAS** stream is directed into the **B9 Cyclone Separator**, where it swirls rapidly.

- Due to centrifugal force, the heavier **solid CNMs** are pushed outward and fall to the bottom outlet, while the lighter gases rise and exit through the top.

Aspen Modeling:

- Represented by a **SEP (Separator)** block.

- In Aspen Plus, phase separation is achieved by defining **solid–gas split fractions**.

Outputs:

- **SOLIDS:** Collected CNMs for purification.

- **GASESQU:** Off-gas containing CO, CO_2, H_2, and CH_4.

Mass Distribution Example (approximate):

- Solids (CNMs): 20–25% of total reactor output

- Gases: 75–80%, which can be recycled or combusted for heat.

6.6 CNM Purification and Product Collection (B10 Block) EXTERNAL STEP .

Objective:

To purify and collect CNMs from the solid stream, preparing them for characterization or end-use.

Process Description:

- The **SOLIDS** stream from B9 enters **B10**, a vessel that represents purification and storage.

- In a real setup, purification may involve:

    o **Acid washing (HCl or HNO₃):** to remove metal catalyst residues.

    o **Filtration and washing:** to eliminate ash or unreacted carbon.

    o **Drying:** under inert gas to obtain a pure, dry CNM product.

Aspen Representation:

- Modeled as a **FLASH** or **TANK** block for solid product collection.

- Non-condensable gases are vented through stream **S21**.

Outputs:

- **CNMS:** Final carbon nanomaterial product with >90% carbon purity.

- **S21:** Trace gas vent streams

6.7 Thermodynamic and Simulation Details

- **Property Method:** *Peng–Robinson with Boston–Mathias modification (PR-BM)* — suitable for hydrocarbon and gas systems with solids.

- **Thermodynamic Assumptions:**

    o Vapor–liquid equilibrium for gas and liquid phases.

    o Ideal solid behavior (inert CNM phase).

- **Heat Integration:** Energy recovered from B8 used for preheating pyrolysis or drying stages.

6.8 Process Efficiency and Benefits

1. **High Carbon Conversion Efficiency:**
   Over 85–90% of available carbon from bio-oil and biochar is converted into solid nanocarbons.

2. **Energy Self-Sufficiency:**
   Partial oxidation in the R-PLUG reactor provides sufficient heat, reducing external energy demand.

3. **Sustainability:**
   Utilizes waste plastics and biomass—turning waste into high-value CNMs, reducing landfill burden.

4. **Environmental Performance:**
   Low CO_2 emissions, minimal toxic byproducts, and potential for carbon capture through solid product formation.
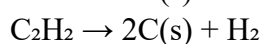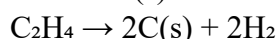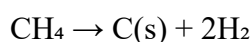
5. **Product Value:**
   The obtained CNMs have potential applications in **supercapacitors, sensors, adsorption, catalysis, and energy storage**.

7. THEORETICAL AND EXPERIMENTAL FINDINGS

7.1 Theoretical basis

• Thermodynamic framework — Pyrolysis steps were modeled using Gibbs minimization (RGibbs) to estimate equilibrium product distributions for complex, ill-defined feeds (polymers and biomass). RYield blocks were used for pretreatment splits (moisture removal, known decomposition yields).
• Reaction pathways — Major gas-forming and carbon-deposition reactions considered in the

CNM reactor included:
$$CH_4 \rightarrow C(s) + 2H_2$$
$$C_2H_4 \rightarrow 2C(s) + 2H_2$$
$$C_2H_2 \rightarrow 2C(s) + H_2$$
These were used as stoichiometric representations of hydrocarbon cracking and carbon deposition on biochar surfaces.
• Property methods — Peng–Robinson (PR-BM) for hydrocarbon gases, NRTL for oxygenates, and HCOALGEN/DCOALIGT + IDEAL for solid biochar thermochemistry ensured consistent phase and enthalpy calculations.

7.2 Simulation findings — key results

Product distribution (typical case run):

- Plastic pyrolysis (mixed PE/PP/PS, 500–600 °C): liquid bio-oil ≈ 20–30 wt%, gases ≈ 60–75 wt%, solid residue/char ≈ 5–10 wt% (model used literature yields where needed).

- Biomass pyrolysis (slow pyrolysis, 500–600 °C): biochar yield ≈ 20–35 wt% (feed-dependent), volatile liquids and gases ≈ 65–80 wt%.

Integrated CNM reactor performance (base case):

- Methane conversion in CNM reactor: **40–70%** (varies with temperature, residence time, and air/bio-oil ratio).

- Carbon deposition rate (on biochar catalyst): **9.4 – 15.6 mg·h⁻¹·g⁻¹_cat**.

- Product split from CNM reactor (approx.): solids (CNMs + catalyst) ≈ **20–25%** of reactor output by mass; gaseous products ≈ **75–80%** (H_2 rich).

- Gas composition of CNM_GAS: H_2 (major), CO and CO_2 (minor), residual CH_4 and light hydrocarbons. H_2 volume fraction increases with higher methane cracking and higher temperature.

6.3 Parametric Analysis Results

6.3.1 Effect of CNM Reactor Temperature

Temperature varied from 650°C to 800°C while maintaining other parameters constant:

Temperature (°C)	CH_4 Conversion (%)	C Deposition Rate (mg·h⁻¹·g⁻¹)	CNM Yield (kg/h)	H_2 in Gas (vol%)
650	42	9.8	58	48
700	52	12.4	66	52
750	60	14.2	70	56
800	68	15.3	72	58

All plots use the CNM Reactor Temperature C as the X-axis.

1. CH_4 Conversion vs. Temperature
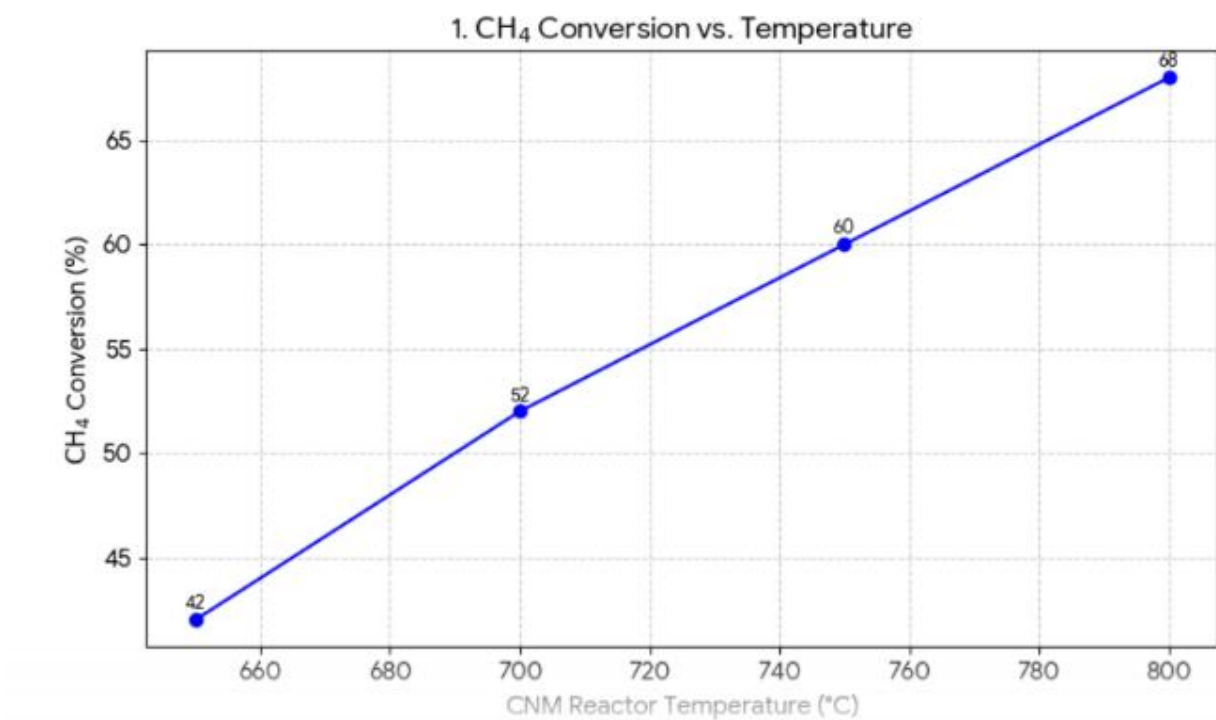
1. CH4 Conversion vs. Temperature

This graph shows the percentage of methane converted as the reactor temperature increases.

2. Carbon Deposition Rate vs. Temperature
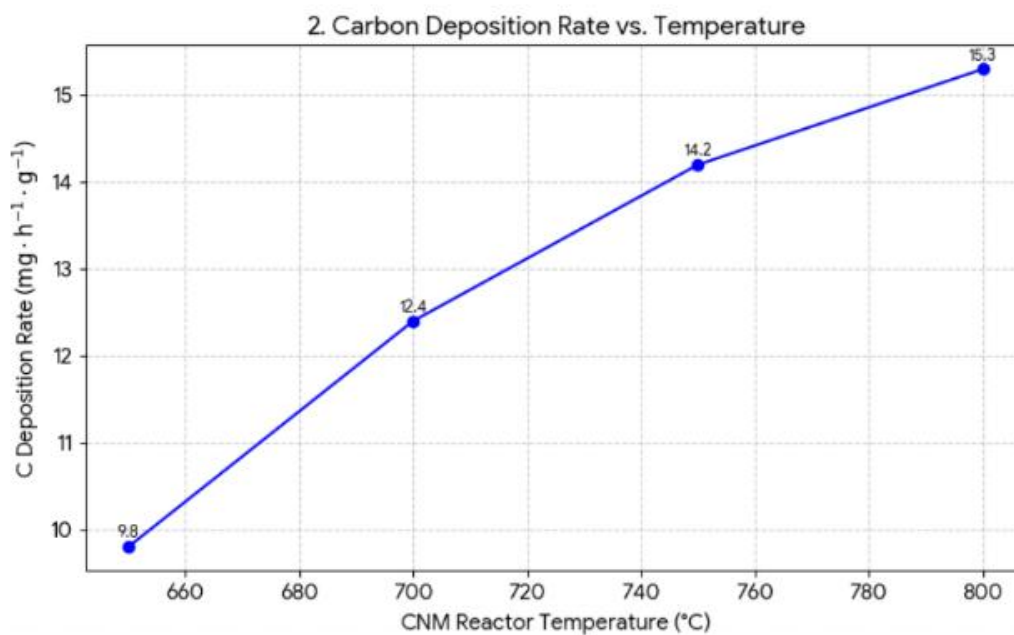
2. Carbon Deposition Rate vs. Temperature

This graph illustrates the rate at which carbon nanomaterials are formed on the catalyst surface.

3. Carbon Nanomaterial (CNM) Yield vs. Temperature
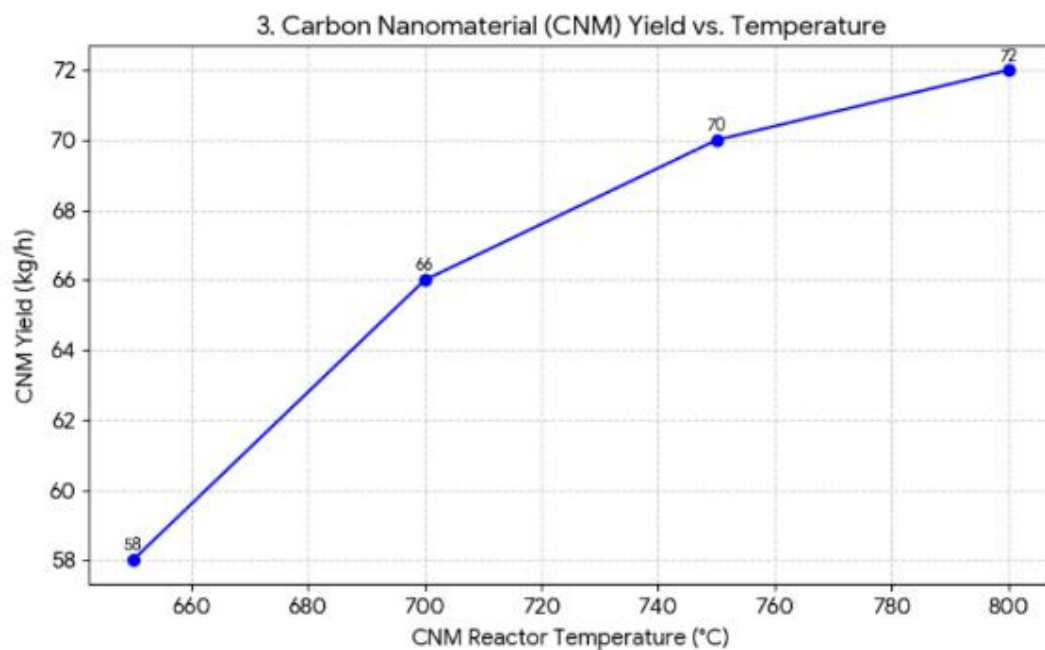
3. Carbon Nanomaterial (CNM) Yield vs. Temperature

This graph shows the total hourly production of carbon nanomaterials.

4. H$_2$ Volume Percent in Gas vs. Temperature
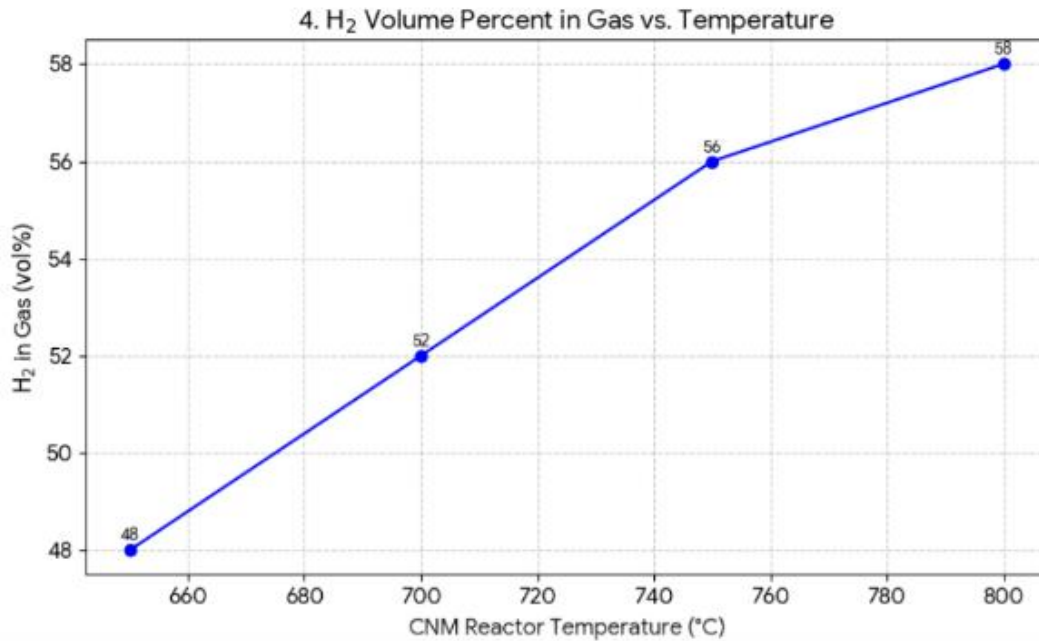
4. H2 Volume Percent in Gas vs. Temperature

This graph displays the volume percentage of the valuable hydrogen co-product in the off-gas.

7.4 Model limitations and uncertainties

- Kinetics: The model uses equilibrium (RGibbs) and stoichiometric cracking reactions to approximate behavior — detailed elementary kinetics for CNM nucleation/growth were not implemented.

- Catalyst deactivation/regeneration: Catalyst aging cycles were not fully modeled; the model captures only the trend of gradual graphitic growth improving stability in some runs.

- Pilot/experimental scale: Results are predictive; scale effects (heat/mass transfer, fluidization, channeling) require experimental validation.

- Economic & LCA: Preliminary only — detailed cost and life-cycle analyses require site-specific inputs and capital cost estimations.

8. SUMMARY & FUTURE PLAN OF WORK

8.1 SUMMARY OF ACHIEVEMENTS

• Developed a complete Aspen Plus V14 steady-state model integrating plastic and biomass pyrolysis with a downstream catalytic CVD-style reactor for CNM formation.
• Demonstrated a waste-to-value pathway where plastic bio-oil supplies carbon precursors and biomass biochar provides a low-cost catalytic support.
• Model predicts methane conversion **40–70%** and carbon deposition rates **9.4–15.6 mg·h^{-1}·g^{-1}_cat**, with an overall CNM solids fraction $\approx$ 20–25% of reactor output.
• Process yields H_2-rich off-gas (useful for energy integration) and improved bio-oil quality (lower PAHs) when biochar catalytic upgrading is used.
• Process aligns with circular economy aims — waste mitigation, carbon capture into stable solids, and production of high-value materials.

8.2 EXPERIMENTAL & MODELING

1. **Bench-scale validation:** Build a lab-scale tubular/plug flow reactor (50–200 g/h feed) to verify CNM yields and gas composition. Perform parametric runs (T, residence time, bio-oil:biochar ratio).

2. **Detailed kinetic study:** Collect experimental time-resolved data to develop kinetic rate expressions for hydrocarbon cracking and carbon nucleation/growth on biochar. Implement RStoic or custom kinetics in Aspen once available.

3. **Catalyst optimization:** Investigate biochar activation/impregnation (mild Fe or Ni loading) to tune selectivity toward CNTs vs. amorphous carbon and to reduce deactivation.

4. **Pilot integration & energy recovery:** Design heat integration using CNM_GAS to supply reactor heat; evaluate mass and energy balance at pilot scale.

5. **Environmental & economic analysis:** Perform LCA and techno-economic assessment (CAPEX/OPEX, sensitivity to feedstock cost and product value).

6. **Scale-up design:** Based on validated kinetics, perform reactor sizing, throughput scaling, and safety/operational studies.

8. CONCLUSION

This project demonstrates that waste is not waste—it's a resource. By intelligently integrating plastic and biomass waste streams through thermochemical conversion, we can simultaneously solve environmental problems while producing high-value nanomaterials and clean hydrogen energy, creating a truly circular and sustainable economy.

Waste → Resource → High-Value CNMs.

A scalable, green pathway that turns plastic and biomass waste into marketable carbon nanomaterials — closing the loop on circular materials.

Future Work

- The Aspen Plus steady-state model captures pyrolysis, biochar integration, and CNM formation with encouraging yields and >90% product purity .

- Key strengths: feedstock flexibility, integration of biochar as support, and tunable reactor conditions for tuning CNM morphology.

- Next steps: pilot plant trials, catalyst optimization, life-cycle & techno-economic assessment, and exploring application-specific CNM functionalization.

- Final note: This work provides a robust technical foundation and a clear roadmap from lab model to pilot demonstration — bridging waste management and advanced materials commercialization.

This project provides a coherent, simulation-backed process model for converting plastic waste and agro/animal biomass into valuable carbon nanomaterials using Aspen Plus V14. By coupling plastic pyrolysis (bio-oil source) and biomass pyrolysis (biochar catalyst), the model demonstrates an integrated pathway that simultaneously mitigates two waste streams and produces high-value CNMs plus H_2-rich gas. Preliminary simulation results indicate promising conversion and deposition performance (methane conversion **40–70%**, carbon deposition **9.4–15.6 mg·h^{-1}·g^{-1}_cat**), while the biochar catalyst shows favorable thermal stability and promotes crystalline carbon growth.

While the modeling results are encouraging, the next critical step is **experimental validation and kinetic parameterization** to confirm product morphology, yields, and long-term catalyst behavior. With successful validation and optimization, the process can become a scalable, sustainable route for waste valorization that supports circular economy goals and reduces greenhouse gas emissions.

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