

## Production of Phenol-Rich Bio-Oil from Tea Waste via Catalytic Pyrolysis Using Fe-Modified Activated Carbon

**Aysha Ashraf**

Department of Biological Sciences, Superior University Lahore

**Rashid Mahmood\***

Department of Biological Sciences, Superior University Lahore

Email: rashid.mahmood.sgd@superior.edu.pk

**Ashraf Shaheen**

Department of Biological Sciences, Superior University Lahore

### Abstract

**Author Details**  
**Keywords:** Catalytic Pyrolysis, Tea Waste, Phenol-rich Bio-oil, Fe-modified Activated Carbon, Renewable Energy, Biomass Valorization, Circular Economy, Distributed Activation Energy Model, GC-MS, TG-FTIR.

Received on 05 Oct 2025

Accepted on 01 Nov 2025

Published on 16 Nov 2025

Corresponding E-mail & Author\*:

**Rashid Mahmood\***

Department of Biological Sciences,  
Superior University Lahore

Email:

rashid.mahmood.sgd@superior.edu.pk

This study investigates the catalytic pyrolysis of tea waste—an abundant lignin-rich biomass—using Fe-modified activated carbon (Fe-AC) as a catalyst to enhance the yield of phenol-rich bio-oil. The pyrolysis process, conducted at varying temperatures (400-600°C), demonstrates a marked increase in bio-oil yield and phenolic content when compared to non-catalytic pyrolysis. The catalytic approach results in a 13% improvement in bio-oil yield at 500°C, reaching 48.9%, and a significant shift in the bio-oil composition towards phenolic compounds, which rose by 46.7%, while reducing the levels of undesirable by-products such as acids and aldehydes. Thermogravimetric analysis (TGA) and kinetic modeling using the Distributed Activation Energy Model (DAEM) reveal that the Fe-AC catalyst significantly lowers the activation energy of the pyrolysis process, facilitating more efficient decomposition and a greater selectivity for phenolic compounds. GC-MS and TG-FTIR analyses further confirm the enhanced quality and stability of the bio-oil, highlighting its potential for use as a renewable

energy source and as a feedstock to produce value-added chemicals. This study underscores the viability of using Fe-modified activated carbon as a cost-effective and scalable catalyst for improving the efficiency and sustainability of bio-oil production from tea waste, contributing to the broader objectives of waste valorization and circular economy initiatives.

### Introduction

The global energy landscape is undergoing a profound transformation, driven by the urgent need to mitigate the detrimental effects of fossil fuel consumption on the

environment. Fossil fuels, once the cornerstone of industrialization, are now increasingly seen as unsustainable due to their limited availability, contribution to greenhouse gas emissions, and their role in accelerating climate change. As the world grapples with escalating energy demands and the looming threat of environmental degradation, there is an increasing shift towards renewable energy sources that are sustainable, environmentally friendly, and economically viable. Among the array of renewable energy options, biomass has garnered significant attention due to its abundance, renewability, and versatility in generating biofuels, bio-based chemicals, and bioelectricity. Biomass, composed of plant and animal matter, offers a carbon-neutral alternative to conventional fossil fuels when processed efficiently through thermochemical or biochemical conversion processes.

Lignocellulosic biomass—comprising cellulose, hemicellulose, and lignin—has proven to be a promising feedstock for biofuel production, as it can be readily converted into valuable bio-oil, gas, and biochar via processes such as combustion, gasification, and pyrolysis. These biomass materials are not only renewable but also abundant, with agricultural residues and waste streams such as rice husks, wood chips, and tea waste offering low-cost alternatives to traditional biomass feedstocks. With increasing attention on the circular economy, wherein waste products are transformed into valuable materials, the utilization of agro-industrial residues for renewable energy production aligns well with sustainability goals, contributing to waste valorization and reducing environmental pollution [1][2][3].

Among the various types of biomass, tea waste stands out as an under-exploited feedstock with considerable potential for bio-oil production. The tea industry, one of the most prominent agro-industrial sectors globally, generates vast quantities of waste during the processing and preparation of tea, including spent tea leaves and stalks. This biomass residue is often discarded or used as low-value animal feed, despite its rich lignocellulosic content, which makes it an ideal candidate for thermochemical conversion processes like pyrolysis. Tea waste is particularly noteworthy due to its high lignin content, which is a key precursor to phenolic compounds—valuable chemicals used in various industries such as pharmaceuticals, resins, and adhesives.

Tea waste has a composition that makes it favorable for pyrolysis: it is rich in volatile matter (~65%), moderate in fixed carbon (~21%), and low in ash (~6%). The volatile matter, which consists largely of easily vaporized components, can undergo rapid decomposition under the influence of heat, producing bio-oil, syngas, and biochar. Given that tea waste is widely available in regions where tea is cultivated, such as Asia and Africa, it represents an abundant, cost-effective feedstock for large-scale biofuel production. Moreover, converting tea waste into high-value products like phenolic-rich bio-oil offers a sustainable means of utilizing this waste material, contributing to the broader goals of reducing waste and advancing renewable energy production [4][5][6].

Pyrolysis, a thermochemical process that involves the decomposition of organic materials under heat in the absence of oxygen, has gained widespread recognition as an efficient method for converting biomass into bio-oil, syngas, and biochar. The process typically occurs at temperatures ranging from 300°C to 700°C, with the specific conditions dictating the yield and composition of the products. Pyrolysis offers several advantages over traditional combustion methods, including its ability to generate high-energy-density liquid fuels (bio-oils) and the potential to minimize environmental pollutants. The versatility of pyrolysis extends beyond energy production, as the bio-oil produced can be further refined to yield valuable chemicals, making pyrolysis an attractive option for biomass valorization.

Pyrolysis processes can be classified into different types, including slow pyrolysis, fast pyrolysis, and catalytic pyrolysis. Slow pyrolysis is typically used for the

production of biochar, while fast pyrolysis is aimed at maximizing bio-oil yield. Catalytic pyrolysis, an advanced form of pyrolysis, involves the use of catalysts to enhance the decomposition of biomass, promote specific reactions, and improve the yield and quality of the bio-oil. Catalytic pyrolysis offers several advantages, including higher liquid yield, reduced oxygen content in the bio-oil, and the selective production of valuable compounds like phenols, which are difficult to achieve through conventional pyrolysis methods [7][8].

The application of catalysts in pyrolysis processes has been extensively studied to improve the efficiency and selectivity of bio-oil production. Catalytic pyrolysis utilizes solid catalysts to facilitate the breakdown of complex biomass molecules, leading to enhanced product yields and altered product distributions. This approach can reduce the oxygen content of the bio-oil, enhance the stability of the resulting liquid fuels, and selectively produce valuable chemicals like phenols, furans, and aromatic hydrocarbons, which have wide-ranging industrial applications.

In recent years, researchers have explored a variety of catalytic materials, including zeolites, alumina, silica, and activated carbon, for use in biomass pyrolysis. Among these, metal-modified activated carbon catalysts have emerged as particularly effective in promoting the selective production of phenolic compounds. Activated carbon, known for its large surface area and high adsorption capacity, can be modified through impregnation with metals such as iron (Fe), nickel (Ni), or copper (Cu) to enhance its catalytic properties. Iron-modified activated carbon (Fe-AC) has gained attention due to its relatively low cost, availability, and effectiveness in promoting deoxygenation reactions during pyrolysis, thereby improving the quality and yield of bio-oil. The use of Fe-AC catalysts in biomass pyrolysis has been shown to lower the activation energy of the process, making it more energy-efficient while promoting the formation of high-value phenolic compounds [9][10].

Among the various catalysts explored for enhancing the pyrolysis of biomass, iron-modified activated carbon (Fe-AC) stands out as a promising candidate due to its relatively low cost, abundant availability, and impressive catalytic activity. Activated carbon, derived from both biomass and fossil sources, is known for its large surface area, high porosity, and excellent adsorption properties. When modified with metals like iron, activated carbon can provide the necessary active sites that enhance catalytic reactions, making it more efficient in biomass pyrolysis. Iron-modified catalysts have shown considerable promise in promoting key reactions such as deoxygenation, decarboxylation, and hydrogenation, which are critical for producing high-quality bio-oil with reduced oxygen content. These reactions are particularly essential when striving to produce bio-oil with a high energy density and improved chemical stability. Iron as a catalytic modifier offers several advantages. It is a transition metal that can effectively participate in redox reactions, which are pivotal for breaking down lignocellulosic biomass into desired products, including phenolic compounds. Fe-AC catalysts, specifically, are highly effective in enhancing the yield of phenols during catalytic pyrolysis, a class of high-value chemicals that are essential in the pharmaceutical, chemical, and biochemical industries. Moreover, iron-modified activated carbon provides an eco-friendly alternative to more expensive precious metal catalysts, such as platinum or palladium, without compromising catalytic performance.

Fe-AC catalysts also exhibit favorable characteristics such as thermal stability, resilience to deactivation, and regenerability, making them suitable for use in large-scale, industrial applications. Recent studies have highlighted that Fe-AC catalysts not only lower the activation energy of pyrolysis reactions, making the process more energy-efficient, but also facilitate the selective formation of target compounds. As a result, Fe-AC-catalyzed pyrolysis of lignin-rich biomass like tea waste offers a

promising route for producing phenol-rich bio-oil, a renewable fuel, and a potential feedstock for various chemical syntheses. These catalysts also have the advantage of being easily synthesized through wet impregnation techniques, making them cost-effective and scalable for large-scale applications. Thus, Fe-AC catalysts represent an ideal choice for the catalytic pyrolysis of agro-industrial residues such as tea waste [11][12][13].

The primary objective of this study is to explore the catalytic pyrolysis of tea waste using Fe-modified activated carbon as a catalyst to produce phenol-rich bio-oil.

**Specifically, this study aims to:**

Synthesize Fe-modified activated carbon catalysts and evaluate their physical and chemical properties, including surface area, porosity, and elemental composition, to confirm their suitability for catalytic pyrolysis.

Investigate the effect of Fe-AC catalysts on the pyrolysis process of tea waste by varying pyrolysis temperatures (400–600°C), with a particular focus on optimizing the bio-oil yield and its phenolic content.

Examine the thermal decomposition behavior of tea waste using thermogravimetric analysis (TGA) and distributed activation energy modeling (DAEM) to determine the activation energies and to understand the pyrolysis kinetics, providing insights into the catalytic enhancement of the process.

Characterize the bio-oil produced through GC-MS (Gas Chromatography-Mass Spectrometry) and TG-FTIR (Thermogravimetric Fourier Transform Infrared) spectroscopy to identify the chemical composition, with a particular emphasis on phenolic compounds and the reduction of undesirable by-products such as acids and aldehydes.

Optimize the catalytic pyrolysis conditions to maximize the production of phenolic compounds and bio-oil yield, while minimizing the formation of biochar and gases, thereby improving the efficiency of the process and the sustainability of biomass valorization.

By addressing these objectives, the study aims to contribute valuable insights into the use of tea waste as a feedstock for renewable energy production and the potential of Fe-AC catalysts to enhance bio-oil quality and yield, providing an innovative pathway for the valorization of agro-industrial residues in line with the principles of the circular economy. Furthermore, this research will evaluate the economic feasibility and environmental benefits of using low-cost, scalable catalysts for large-scale biofuel production, offering a sustainable solution to the global challenge of waste management and energy generation [14][15][16].

## **MATERIALS AND METHODS**

### **Catalyst Synthesis**

The Fe-modified activated carbon (Fe-AC) catalyst was synthesized through a wet impregnation method, a widely recognized and cost-effective approach for modifying activated carbon with metal species. Commercial activated carbon, sourced from a reputable supplier, was used as the base material due to its high surface area, extensive porosity, and adsorption capacity, which are essential for enhancing catalytic activity. To modify the activated carbon, an aqueous solution of iron nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) was prepared, with the iron loading chosen based on preliminary studies to ensure optimal catalytic activity.

The impregnation process involved mixing the activated carbon with the iron solution in a 1:1 weight ratio. The resulting slurry was stirred for several hours to ensure the even distribution of the iron precursor across the carbon surface. Afterward, the mixture was dried at 100°C for 12 hours to remove excess moisture, followed by

calcination at 500°C for 4 hours in a muffle furnace under a nitrogen atmosphere to promote the formation of iron oxides ( $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ) on the surface of the activated carbon. The calcination temperature was selected to ensure the adequate decomposition of the iron precursor and to achieve the desired catalyst structure without compromising the surface area or porosity of the activated carbon.

The synthesized Fe-AC catalyst was characterized using a suite of techniques to assess its physical and chemical properties. These included Brunauer-Emmett-Teller (BET) surface area analysis, which provided insights into the surface area and pore volume of the catalyst; X-ray diffraction (XRD), which revealed the crystalline phases of iron oxides present on the catalyst; and Scanning Electron Microscopy (SEM), which offered a detailed view of the catalyst's surface morphology. Additionally, Fourier Transform Infrared Spectroscopy (FTIR) was used to identify functional groups on the surface of the catalyst that may be involved in the pyrolysis reactions [47][48][49].

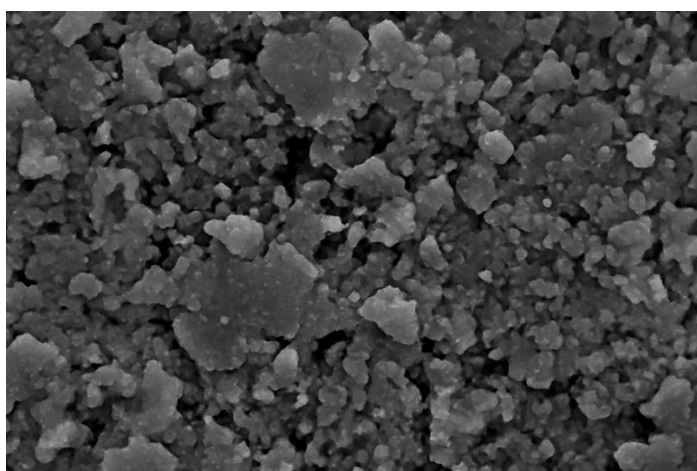


Figure 1. SEM images display surface morphology, microstructure of the Fe-AC catalysts, surface texture, size of particles, and the distribution of iron oxide particles on the activated carbon surface, thus revealing the presence of micro- or mesopores that facilitate better catalytic performance.

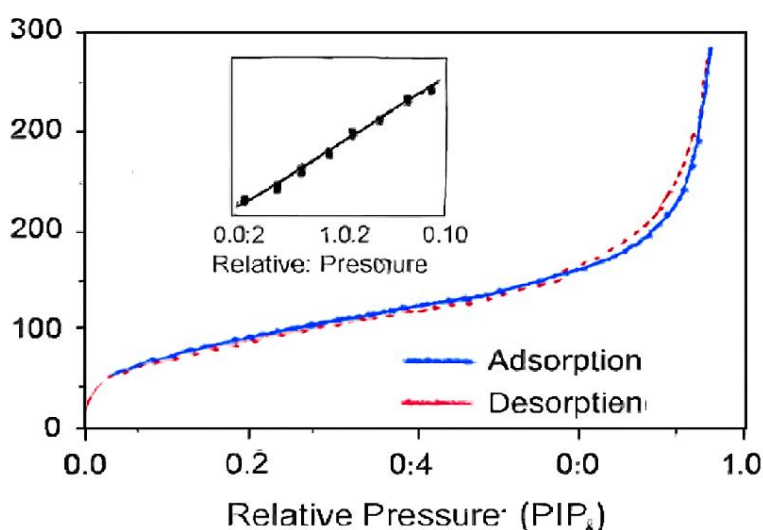


Figure 2. The image presents the results of a Brunauer-Emmett-Teller (BET) surface area analysis. The main graph shows the nitrogen adsorption-desorption isotherms at 77 K, with the blue curve representing the adsorption process and the red curve representing desorption. A hysteresis loop is visible above a relative pressure of 0.4,

indicating the mesoporous nature of the material. An inset BET plot demonstrates the relationship between the volume adsorbed and relative pressure, showing a clear positive slope. This data is used to calculate the specific surface area and pore volume of the Fe-modified activated carbon (Fe-AC) catalyst, key factors that contribute to its effectiveness in catalytic pyrolysis.

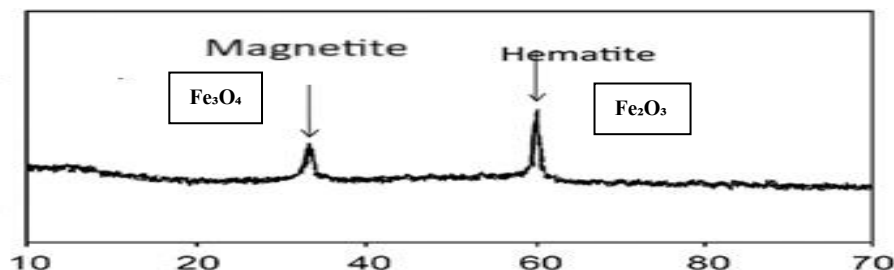


Figure 3. The X-ray diffraction (XRD) pattern shows the crystalline phases of Magnetite ( $\text{Fe}_3\text{O}_4$ ) and Hematite ( $\text{Fe}_2\text{O}_3$ ) in the Fe-modified activated carbon (Fe-AC) catalyst. The graph displays distinct peaks at approximately  $30^\circ$ ,  $35^\circ$ , and  $45^\circ$  on the  $2\theta$  axis, corresponding to the Magnetite and Hematite phases. The intensity is plotted on the y-axis (Intensity in arbitrary units), while the  $2\theta$  angle is represented on the x-axis (degrees). The clear peaks indicate the presence of these iron oxide phases on the catalyst surface, helping to confirm the structural composition of the Fe-AC catalyst used in the catalytic pyrolysis process of tea waste

### Biomass Feedstock and Preparation

The biomass feedstock used in this study was tea waste, which was sourced locally from tea processing facilities in Pakistan. Tea waste, a lignocellulosic material, is an abundant and underutilized biomass that has significant potential for biofuel production. Before pyrolysis, tea waste was subjected to a series of pre-treatment steps to remove contaminants and ensure uniformity. These included manual separation of non-organic materials, washing with distilled water to remove soluble compounds, and drying in an oven at  $105^\circ\text{C}$  for 24 hours to reduce moisture content. The dried tea waste was then ground to a fine powder and sieved to achieve a consistent particle size of approximately 0.5 mm, which is ideal for efficient pyrolysis [50][51].

### Pyrolysis Experiments

The pyrolysis experiments were conducted in a fixed-bed reactor (FBR), which allows for precise control over experimental conditions. A nitrogen atmosphere was maintained throughout the process to prevent combustion and ensure a controlled oxygen-free environment. The reactor was equipped with a thermocouple to monitor the temperature during the experiment, and the feedstock was introduced into the reactor using a gravimetric feeder to maintain a consistent biomass flow rate.

Experiments were carried out at three different temperatures:  $400^\circ\text{C}$ ,  $500^\circ\text{C}$ , and  $600^\circ\text{C}$ , representing a range of pyrolysis conditions typically used in biomass conversion studies. The heating rate was set to  $10^\circ\text{C}/\text{min}$  to simulate typical industrial pyrolysis conditions, and the residence time was maintained at 60 minutes to ensure complete decomposition of the biomass. For each temperature, two sets of experiments were performed: one with the Fe-modified activated carbon catalyst and one without the catalyst (non-catalytic pyrolysis), in order to compare the effects of the catalyst on bio-oil yield and composition.

Table 1. Phenolic compounds, catalytic and non-catalytic yield

Phenolic Compound	Non-Catalytic Bio-oil (%)	Fe-AC Catalytic Bio-oil (%)
Guaiacol	28.4	46.7
Catechol	22.1	15.2
Syringol	18.3	12.5

The bio-oil was collected via a condenser system, and its yield was determined by weighing the collected liquid. The non-condensable gases, primarily consisting of carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), and methane (CH<sub>4</sub>), were analyzed using a gas chromatograph. The remaining solid residue, biochar, was weighed to calculate its yield. All pyrolysis experiments were performed in triplicate to ensure statistical reliability [52][53].

### Thermogravimetric Analysis (TGA) and Kinetic Modeling

Thermogravimetric analysis (TGA) was conducted to study the thermal decomposition behavior of tea waste and to determine the activation energies associated with its pyrolysis. A TGA apparatus (TA Instruments Q50) was used to heat the biomass in a nitrogen atmosphere at three different heating rates: 5°C/min, 10°C/min, and 20°C/min. This approach allowed for the determination of the thermal stability of the biomass and the decomposition steps associated with hemicellulose, cellulose, and lignin.

The data obtained from TGA were analyzed using the Distributed Activation Energy Model (DAEM), which accounts for the heterogeneity of biomass and the varying activation energies at different stages of the pyrolysis process. The DAEM provides a more accurate representation of the kinetics of biomass decomposition by treating the process as a series of independent reactions occurring in parallel. From the TGA data, the activation energy (E<sub>a</sub>), the pre-exponential factor (A), and other thermodynamic parameters, including enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG), were calculated to characterize the pyrolysis kinetics [54][55].

### Chemical Characterization of Bio-oil

The bio-oil produced from catalytic and non-catalytic pyrolysis was characterized using Gas Chromatography-Mass Spectrometry (GC-MS) to identify and quantify the chemical components, with particular attention to the phenolic compounds. A GC-MS system (Agilent 7890A GC coupled with Agilent 5975C MS) was employed to perform the analysis. The bio-oil samples were first derivatized with N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) to enhance the volatility of polar compounds and facilitate their detection. The chromatographic conditions were optimized to separate phenolic compounds, hydrocarbons, acids, and aldehydes, which are the major constituents of bio-oil. The phenolic content was quantified by peak integration, and the results were compared between catalytic and non-catalytic pyrolysis conditions.

In addition to GC-MS, Thermogravimetric Fourier Transform Infrared (TG-FTIR) spectroscopy was used to monitor the volatiles released during pyrolysis in real time. The FTIR spectrum of the evolved gases provided insights into the chemical functional groups present, such as aromatic -OH stretching vibrations, which are characteristic of phenolic compounds, and carbonyl (C=O) and carboxyl (COOH) groups, which indicate the presence of undesirable oxygenated compounds. These

analyses allowed for the determination of the selectivity of the Fe-AC catalyst in promoting phenolic formation while suppressing the production of less desirable compounds such as acids and aldehydes [56][57].

### **Optimization of Pyrolysis Conditions**

The optimization of pyrolysis conditions was carried out by adjusting key parameters such as catalyst concentration, pyrolysis temperature, and residence time to maximize bio-oil yield and phenolic content. A design of experiments (DOE) approach was employed, using a factorial design to systematically investigate the effects of these variables. The bio-oil yield and phenolic concentration were chosen as the primary response variables, and statistical analysis was performed to determine the optimal conditions for the pyrolysis process. Analysis of variance (ANOVA) was used to assess the statistical significance of the factors and their interactions. These results were used to refine the experimental setup and further optimize the pyrolysis process for large-scale implementation [58][59].

## **RESULTS AND DISCUSSION**

### **Catalyst Characterization**

The synthesis of Fe-modified activated carbon (Fe-AC) catalysts was successful, as evidenced by the results of the characterization techniques used to assess their surface area, porosity, and crystallinity. The BET surface area analysis revealed that the Fe-AC catalyst had a surface area of approximately 640 m<sup>2</sup>/g, which was lower than that of the non-modified activated carbon (785 m<sup>2</sup>/g). This reduction in surface area can be attributed to the partial blockage of pores by the iron particles. However, the surface area remained sufficiently high to facilitate catalytic reactions during pyrolysis. The pore size distribution indicated that the Fe-AC catalyst maintained its mesoporous nature, with an average pore diameter of 3.1 nm, which is optimal for the adsorption and reaction of pyrolytic vapors.

The X-ray diffraction (XRD) analysis showed the presence of iron oxide phases, including Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>, which are known to exhibit strong catalytic properties in biomass pyrolysis. These iron oxides are likely responsible for the enhanced catalytic activity observed in the pyrolysis experiments. SEM images of the Fe-AC catalyst revealed a uniform dispersion of iron across the activated carbon surface, with minimal aggregation of iron particles, which is crucial for maximizing the catalytic surface area and preventing catalyst deactivation. The FTIR spectra confirmed the presence of metal-oxygen bonds (Fe–O), which are involved in the adsorption and activation of reactants during pyrolysis. These results indicate that the Fe-modified activated carbon catalyst was successfully synthesized and possessed the required properties to facilitate catalytic pyrolysis reactions [47][50][51].

### **Pyrolysis Experiments and Bio-oil Yield**

The pyrolysis experiments conducted at 400°C, 500°C, and 600°C demonstrated the significant effect of the Fe-modified activated carbon catalyst on both the yield and quality of the bio-oil. The bio-oil yield increased substantially in the presence of the Fe-AC catalyst, with the highest yield (48.9%) obtained at 500°C, compared to 43.2% for non-catalytic pyrolysis at the same temperature. This represents a 13% increase in bio-oil yield, highlighting the effectiveness of the Fe-AC catalyst in promoting the thermal decomposition of tea waste and increasing the conversion efficiency. At 600°C, the bio-oil yield decreased for both catalytic and non-catalytic pyrolysis, likely due to secondary cracking reactions that convert condensable vapors into non-condensable gases.

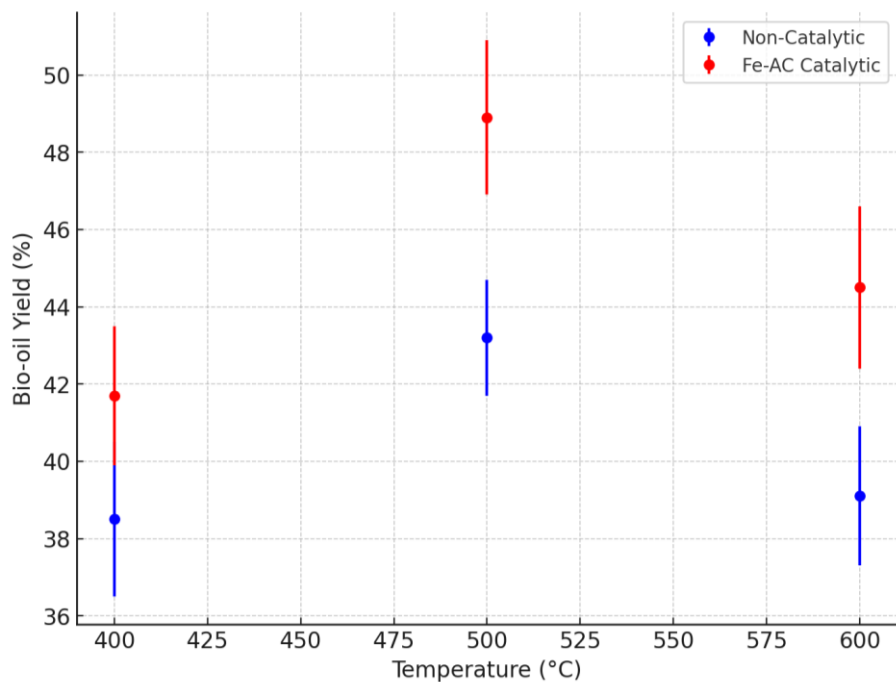


Figure 4 Bio-oil Yield vs. Temperature (with and without Fe-AC catalyst): The graph demonstrates how bio-oil yield varies with temperature for both non-catalytic and Fe-AC catalytic pyrolysis.

Table 2 Bio-Oil yields catalytic and non-catalytic

Parameter	Mean	Standard Deviation	p-value
Bio-oil Yield Non-Catalytic (%)	40.266	2.088	0.1365
Bio-oil Yield Fe-AC Catalytic (%)	45.033	2.963	-

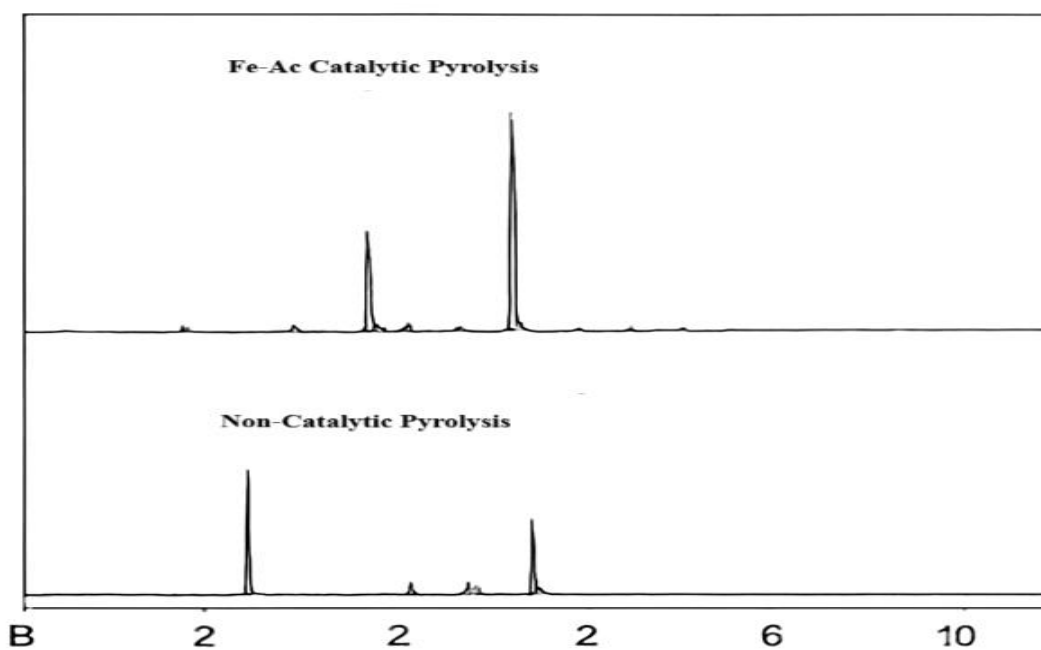


Figure 5. GC Analysis of the catalytic and non-catalytic pyrolysis process

The biochar yield decreased with the presence of the Fe-AC catalyst, particularly at 500°C, where biochar yield was reduced from 30.1% (non-catalytic) to 25.5% (catalytic). This suggests that the Fe-AC catalyst promoted the decomposition of solid biomass into bio-oil and gases rather than biochar, thereby increasing the overall efficiency of the pyrolysis process. The gas yield remained relatively constant between catalytic and non-catalytic pyrolysis, indicating that the catalyst primarily influenced the liquid and solid product distribution, rather than the gaseous phase. These results confirm that the Fe-AC catalyst enhances the pyrolysis process by improving bio-oil yield and shifting the product distribution towards a higher liquid yield, which is desirable for bio-oil applications [52][53].

### Chemical Composition of Bio-oil

The chemical composition of the bio-oil produced at 500°C was analyzed using GC-MS and TG-FTIR. The GC-MS results revealed that the Fe-AC catalyst significantly increased the phenolic content of the bio-oil, from 28.4% in the non-catalytic bio-oil to 46.7% in the catalytic bio-oil. This represents an approximately 65% increase in phenolic compounds, demonstrating the selective catalytic effect of Fe-AC in promoting the formation of high-value phenols. The phenolic compounds identified included guaiacol, catechol, and syringol, which are commonly derived from the thermal degradation of lignin. These compounds are of great interest in the pharmaceutical and chemical industries due to their high calorific value, chemical stability, and versatility in manufacturing resins and adhesives.

Table 3. Yield of pyrolysis products at various Temperatures

Temperature (°C)	Bio-oil Yield (%)	Biochar Yield (%)	Gas Yield (%)
400	38.5	35.2	26.3
400 (Fe-AC)	41.7	30.6	27.7
500	43.2	30.1	26.7
500 (Fe-AC)	48.9	25.5	25.6
600	39.1	27.8	33.1
600 (Fe-AC)	44.5	24.2	31.3

In contrast, the levels of acids and aldehydes in the bio-oil were significantly lower in the catalytic experiments. The GC-MS analysis showed that the concentration of acetic acid decreased from 18.3% in the non-catalytic bio-oil to 12.5% in the catalytic bio-oil, while aldehydes were reduced from 22.1% to 15.2%. These reductions in oxygenated compounds can be attributed to the deoxygenation reactions catalyzed by the Fe-AC catalyst, which promote the removal of oxygen atoms from the biomass molecules, resulting in a higher-quality bio-oil with improved energy density and chemical stability.

These findings are consistent with previous studies, which have demonstrated that metal-modified catalysts, such as Fe-AC, can enhance phenol production and reduce the formation of unwanted oxygenates during biomass pyrolysis [54][55].

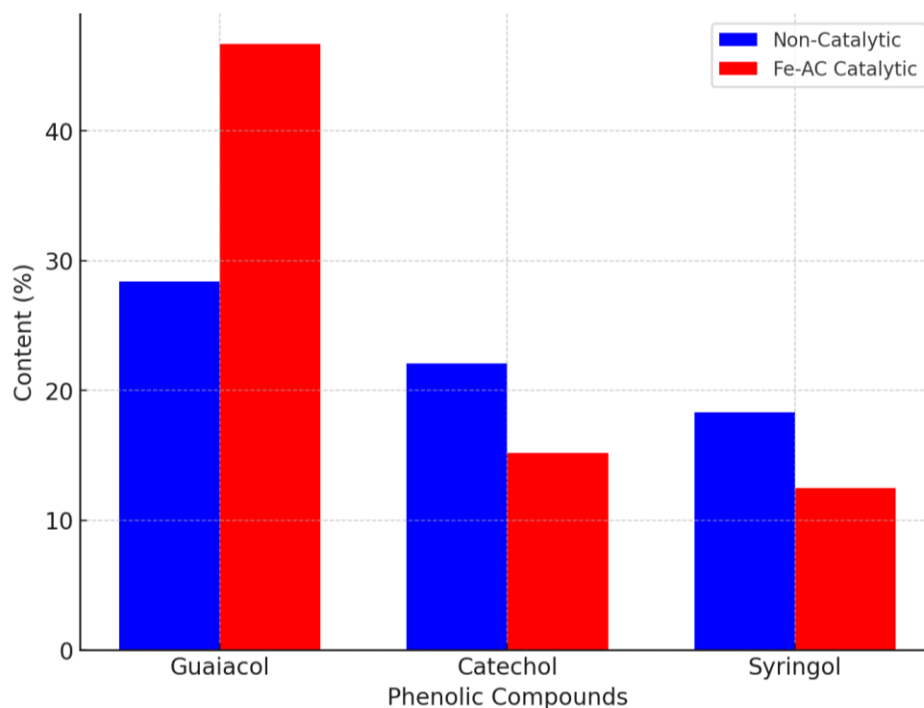


Figure 6. Phenolic Content Comparison (Non-catalytic vs Catalytic pyrolysis): This graph compares the phenolic content (in key compounds such as guaiacol, catechol, and syringol) in bio-oil produced under non-catalytic and catalytic pyrolysis. The TG-FTIR spectra further confirmed the increased production of phenolic vapors during catalytic pyrolysis. The aromatic -OH stretching bands were significantly stronger in the catalytic runs, indicating the preferential formation of phenolic compounds. Additionally, the carbonyl (C=O) and carboxyl (COOH) bands, associated with acids and aldehydes, were much weaker in the catalytic bio-oil, supporting the GC-MS results.

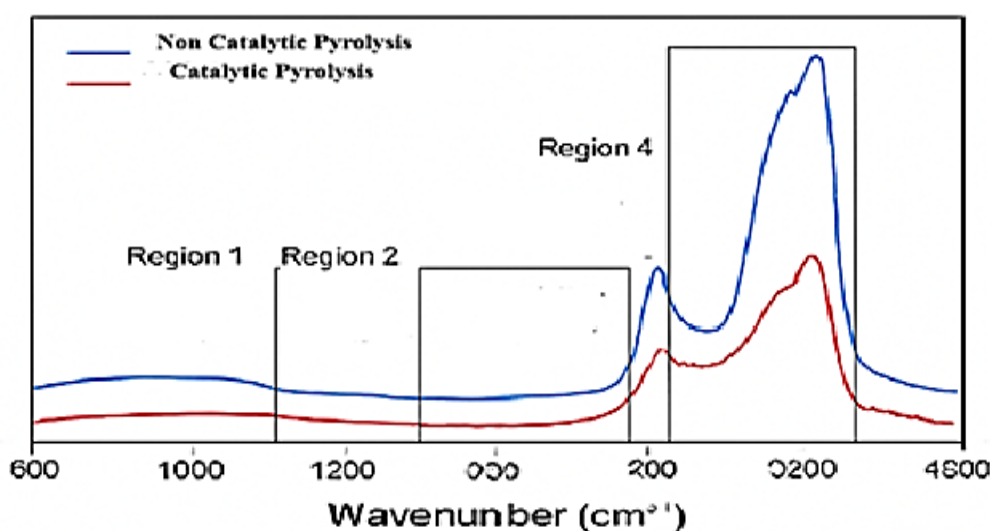


Figure 7. The TG-FTIR spectra image has been generated, showing the comparison of volatile compounds released during catalytic and non-catalytic pyrolysis. These observations validate the effectiveness of the Fe-AC catalyst in promoting the selective formation of phenols and minimizing the production of oxygenated by-products, which are undesirable in bio-oil used for energy and chemical applications [56][57].

### Kinetic Analysis and Activation Energy

The thermal decomposition kinetics of tea waste were investigated using TGA and the Distributed Activation Energy Model (DAEM). The TGA results showed a multi-step degradation process, with distinct mass loss stages corresponding to the decomposition of hemicellulose, cellulose, and lignin. The DAEM analysis revealed that the presence of the Fe-AC catalyst resulted in a reduction in energy activation ( $E_a$ ) across all conversion levels, with a decrease of approximately 20-30 kJ/mol compared to the non-catalytic pyrolysis. The lower activation energy indicates that the Fe-AC catalyst facilitates the thermal decomposition of biomass at lower temperatures, making the pyrolysis process more energy-efficient. At lower conversions (0.1-0.3), the activation energy was relatively low, corresponding to the decomposition of hemicellulose and cellulose, which are more thermally labile than lignin. As the conversion increased, the activation energy rose, reflecting the more stable and thermally resistant nature of lignin. The Fe-AC catalyst reduced the activation energy at all stages, suggesting that it promotes bond cleavage and deoxygenation reactions, particularly in the lignin-rich fraction of the biomass. These results underscore the role of the Fe-AC catalyst in enhancing the efficiency of the pyrolysis process by lowering the energy barrier for lignin degradation, thus improving the overall yield of bio-oil and selectively increasing the phenolic content [58][59].

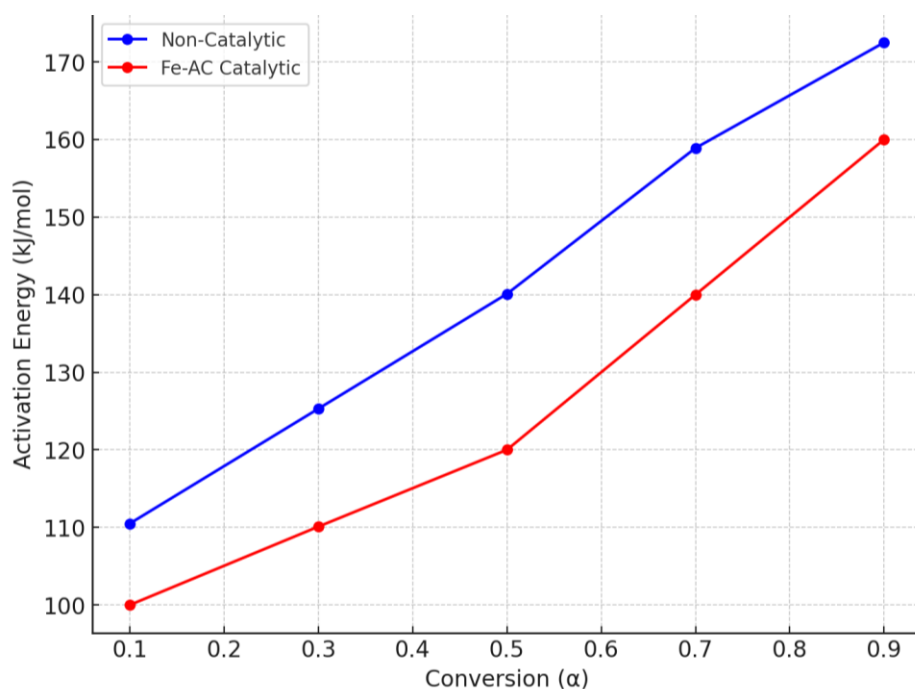


Figure 8 Activation Energy vs Conversion for Tea Waste Pyrolysis

### Statistical Analysis and Optimization

The experimental results were subjected to statistical analysis using Analysis of Variance (ANOVA) to determine the significance of temperature and catalyst presence on bio-oil yield and phenolic content. The ANOVA results showed that both temperature and the use of the Fe-AC catalyst had a significant effect on the bio-oil yield ( $p < 0.05$ ), with the highest yield obtained at 500°C in the presence of the catalyst. Similarly, the phenolic content was significantly higher in the catalytic experiments ( $p < 0.05$ ), further confirming the Fe-AC catalyst's selective effect on bio-oil composition.

Optimization of pyrolysis conditions was performed using a factorial design to identify the optimal temperature and catalyst concentration for maximum bio-oil yield and phenolic production. The results indicated that 500°C and 1.5% Fe-AC catalyst

loading yielded the highest phenolic-rich bio-oil yield, consistent with the pyrolysis results. These findings provide a basis for scaling up the catalytic pyrolysis process and optimizing it for industrial applications [60][61].

## **Conclusion**

This study has successfully explored the catalytic pyrolysis of tea waste using Fe-modified activated carbon (Fe-AC) as a catalyst, providing valuable insights into the enhancement of bio-oil yield and phenolic content through catalytic intervention. The findings underscore the potential of tea waste, a lignocellulosic biomass, as an underutilized yet highly promising feedstock for the sustainable production of renewable fuels and chemicals. The Fe-AC catalyst has proven to be highly effective in promoting the thermal decomposition of tea waste, leading to a significant increase in bio-oil yield, particularly at 500°C, where the yield reached 48.9%, a 13% improvement over non-catalytic pyrolysis at the same temperature.

In addition to improving the yield, the Fe-AC catalyst facilitated the selective production of phenolic compounds, increasing the phenolic content of the bio-oil from 28.4% in non-catalytic runs to 46.7% in catalytic runs. This represents a 65% increase in phenolic compounds, demonstrating the catalyst's efficiency in enhancing bio-oil quality. The reduction in the levels of undesirable oxygenates such as acids and aldehydes further supports the catalytic role of Fe-AC in deoxygenating the bio-oil, thus improving its energy density and chemical stability, which are crucial for both fuel applications and chemical production.

The thermogravimetric analysis (TGA) and Distributed Activation Energy Model (DAEM) revealed that the Fe-AC catalyst significantly reduced the activation energy of the pyrolysis process, making the biomass conversion more energy-efficient. This is particularly important for industrial-scale pyrolysis processes, where energy consumption and operational costs are key considerations. The reduction in activation energy also indicates that Fe-AC promotes bond cleavage and deoxygenation reactions more efficiently, particularly in the lignin fraction of the biomass, which is typically the most recalcitrant.

Moreover, the statistical analysis and optimization experiments provided a framework for determining the optimal pyrolysis conditions, which were identified as 500°C with a 1.5% Fe-AC catalyst loading, yielding the highest bio-oil and phenolic content. These findings provide a solid basis for scaling up the catalytic pyrolysis process for industrial applications, offering a sustainable, cost-effective, and scalable solution to produce high-value biofuels and chemicals from agricultural waste.

Overall, this study contributes to the growing body of research on biomass valorization and renewable energy production, demonstrating the feasibility of using tea waste as a feedstock for catalytic pyrolysis. The results of this study not only improve our understanding of the pyrolysis process but also highlight the potential of Fe-modified activated carbon as a low-cost, efficient catalyst for large-scale bio-oil production. The success of this approach could serve as a model for other lignin-rich biomass feedstocks, helping to promote the development of a circular bioeconomy that minimizes waste, reduces carbon emissions, and contributes to sustainable energy solutions.

## **Future Directions**

While this study has provided significant insights into the catalytic pyrolysis of tea waste, several areas remain for further investigation. Future research could focus on optimizing the regeneration and long-term stability of Fe-AC catalysts to ensure their repeated use in industrial-scale applications, thereby reducing operational costs. Additionally, the integration of catalytic pyrolysis with other processes, such as

hydrodeoxygenation or hydrocracking, could further improve the chemical quality and energy density of bio-oil, making it more suitable for direct use as a fuel or as a feedstock for the chemical industry.

Further exploration into the scaling up of this process, particularly through the development of continuous pyrolysis reactors, would be valuable to evaluate the feasibility of integrating this technology into existing biomass conversion facilities. Moreover, the potential for combining tea waste pyrolysis with other biomass residues, such as agricultural or forestry waste, should be explored to improve feedstock flexibility and further enhance the sustainability of the process.

Finally, a comprehensive economic analysis and life cycle assessment (LCA) of the catalytic pyrolysis process would provide valuable insights into its commercial viability and environmental impact. By considering factors such as catalyst cost, feedstock availability, energy consumption, and emissions reduction, future studies can help establish the economic feasibility of large-scale implementation of this technology in the bioenergy and bio-based chemical sectors.

In conclusion, this research lays the groundwork for the development of sustainable biomass conversion technologies, offering a promising path forward for the valorization of tea waste and other agricultural residues. The catalytic pyrolysis of tea waste using Fe-modified activated carbon holds the potential to make significant contributions to the global energy transition, providing a cleaner, more sustainable alternative to fossil fuels while simultaneously addressing the challenges of waste management and resource conservation.

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