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Special Issue
A Themed Issue in Honour of Professor Onukwuli Okechukwu Dominic (FAS).

This special issue is dedicated to Professor Onukwuli Okechukwu Dominic (FAS), marking his retirement and celebrating a remarkable career. His legacy of exemplary scholarship, mentorship, and commitment to advancing knowledge is commemorated in this collection of works.

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Sustainable Bio-Aviation Fuel Production from Biobased Oil: A Novel Hydrogen-Free Biorefinery Approach

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Abstract
This study investigates a novel biorefinery strategy for the sustainable production of bio-aviation fuel. The process involves a single-step, hydrogen-free simultaneous (heterogeneous) fluid catalytic conversion and recovery (SFCCR) of Jatropha seed oil (JO) using a low-cost oxalic acid functionalized-activated carbon catalyst from rice husk. To optimize the process, response-surface-methodology (RSM) was employed using a central composite rotatable design (CCRD). The study examined the influence of temperature, catalyst loading, and reaction time on the SFCCR process and evaluated its kinetics and thermodynamics. A maximum bio-aviation fuel yield of 88.60% was achieved under optimized conditions: 394.69 °C, 4.67 g catalyst loading, and 62.25 minutes reaction time. Kinetic analysis revealed that the SFCCR process best fit a pseudo-second-order model, characterized by a high coefficient of determination ($R^2 = 0.96$), adjusted R^2 (0.94), and low values for the sum of squares of errors (SSE = 4.75) and root mean squared error (RMSE = 1.0). Thermodynamic analysis yielded a negative Gibbs free energy ($\Delta G = -13.66$ kJ/mol), indicating a spontaneous reaction. Furthermore, the process was found to be endothermic ($\Delta H = 389.32$ kJ/mol) and irreversible ($\Delta S = 0.61$ kJ/mol). The resulting bio-aviation fuel, composed of hydrocarbons in the C9-C16 range, met ASTM specifications for aviation turbine fuel. This study demonstrates the potential of this hydrogen-free, single-step catalytic process for sustainable bio-aviation fuel production, highlighting the viability of utilizing functionalized activated carbon catalysts in biorefinery systems.

Keywords: Biorefinery, Bio-aviation fuel, Activated carbon catalyst, Kinetics and Thermodynamics, Jatropha oil

1. Introduction

The aviation industry's pursuit of sustainable alternatives to conventional jet fuels has intensified recently, driven by concerns over fossil fuel depletion and environmental degradation. Bio-aviation fuel production has emerged as a promising solution, with Jatropha oil garnering significant interest as a feedstock. Jatropha's high oil content, ability to grow on non-arable land, and resilience in poor soil conditions make it particularly attractive for biofuel production (Yang et al., 2019; Tan et al., 2020). However, despite progress in the biofuel sector, significant challenges persist in optimizing biorefinery processes, developing efficient catalyst systems, and managing feedstock variability, necessitating further research and innovation.

Current biorefinery approaches to biofuel production, particularly for aviation fuels, face several limitations. High hydrogen consumption and poor catalyst stability during the hydrodeoxygenation process are notable drawbacks. For instance, catalysts such as Ni2P/Zr-SBA-15 and WO3-ZrO2 have demonstrated high deoxygenation efficiencies but require hydrogen supplementation, which adds to the production cost and complexity (Tan et al., 2020; Lin et al., 2022). Additionally, many existing processes rely on high temperatures and pressures, leading to energy inefficiencies and reduced economic viability for large-scale operations (Duan et al., 2019).

To address these issues, decarboxylation and decarbonylation processes have gained attention as alternatives to hydrogenation. These processes do not require hydrogen, significantly reducing the overall energy requirements (Asikin-Mijan et al., 2020). Catalysts such as activated carbon (AC) from agricultural waste can promote decarboxylation reactions, leading to high hydrocarbon yields in the C8–C18 range without external hydrogen (Lin et al., 2022). While activated carbon derived from biomass, such as rice husk, has shown potential for improving catalytic efficiency, its use in aviation biofuel production is still in its nascent stages, and further optimization is needed to meet aviation fuel standards (Duan et al., 2019; Lin et al., 2022).

The choice of catalyst is critical in biorefinery processes. Nickel- and palladium-based catalysts have been commonly employed in hydrogenation reactions due to their high activity in hydrodeoxygenation and cracking reactions. However, these metals are expensive, and their long-term stability is often compromised by sintering and poisoning during the reaction (Verma et al., 2015). In contrast, activated carbon (AC) catalysts, especially those derived from renewable resources like rice husk and coconut residues, offer a low-cost, sustainable alternative with good catalytic performance for decarboxylation and decarbonylation processes (Asikin-Mijan et al., 2020). Feedstock variability also plays a significant role in the efficiency of biofuel production. The high free fatty acid (FFA) content in Jatropha oil can lead to undesirable side reactions, such as saponification, which reduces catalyst efficiency and overall fuel yield (Moreira et al., 2020). Therefore, feedstock pre-treatment, the development of more robust catalysts, and catalyst regeneration are crucial for addressing these limitations, but significant advances are still required for commercial viability.

Recent studies have focused on addressing various limitations of bio-aviation fuel production, including the high cost of raw materials, low yield, and suboptimal process conditions (Wang et al., 2018). The optimization of catalyst systems remains a major challenge, with recent works exploring multifunctional catalysts such as Ni2P/Zr-SBA-15, which significantly enhance the deoxygenation of Jatropha oil for aviation fuel production (Tan et al., 2020). Nevertheless, issues such as catalyst deactivation and high hydrogen consumption continue to hinder scalability (Lin et al., 2022).

One of the key challenges in optimizing biorefinery processes is the complexity of reaction kinetics and thermodynamics. Many biofuel production processes exhibit nonlinear kinetics, where reaction rates are affected by multiple interacting factors such as temperature, catalyst loading, and reaction time (Romero et al., 2015). Studies have applied pseudo-second-order kinetic models to better understand the catalytic reactions in biofuel production, demonstrating high accuracy in predicting conversion rates (Zulfiqar et al., 2021). Furthermore, thermodynamic evaluations of processes, such as those conducted with activated carbon catalysts, show that these processes are typically spontaneous, endothermic, and irreversible, which provides valuable insights for optimization (Tan et al., 2020).

The proposed study on biorefinery process optimization and non-linear kinetic modeling for bioaviation-fuel production from Jatropha oil with activated-carbon catalysts addresses key limitations in current methodologies. By utilizing a low-cost, sustainable catalyst derived from rice husks, without external hydrogen addition and applying response-surface-methodology (RSM) for process optimization, this study aims to enhance fuel yield, reduce production costs, and minimize environmental impact. Moreover, optimizing the process using response-surface-methodology (RSM) and investigating the non-linear kinetics will lead to better control over reaction parameters, thus improving overall efficiency and sustainability (Zulfiqar et al., 2021). This approach will significantly contribute to more sustainable and efficient biorefinery systems development for aviation fuel production, potentially revolutionizing the bio-aviation fuel sector and offering a viable path toward reducing the carbon footprint of air travel while meeting the growing global demand for aviation fuel.

A key innovation of this study lies in the utilization of a low-cost oxalic acid functionalized-activated carbon catalyst derived from rice husk. This approach eliminates the need for external hydrogen, significantly reducing energy consumption and production costs. Furthermore, the use of a readily available and renewable resource like rice husk for catalyst production enhances the sustainability and economic viability of the process. The study also employs response-surface-methodology (RSM) to optimize the process parameters, enabling precise control and maximizing biofuel yield while minimizing resource consumption.

This research addresses several critical gaps in the existing literature. Firstly, it explores a hydrogen-free biorefinery pathway, offering a more sustainable and cost-effective alternative to conventional hydrogenation-based approaches. Secondly, it investigates the use of a low-cost, biomass-derived catalyst for bio-aviation fuel production, demonstrating the potential for utilizing renewable resources to enhance process sustainability. Finally, the study employs RSM to optimize the process, providing valuable insights into the influence of various parameters on biofuel yield and paving the way for improved process control and scalability. These novel aspects contribute to the advancement of sustainable bio-aviation fuel production and address the pressing need for innovative and environmentally friendly solutions for the aviation industry.

2.0 Materials and methods

2.1. Preparation of Feedstock and Oil Extraction

Jatropha seeds were subjected to a meticulous cleaning and screening process to remove impurities such as seed coats, chaff, debris, and damaged seeds. The cleaned seeds were then cracked, sieved, and dried in an oven at 65°C to achieve a moisture content of 1.3%. Subsequently, the dried seeds were milled into a fine powder using an electric grinder and sieved to a particle size of 0.1 mm.

Oil extraction was carried out using a Soxhlet apparatus with petroleum ether as the solvent. A known quantity of milled seeds was placed in the Soxhlet thimble, and the extraction was conducted at 74°C for 180 minutes. The solvent was then removed from the oil extract using a rotary evaporator at 65°C or through simple evaporation. The percentage oil yield was determined gravimetrically using the following equation (1) (John et al., 2021a, b). This comprehensive approach ensured the preparation of high-quality feedstock for subsequent biofuel production processes.

$$Oil\ yield\ (\%) = \frac{weight\ of\ extracted\ oil\ (g)}{weight\ of\ sample\ (g)}\ x\ 100 \tag{1}$$

2.2 Catalyst Preparation

Samples of rice husk were well-dried and ground. Then ground rice husk as a source of carbon was impregnated with phosphoric acid. The impregnated carbon was dried for 24 hours at 120 ^{o}C in an oven. The concentration of acid was 0.1M while the ratio of acid to rice husk samples by weight basis (g: g or ml: g) was 1:1. The reaction time was 60 min at 40 ^{o}C. 100 g of raw rice husk was impregnated with 100 ml of dilute acid. One-step activation was conducted in a muffle-furnace. 250 g of the impregnated and dried samples were carbonized for 1 hour at temperature (450 ^{o}C). At the end of each reaction time, the samples were cooled to the ambient temperature and weighed to estimate the yield of activated carbon. The samples were repeatedly washed and filtered using distilled water and Whatman No.1 filter paper to pH 6-7. The samples were further dried at 110^{0}C in the oven for 8 hours. The well-dried samples were subsequently pulverized, and sieved (0.1- 0.3 mm). The dried activated carbon was functionalized with oxalic acid (0.1 M) via impregnation to the pH of 5.4. The functionalized activated carbon was further dried at 110 ^{o}C, and airtight stored, ready for use in bottles.

2.3 Bio aviation fuel production process

2.3.1 Proposed experimental setup and procedure

The proposed methodology for bio-aviation fuel production involves several stages, beginning with the collection and preparation of raw materials and culminating in product collection and analysis. A model-scale Multi-product biorefinery set up was used for the BAF production. A single-step process (SSP) method was employed for the SFCCR of bio-aviation fuel from Jatropha Oil. This process involves only the SFCCR stage, where the raw oil feedstock is directly subjected to fluid catalytic conversion and bio-aviation fuel recovery. In the SSP, the JO was introduced into a batch reactor for the SFCCR process, which is conducted without the addition of hydrogen. The biorefinery setup includes a reactor unit, thermometer (capable of measuring temperatures up to 600 °C), vapor channels, lagging materials, an overhead constant water circulator, cooling unit, reservoir tank and water pump, distillation unit and an extraction chamber for seed Oil extraction. The reactor is loaded with the raw JO as the feedstock and the AC catalyst. The system temperature was increased gradually by 1°C to 2 °C per minute. After each temperature increment, the system is allowed to recover the bio-aviation product formed at that temperature before further increasing the temperature. This stepwise temperature increment and product recovery continue until the system reaches the desired reaction temperature. The system is then maintained at the target temperature for a specified duration to ensure complete recovery of the bio-aviation fuel.

Once the reaction time is completed, the recovered bio-aviation product is centrifuged to separate any dissolved solid catalysts from the liquid phase products. The yield of the liquid bio-aviation fuel product is calculated using the following equation (2):

$$\text{Liquid bio} - \text{aviation fuel (LBFP) product yield (wt.\%)} = \frac{\text{LBFP}}{\text{Feed}} \text{ x } 100\% \qquad (2)$$

where LBFP represents the mass or volume of the liquid bio-aviation fuel product. The optimized samples are characterized for total hydrocarbon composition (THC) using a gas chromatograph (GC).

2.4 Total Hydrocarbon Compound (THC) Analysis

The Total Hydrocarbon Compound (THC) content of bioaviation-fuel from Jatropha was analyzed with gas-chromatography fixed with flame-ionization-detection (GC-FID). Before analysis, the bio-aviation fuel samples were prepared by diluting them in an appropriate solvent. The GC-FID system used for the analysis was equipped with a capillary column suitable for separating hydrocarbon compounds. The GC oven temperature program was optimized to achieve proper separation of the hydrocarbon components. Initially, the oven was held at a starting temperature for a set time, followed by a programmed temperature ramp to a final temperature. Helium was applied as the carrier-gas while the injector and detector-temperatures were set to ensure complete vaporization of the sample and optimal detection sensitivity. An automated calibration of the GC-FID system was performed using hydrocarbon standards of known concentrations. These standards covered the expected range of hydrocarbons present in the bio-aviation fuel. An automated calibration curve was constructed to relate peak areas to hydrocarbon concentrations. For the analysis, a measured volume of the prepared bio-aviation fuel sample was injected into the GC-FID system. The sample components were separated as they passed through the column and were detected by the FID. The resulting chromatogram displayed peaks corresponding to the various hydrocarbon compounds present in the fuel. Automated peak identification was carried out by comparing retention times with those of the calibration standards. Automated quantification of the THC content was accomplished by integrating the peak areas and relating them to the calibration curve. The total hydrocarbon content was calculated as the sum of all identified hydrocarbon peaks. Multiple replicate analyses were performed to ensure the repeatability and accuracy of the results. Quality control measures, including the analysis of blanks and known standards, were implemented throughout the analytical process to validate the method's performance and reliability.

2.5 Experimental Design

This study employed a central composite design (CCD) to optimize the SFCCR process for bio-aviation fuel synthesis from decarboxylation of crude Jatropha oil (JO). Three independent variables, namely temperature, catalyst loading, and reaction time, were investigated at five levels. A total of 20 experimental runs were conducted according to the CCD matrix, as outlined in Table 1. The primary response variable was the liquid bio-aviation fuel yield (%). The optimization of SFCCR process parameters is crucial for achieving a balance between high yield and desirable cold flow properties. Producing highly branched iso-paraffins requires operating under higher severity conditions, which may involve hydrocracking reactions. These conditions are necessary to meet stringent aviation fuel specifications, including cloud point, pour point, boiling point, freezing point, and cold filter plugging point (CFPP) (Scharff et al., 2019).

The ranges for the process variables in the SFCC experiments were established based on preliminary studies and a comprehensive review of relevant literature, considering experimental conditions reported in similar studies conducted with different catalysts. From the literature search, with external hydrogen addition, the de-oxygenation and isomerization reaction over AC catalysts is suggested to yield the best results over a range of temperatures between 270 °C – 300ºC, although, little or no literature report exists on AC on the conversion of any reactant sample via decarboxylation without addition of external hydrogen. For this investigation, the temperature range of 300 – 395ºC was chosen to study the SFCCR efficiency, selectivity and catalytic activity of functionalized activated carbon. The factor levels of the process conditions and the design matrix for the SFCCR optimization experiments were presented in Tables 1 and 2.

Table 1. Factor levels of independent biorefinery process variables

Factor	Name	Low Actual	Mean	High Actual
A	Temp (°C)	340	367.5	395
B	Catalyst loading (g)	1	3	5
C	Reaction time (min)	30	120	90

Table 2 Experimental design matrix

Run	Factor 1 X_1:Temp (°C)	Factor 2 X_2:Catalyst loading (g)	Factor 3 X_3:Reaction time (min)
1	367.5	3	20.52
2	395	5	90
3	395	1	30
4	340	1	30
5	340	5	30
6	340	5	90
7	367.5	0.37	60
8	395	1	90
9	367.5	3	60
10	367.5	3	60
11	367.5	3	60
12	403.69	3	60
13	367.5	3	60
14	331.31	3	60
15	340	1	90
16	367.5	3	60
17	395	5	30
18	367.5	3	99.48
19	367.5	5.6	60
20	367.5	3	60

2.6 Kinetic Models

The single-step biorefinery-process kinetics for producing bio-aviation fuel from jatropha seeds-oil using AC catalyst were studied. The process involved simultaneous fluid catalytic conversion and recovery (SFCCR) of bio-aviation fuel and was modeled using non-linear pseudo-first-order and pseudo-second-order models. The SFCCR experimental data were used to fit the kinetic models using Matlab software. To fit the selected models to the experimental data, parameters such as the Nonlinear least squares method, Robust (Off, Bisquare, LAR), Trust-region, and Levenberg-Marquardt Algorithm were employed. The Table 3 provides the kinetic model-equations.

Table 3. Kinetic model equations

Kinetic models	Nonlinear equation	Linear equation
Pseudo 1st order	$Y,(\%) = \frac{d(q_t)}{dt} = K(q_e - q_t)$	$Ln(q_e - q_t) = Inq_e - Kt$
Pseudo 2nd order	$Y,(\%) = \frac{{q_e}^2Kt}{1+q_eKt}$	$\frac{t}{q_t} = \frac{1}{K{q_e}^2} + \frac{t}{q_e}$

2.7 Thermodynamic Parameters

A crucial initial step in developing a comprehensive mathematical model for simultaneous catalytic conversion and bio-aviation fuel recovery is conducting a rigorous thermodynamic analysis. This analysis provides valuable insights into the feasibility and characteristics of the proposed process by evaluating key thermodynamic parameters, namely enthalpy, Gibbs free energy, and entropy. These parameters were calculated using equations (3) - (4) to assess the thermodynamic potential and feasibility of the concurrent fluid cracking and product recovery process.

$$\Delta G = -RTln\,K \tag{3}$$

$$In\,K \ = \frac{-\Delta G}{RT} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{4}$$

The Gibbs free energy (ΔG), measured in kJ/mol, is a thermodynamic property that quantifies the spontaneity of a chemical reaction. It is related to the enthalpy change (ΔH), entropy change (ΔS), and temperature (T) through the equation ΔG = ΔH - TΔS, where R is the universal gas constant (8.314 J/mol·K). A negative ΔG value indicates a spontaneous reaction, while a positive ΔG value suggests a non-spontaneous reaction. The magnitude of ΔG provides valuable insights into the reaction's likelihood and driving force. In the context of hydrocarbon conversion processes, such as fluid catalytic cracking, the Gibbs free energy values play a crucial role in formalizing the chemical reaction pathways and establishing the basis for kinetic models that predict reaction rates and product yields (Nazarova et al., 2015).

$$\mathrm{K} \ = \frac{\mathrm{Y_{Te}}}{\mathrm{Y_{Ue}}} \tag{5}$$

The thermodynamic parameters, enthalpy (ΔH) and entropy (ΔS), associated with the bio-aviation fuel production process can be determined through Arrhenius-type analysis. By plotting the natural logarithm of the rate constant (lnk) against the reciprocal of temperature (1/T), a linear relationship is obtained. The slope of this line yields -ΔH/R, where R is the universal gas constant. Similarly, the intercept of the line corresponds to ΔS/R. From these values, the enthalpy and entropy changes of the reaction can be calculated. Subsequently, the Gibbs free energy (ΔG*) can be determined using equation (6), where T is the absolute temperature. This thermodynamic analysis provides valuable insights into the reaction mechanism and energetics, enabling a deeper understanding of the factors influencing the bio-aviation fuel production process.

$$\Delta G = \ \Delta H - T\Delta S \tag{6}$$

2.8 Evaluation of Kinetic Model Fitness

To assess the fitness of the kinetic models to the experimental data, a statistical evaluation was conducted. The performance of each model was evaluated using a combination of metrics, including the root mean squared error (RMSE), coefficient of determination (R^2), adjusted coefficient of determination (adj-R^2), and the sum of squares of the errors (SSE). These statistical parameters, calculated using equations (7) - (10), provide quantitative measures of how well the model predictions align with the experimental observations.

$$RSME \ = \sqrt{\frac{\sum\left[\frac{q_{\exp(i)} - q_{model(i)}}{q_{exp(i)}}\right]^2}{n}} \tag{7}$$

$$R^2 = 1 - \ \frac{\sum(y_i - \hat{y})^2}{\sum(y_i - \overline{y})^2} \tag{8}$$

$$SSE = \frac{\sum_{i=0}^{n}(y_i - \hat{y})^2}{n} \tag{9}$$

$$Adj - R^2 = \frac{(1 - R^2)(N - 1)}{N - P_r - 1} \tag{10}$$

The goodness-of-fit of the regression model is assessed by comparing the experimental response values (yi) with the predicted response values (ŷi). The model's accuracy is evaluated using metrics such as the coefficient of determination (R-squared), adjusted R-squared, root mean squared error (RMSE), and sum of squared errors (SSE). R-squared and adjusted R-squared quantify the proportion of variance in the experimental data explained by the model. Higher values of these metrics indicate a better fit. Conversely, lower values of RMSE and SSE, which represent the average deviation and the sum of squared differences between predicted and actual values, respectively, signify a more accurate and reliable model. In essence, a combination of high R-squared and adjusted R-squared values, along with low RMSE and SSE values, suggests a model that effectively captures the underlying trends in the data and provides accurate predictions (John et al., 2021a, b).

3.0 Results and Discussion

3.1. Kinetic Model Parameters and Interpretation

Table 4 presents the kinetic parameters, including the rate constant (K) and equilibrium adsorption capacity (qe), for both pseudo-first-order and pseudo-second-order models, determined at various temperatures and catalyst loadings during bio-aviation fuel production from Jatropha Oil (JO) over activated carbon (AC) catalyst. The kinetic parameters for the first-order model exhibited an inconsistent relationship with increasing temperature and catalyst loading. While an increase in temperature and catalyst loading generally led to higher K and qe values, the observed trend was not consistently proportional. This variability in the kinetic parameters can be attributed to the complex interplay of factors influencing the reaction kinetics, such as mass transfer limitations, catalyst deactivation, and the inherent heterogeneity of the reaction system.

The observed increase in K and qe values with increasing temperature and catalyst loading for the second-order model aligns with the improved rate of bio-aviation fuel recovery observed under these conditions. This trend suggests that the second-order model more accurately captures the underlying reaction mechanisms and the influence of operating parameters on the reaction kinetics. A comparative analysis of the kinetic parameter values for the first-order and second-order models revealed comparable magnitudes for both K and qe. This observation suggests that both models, despite their different underlying assumptions, can provide reasonable estimates of the reaction rate and equilibrium adsorption capacity. However, the consistent trend of increasing K and qe values with increasing temperature and catalyst loading for the second-order model, coupled with its superior fit to the experimental data as demonstrated in the previous section, indicates a more robust and reliable representation of the reaction kinetics.

The kinetic parameters, K and qe, provide valuable insights into the reaction mechanism and the performance of the catalyst. The rate constant, K, reflects the intrinsic reactivity of the system and is influenced by factors such as the activation energy of the reaction, the strength of adsorption between the reactants and the catalyst, and the presence of any mass transfer limitations. The equilibrium adsorption capacity, qe, represents the maximum amount of bio-aviation fuel that can be adsorbed onto the catalyst surface under given conditions. Higher qe values generally indicate higher catalyst activity and potentially higher product yields.

Implications for Process Optimization and Future Research Directions. The insights gained from the kinetic analysis can be leveraged to optimize the bio-aviation fuel production process. By understanding the influence of temperature and catalyst loading on the reaction kinetics, process parameters can be adjusted to maximize product yield, minimize reaction time, and improve overall process efficiency. Furthermore, the kinetic models can be used to predict the performance of the catalyst under different operating conditions, enabling the development of more robust and efficient process designs.

Further research is warranted to investigate the effects of other operating parameters, such as reactant concentration and stirring speed, on the reaction kinetics. Additionally, exploring the use of different catalysts and feedstocks can provide valuable insights into the versatility and applicability of the developed kinetic models.

Comparison with recent Advanxcement. Recent advancements in biofuel production technologies have focused on developing more efficient and sustainable processes. For example, Raji et al., (2023) conducted a comparative analysis of combustion and emission characteristics of biojet and conventional jet fuels, highlighting the need for continued research and development to improve the performance and environmental compatibility of biofuels. Studies like Task, (2024) have emphasized the importance of technological innovation and policy support to accelerate the commercialization of biojet/sustainable aviation fuels (SAFs). The current study contributes to this body of research by providing a detailed kinetic analysis of bio-aviation fuel production from Jatropha Oil (JO), which can inform the development of more efficient and optimized processes.

The kinetic analysis presented in this study holds significant implications for the industrial-scale deployment of bio-aviation fuel production. Establishing kinetic parameters and developing predictive models are fundamental for several critical aspects of industrial implementation. Firstly, in process design and optimization, kinetic models offer a powerful tool for optimizing key process parameters such as temperature, catalyst loading, and residence time. This optimization aims to maximize product yield, minimize reaction time, and enhance overall process efficiency, leading to a more economically viable and productive industrial operation. Secondly, in reactor design, the derived kinetic data plays a crucial role in the design and scale-up of reactors for industrial-scale production. This ensures optimal reactor performance at larger scales while simultaneously minimizing capital investment by informing efficient reactor design and avoiding costly over-engineering. Thirdly, cost estimation benefits significantly from kinetic analysis. By understanding the reaction kinetics, accurate estimations of production costs, including raw material costs, energy consumption, and catalyst costs, become possible. This detailed cost assessment is essential for evaluating the economic feasibility and potential profitability of the bio-aviation fuel production process at an industrial level. Fourthly, logistics and supply chain management rely heavily on an understanding of reaction kinetics. This knowledge is crucial for optimizing various logistical aspects, including feedstock transportation, efficient product distribution networks, and effective catalyst management strategies. Finally, the scalability of catalyst synthesis and process operations is paramount for industrial success. Kinetic analysis provides valuable insights for identifying potential bottlenecks in scaling up these operations and enables the optimization of process operations to ensure efficient, cost-effective, and large-scale production.

Moving beyond immediate industrial implications, several avenues warrant further exploration to facilitate the widespread commercialization of sustainable bio-aviation fuels. One critical area is the investigation of the behavior of other feedstocks. The kinetic analysis presented should be expanded to encompass a broader range of feedstocks, including lignocellulosic biomass, algal oils, and waste cooking oils. This expansion aims to assess their suitability for bio-aviation fuel production and, importantly, to identify potential synergies with existing biorefinery operations. Utilizing diverse feedstocks can enhance the sustainability and economic viability of bio-aviation fuel production by leveraging existing infrastructure and potentially reducing feedstock costs. Another crucial area of investigation is long-term catalyst stability. Understanding the long-term stability and deactivation behavior of catalysts under continuous operating conditions is essential for assessing the long-term economic viability of the process. Investigating deactivation mechanisms allows for the development of strategies for catalyst regeneration or replacement, minimizing downtime and maintaining consistent production levels. Furthermore, exploring the potential for integrating bio-aviation fuel production into existing refinery systems presents a significant opportunity. Such integration can improve overall energy efficiency by sharing resources and infrastructure, reduce environmental impact through optimized resource utilization, and facilitate the wider adoption of biofuels by leveraging established distribution networks. Finally, conducting a comprehensive life cycle assessment (LCA) of the entire bio-aviation fuel production process is essential. This LCA should encompass all stages, from feedstock cultivation and harvesting to fuel production and end-use. A thorough LCA provides a holistic understanding of the environmental and economic sustainability of the technology, considering factors such as greenhouse gas emissions, land use, water consumption, and economic costs associated with each stage of the process.

In conclusion, the kinetic analysis presented in this study offers valuable insights into the reaction mechanisms and process parameters that govern bio-aviation fuel production. By comparing these findings with recent advancements in biofuel technology and carefully considering the implications for industrial-scale application, this research contributes to the development of more sustainable and economically viable biofuel production processes. Continued research and development efforts focusing on feedstock diversity, long-term catalyst stability, efficient process integration with existing infrastructure, and comprehensive life cycle assessments are crucial to accelerate the commercialization of bio-aviation fuels and pave the way for a more sustainable future for the aviation industry. This multi-faceted approach, combining kinetic understanding with technological advancements and holistic sustainability assessments, is essential for realizing the full potential of bio-aviation fuels as a viable alternative to conventional jet fuels.

Table 4. SFCCR kinetic parameters at different temperatures and catalyst loading

Variable	340 (°C)	350 (°C)	365 (°C)	375 (°C)	385 (°C)	395 (°C)	Temp. Ave.	1 (g)	2 (g)	3 (g)	4 (g)	5 (g)	Cat. Ave.	Total Ave.
First-order														
K	0.01	0.07	0.07	0.19	0.09	0.11	0.09	0.23	0.19	0.20	0.16	0.20	0.20	0.14
q_e	10.00	35.35	54.16	70.14	82.93	88.62	56.87	39.84	53.25	63.65	77.31	88.44	64.50	60.68
Second-order														
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00
q_e	10.44	80.07	71.91	78.51	90.46	91.90	70.55	42.04	67.37	71.40	85.70	90.54	71.41	70.98

3.1.1 Kinetic model evaluation and comparison

The evaluation of kinetic models for bio-aviation fuel (BAF) production from Jatropha oil (JO) over an activated carbon (AC) catalyst was conducted using established statistical criteria, namely Sum of Squared Errors (SSE), coefficient of determination (R^2), adjusted R^2 (Adj-R^2), and Root Mean Square Error (RMSE). Higher R^2 and Adj-R^2 values, along with lower SSE and RMSE values, generally indicate a better fit of the model to the experimental data (Soroosh et al., 2019; Buffi et al., 2020; John et al., 2021a, b). Analysis of the results revealed distinct trends for the first-order and second-order kinetic models. For the second-order model, SSE and RMSE values decreased with increasing temperature and catalyst loading, while R^2 and Adj-R^2 values exhibited a directly proportional relationship. This trend suggests that the second-order model effectively captures the increasing rate of BAF recovery observed at elevated temperatures and catalyst loadings. The model's ability to account for a greater proportion of the total variation in the data, as evidenced by the increasing R^2 and Adj-R^2 values, further supports its suitability for describing the reaction kinetics under these conditions.

In contrast, the first-order model demonstrated inconsistent trends in kinetic parameter variation with respect to temperature and catalyst loading. While higher R^2 and Adj-R^2 values, along with lower SSE and RMSE values, were observed at higher temperatures and catalyst dosages, the overall trend was less pronounced and less consistent compared to the second-order model. A comparative analysis of the average values across all experimental conditions provided further evidence for the superior performance of the second-order model. The average SSE and RMSE values for the first-order model were significantly higher (15.995 and 1.938, respectively) compared to the second-order model (4.75 and 0.996, respectively). Similarly, the average R^2 and Adj-R^2 values for the second-order model (0.9576 and 0.9435) were substantially higher than those for the first-order model (0.7583 and 0.8367). These findings consistently indicate that the second-order kinetic model provides a more accurate and robust description of the BAF production kinetics under the investigated experimental conditions.

Based on the comprehensive analysis of SSE, RMSE, R^2 and Adj-R^2 values, the degree of fitness to the experimental data was determined to be higher for the second-order model compared to the first-order model. This observation is supported by the consistently higher R^2 and Adj-R^2 values and lower SSE and RMSE values obtained for the second-order model across all experimental conditions. Therefore, the second-order kinetic model, characterized by the highest R^2 and Adj-R^2 values and the lowest average SSE and RMSE values, was deemed the most suitable model for describing the experimental kinetics data of BAF production from JO over the AC catalyst. This analysis provides valuable insights into the reaction mechanism and can be utilized to optimize process parameters for maximizing BAF yield and minimizing production costs.

Table 5. Statistical fitness degree for the kinetic of SFCCR for BAF from JO using AC as a catalyst

Variable	340 (ºC)	350 (ºC)	365 (ºC)	375 (ºC)	385 (ºC)	385 (ºC)	Temp. Ave.	1 (g)	2 (g)	3 (g)	4 (g)	5 (g)	Cat. Ave.	Total Ave.
First-order														
SSE	0.09	10.89	55.38	14.93	2.74	0.45	14.08	1.01	52.63	18.18	16.81	0.92	17.91	16.00
R^2	0.98	0.96	0.75	0.80	0.97	0.98	0.91	0.84	0.64	0.70	0.79	0.86	0.77	0.84
Adj-R^2	0.98	0.95	0.67	0.73	0.96	0.97	0.88	0.79	0.28	0.60	0.72	0.81	0.64	0.76
RMSE	0.17	1.91	4.30	2.23	0.96	0.39	1.66	0.58	5.13	2.46	2.37	0.55	2.22	1.94
Second-order														
SSE	0.04	14.33	21.06	0.69	3.93	1.08	6.86	0.27	7.97	1.58	3.13	0.28	2.65	4.75
R^2	0.99	0.95	0.91	0.99	0.95	0.94	0.96	0.96	0.95	0.97	0.96	0.96	0.96	0.96
Adj-R^2	0.99	0.94	0.87	0.99	0.94	0.92	0.94	0.94	0.93	0.97	0.95	0.94	0.95	0.94
RMSE	0.11	2.19	2.65	0.48	1.15	0.60	1.19	0.30	1.63	0.73	1.02	0.31	0.80	1.00

3.2 Thermodynamics of Bio-aviation Fuel Production from Jatropha Oil

The thermodynamic parameters for the simultaneous fluid catalytic conversion and recovery (SFCCR) of bioaviation fuel from Jatropha oil (JO) with activated carbon (AC) catalyst were evaluated to assess the feasibility and spontaneity of the process. Table 6 presents the thermodynamic parameters, including Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS), calculated for different catalyst particle sizes (0.1 mm, 0.3 mm, and 0.45 mm) at varying temperatures. The results indicate that the SFCCR reaction is endothermic, requiring external energy input, consistent with findings from previous studies (John et al., 2021a,b; Buffi et al., 2020; Silmara et al., 2015). This energy input is necessary to overcome the activation energy barrier and break the strong bonds within the JO molecules.

The positive values of ΔH observed for all particle sizes (ranging from 369.77 to 389.32 kJ/mol) confirm the endothermic nature of the process. The positive values of ΔS suggest an increase in the degree of molecular disorder during the reaction, which is expected due to the conversion of complex JO molecules into smaller hydrocarbon chains and the interaction between the reactants and the catalyst surface. The ΔS values varied slightly with particle size, indicating that the catalyst surface area and pore structure can influence the extent of molecular disorder. The negative values of ΔG at all temperatures studied indicate that the SFCCR reaction is thermodynamically feasible and spontaneous under the experimental conditions. The magnitude of ΔG decreases with increasing temperature, suggesting that the reaction becomes more spontaneous at higher temperatures. These findings align with previous studies on biofuel production using catalytic processes (Silmara et al., 2015; John et al., 2021a,b). The most favorable reaction conditions were observed with the smallest catalyst particle size (0.1 mm), resulting in the lowest ΔG value. This suggests that smaller particles provide a larger surface area for interaction with the reactants, enhancing the reaction kinetics and driving the process towards spontaneity.

Implications for Industrial-Scale Application in Thermodynamics. The thermodynamic analysis of the simultaneous fluid catalytic conversion and recovery (SFCCR) of bioaviation fuel from Jatropha oil with activated carbon catalyst offers key insights for the scaling up of this process for industrial bio-aviation fuel production. The endothermic nature of the SFCCR reaction, as indicated by the positive enthalpy changes, necessitates an effective heat management strategy. This means that industrial applications must incorporate advanced heat exchange systems to supply the substantial energy required to drive the reaction forward, overcoming the activation energy barrier to break down the complex Jatropha oil molecules. Moreover, the study on the effects of catalyst particle size on the reaction thermodynamics reveals the importance of catalyst design in enhancing reaction spontaneity and efficiency. The observed trend where smaller catalyst particles (like 0.1 mm) lead to lower Gibbs free energy values suggests that maximizing the catalyst's surface area could significantly improve reaction kinetics. This insight directs the focus towards optimizing the catalyst synthesis process, aiming for smaller, more uniformly sized particles that could offer a larger active surface for interaction with the reactants, thereby promoting a more thermodynamically favorable environment for the reaction at industrial scales.

Future Research Directions. Thermodynamic considerations in the SFCCR of bioaviation fuel from Jatropha oil open several avenues for research. One crucial area is the exploration of feedstock versatility. Understanding how the thermodynamic parameters like Gibbs free energy, enthalpy, and entropy change with different feedstocks such as waste cooking oils, algae oils, or animal fats could lead to more adaptable and efficient processes. This would not only diversify the input materials but also potentially improve the thermodynamic efficiency of the reaction by tailoring conditions to different molecular structures. Another important aspect is the stability and deactivation of the activated carbon catalyst under varying thermodynamic conditions. Research should focus on how temperature, pressure, and reactant composition affect catalyst performance over time. This includes studying the mechanisms by which the catalyst might degrade or deactivate, which could inform strategies for catalyst regeneration or the design of more robust catalysts that can withstand the harsh conditions of SFCCR while maintaining favorable thermodynamic outcomes.

Moreover, integrating the SFCCR process into existing industrial infrastructures could benefit from a thermodynamic perspective. This involves optimizing the energy input required for the endothermic reaction, possibly through heat integration across different stages of the refinery process. Understanding the thermodynamics here would help in designing systems that minimize energy losses and enhance overall process efficiency. Lastly, a comprehensive life cycle assessment from a thermodynamic viewpoint would be beneficial. This would involve analyzing the energy balance, entropy changes, and exergy efficiency throughout the lifecycle of bio-aviation fuel production. Such an assessment would not only highlight areas where thermodynamic efficiency could be improved but also quantify the energy footprint of the process, guiding more sustainable practices in biofuel production.

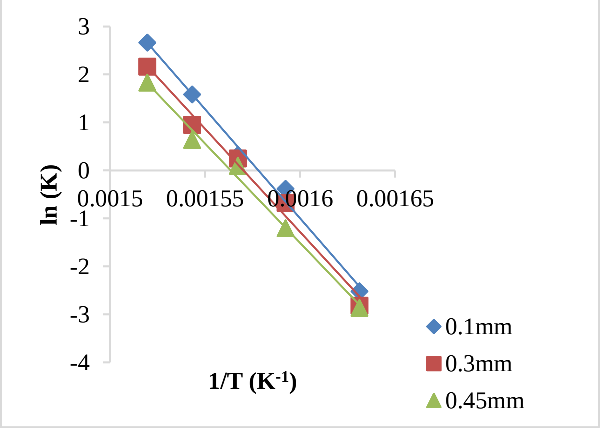

Figure 1: Plot of In K (equilibrium constant) vs. 1/T (temperature, K^{-1}) for different particle sizes for BAF from JO using AC catalyst

Table 6. Thermodynamic parameters

	0.1mm				**0.3mm**				**0.45mm**					**Average**		
Temp (K)	**(Δ)G (KJ/mol)**	**K**	**(Δ)H (KJ/mol)**	**(Δ)S (KJ/mol)**	**(Δ)G (KJ/mol)**	**K**	**(Δ)H (KJ/mol)**	**(Δ)S (KJ/mol)**	**(Δ)G (KJ/mol)**	**K**	**(Δ)H (KJ/mol)**	**(Δ)S (KJ/mol)**	**Ave. (Δ)G (KJ/mol)**	**Ave. K**	**Ave. (Δ)H KJ/mol)**	**Ave. (Δ)S (KJ/mol)**
613	12.59	0.07	381.45	0.60	13.90	0.06	389.32	0.61	15.05	0.05	369.77	0.58	13.85	0.06	380.18	0.60
628	3.56	0.66			4.72	0.57			6.37	0.32			4.88			
638	-2.45	1.75			-1.41	1.10			0.58	1.01			-1.09			
648	-8.47	4.11			-7.53	3.65			-5.20	2.81			-7.07			
658	-14.49	13.81			-13.66	12.97			-10.99	6.40			-13.05			

3.3 Statistical Analysis of the Biorefinery Process using Response Surface Model (RSM)

A comprehensive statistical analysis of the biorefinery process, involving the simultaneous fluid catalytic conversion (SFCC) of Jatropha Oil (JO) and recovery of bio-aviation fuel using activated carbon (AC) catalysts, was performed using Response Surface Methodology (RSM). The experimental data were analyzed to assess the main effects, interaction effects, and quadratic effects of the process variables, including temperature, catalyst dosage, and time, on the conversion of JO to bio-aviation fuel. The results indicated a direct correlation between increased temperature, catalyst loading, reaction time, and the degree of SFCC and fuel recovery. To accurately model the quadratic response surface of this process, a multi-regressional analysis was conducted, leading to the derivation of a second-order (quadratic) polynomial equation. The equation captures the influence of both linear and interactive effects of the process variables. The coded polynomial equation for predicting the yield of bio-aviation fuel is as follows (equation 11):

$$\textbf{\% \% Yield}_{\mathbf{JO}}\ \textbf{(AC)} = 18.9677 + 26.8455X_1 + 17.8464X_2 + 5.27005X_3 + 13.7625X_1X_2 + 0.6075X_1X_3 + -1.9025X_2X_3 + 11.3066X_1\text{^}2 + 10.9602X_2\text{^}2 + -7.8614X_3\text{^}2 \quad (11)$$

This coded equation, derived from the experimental data, allows for the prediction of bio-aviation fuel yield at various levels of the process variables, with high levels coded as +1 and low levels as -1. The relative influence of each factor can be interpreted by comparing the coefficients, with temperature (X_1) showing the most substantial effect on fuel yield, followed by catalyst loading (X_2) and reaction time (X_3). Additionally, the positive interaction between temperature and catalyst loading (X_1X_2) further amplifies the fuel yield, highlighting the importance of optimizing these variables for improved biorefinery process efficiency. This model provides valuable insight into optimizing the biorefinery process for maximum bio-aviation fuel yield and demonstrates the effectiveness of RSM in refining and analyzing complex catalytic processes.

The experimental results for bio-aviation fuel production from Jatropha Oil via the solid-fluid catalytic conversion reaction (SFCCR) using activated carbon AC catalyst were analyzed using analysis of variance (ANOVA) to validate the Response Surface Quadratic models developed for this process. Table 7 presents the ANOVA outcomes and coefficient values, focusing on significant terms in the model. The ANOVA results confirmed the model's significance, with an F-value of 42.94, indicating a strong model fit for predicting biofuel yield from JO. The probability of obtaining an F-value this large due to random noise is only 0.01%, reinforcing the model's robustness. The F-value was calculated by dividing the adjusted mean square of the regression by the adjusted mean square of the residuals, which further illustrates the model's predictive power.

The model's P-value (Prob. > F) was found to be very low, emphasizing the statistical significance of the model terms. A P-value less than 0.05 denotes significant terms, while values greater than 0.1 indicate non-significant terms that could be candidates for removal to refine the model, except those needed for maintaining the model hierarchy. The analysis showed that the model terms X_1 (temperature), X_2 (catalyst dosage), X_3 (reaction time), and their interaction and quadratic terms—X_1X_2, X_1^2, X_2^2, and X_3^2—are significant in predicting bio-aviation fuel yield. The reduced quadratic model equation incorporating these significant terms is presented in equation (12):

$$\% \textbf{Yield}_{\textbf{JO}} \textbf{ (AC)} = 18.9677 + 26.8455X_1 + 17.8464X_2 + 5.27005X_3 + 13.7625X_1X_2 + 0.6075X_1X_3 + -1.9025X_2X_3 + 11.3066X_1\hat{}2 + 10.9602X_2\hat{}2 + -7.8614X_3\hat{}2 \quad (12)$$

This equation demonstrates how variations in temperature, catalyst dosage, and reaction time, along with their interactions and quadratic effects, significantly impact the bio-aviation fuel yield from JO using AC catalysts.

Table 7. ANOVA for Reduced Response Surface Quadratic Model

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	15901.94	7	2271.71	42.94	< 0.0001	Significant
X_1-Temp	8261.96	1	8261.96	156.17	< 0.0001	Significant
X_2-Catalyst loading	3651.25	1	3651.25	69.02	< 0.0001	Significant
X_3-Reaction time	318.40	1	318.40	6.02	0.0304	Significant
X_1X_2	1515.25	1	1515.25	28.64	0.0002	Significant
X_1^2	890.76	1	890.76	16.84	0.0015	Significant
X_2^2	837.02	1	837.02	15.82	0.0018	Significant
X_3^2	430.62	1	430.62	8.14	0.0145	Significant
Residual	634.83	12	52.90			
Lack of Fit	281.99	7	40.28	0.5708	0.7587	not significant
Pure Error	352.85	5	70.57			
Cor Total	16536.78	19				
Fit statistics						
Std. Dev.	7.27		R^2		0.9616	
Mean	27.23		Adjusted R^2		0.9392	
C.V. %	26.72		Predicted R^2		0.8995	
			Adeq Precision		21.7220	

The model adequacy for the SFCCR process of bio-aviation fuel (BAF) production from Jatropha Oil JO using activated carbon catalyst was evaluated using sequential model sum of squares and model summary statistics. The quadratic regression models exhibited coefficients of determination (R^2) values of 0.9635, indicating that the models accounted for 96.35% of the variation in SFCCR performance. The adjusted R^2 value of 0.9307 was in reasonable alignment with the predicted R^2 of 0.8277, further validating the models' accuracy in fitting the experimental data. This agreement underscores the robustness of the predictive model for SFCCR using AC catalysts. The regression analysis, performed using Design Expert Software (V11), revealed that key process parameters such as SFCCR temperature, catalyst loading, and contact time, as well as the interaction between temperature and catalyst loading, significantly influenced the BAF yield ($p<0.05$). Fischer's F-test confirmed the importance of these factors and their quadratic terms, affirming the strong predictive power of the response surface models for optimizing BAF production from JO using AC catalysts. These findings suggest that the SFCCR process can be accurately modeled and optimized, leading to effective biofuel yield predictions under various operating conditions. The Lack of Fit F-values of 0.57 for SFCCR from JO using AC catalyst indicates the Lack of Fit is not significant relative to the pure error. There are 75.87% chance for AC catalysts that a "Lack of Fit F-value" this large could occur due to noise. The non-significant lack of fit is good -- we want the model to fit. The predicted R-squared values are in passable agreement with the Adj R-Squared values; i.e. the difference is less than 0.2. The 'Adeq Precision' measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The estimated ratios of 5.20 for AC catalyst designate an adequate signal, hence, the model can be used for design space navigation. The normal probability plots shown in Figure 2 indicate that the residuals follow a normal distribution, in which instance the points follow a straight line. Significant patterns like an "S-shaped" curve, signify that a response transformation may offer better analysis. The plot of the residuals versus the climbing predicted response values is shown in Figure 3. This tries out the assumption of constant variance. The observed random scatters in the plot indicate the constant range of residuals across the graph. A plot with expanding variance ("megaphone pattern <") signals the essential for a transformation. The plot of the predicted response values versus the actual response values for AC catalysts drives to discover a value, or group of values, difficult to be predicted by the models. Table 8 presents the model-predicted percentage bio-aviation fuel yield and the corresponding experimental values. It could be seen that the model predicted results are in close agreement with the experimental response values. This indicates the capability of the model for future prediction.

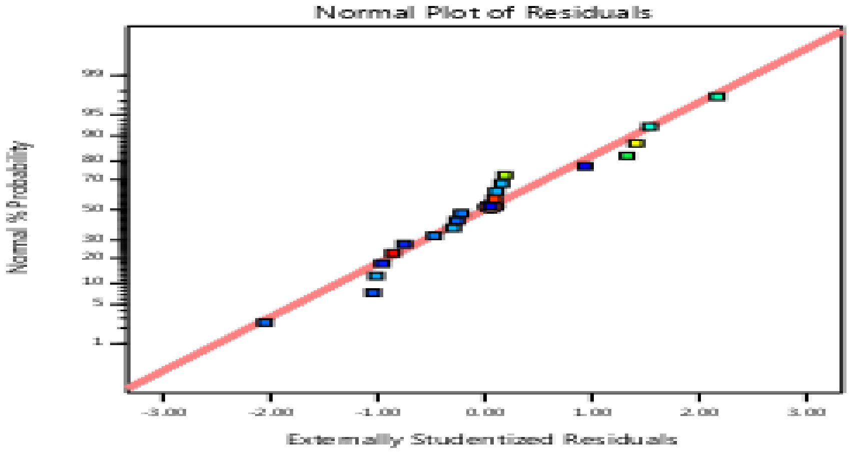

Figure 2: plot of normal probability Vs residuals

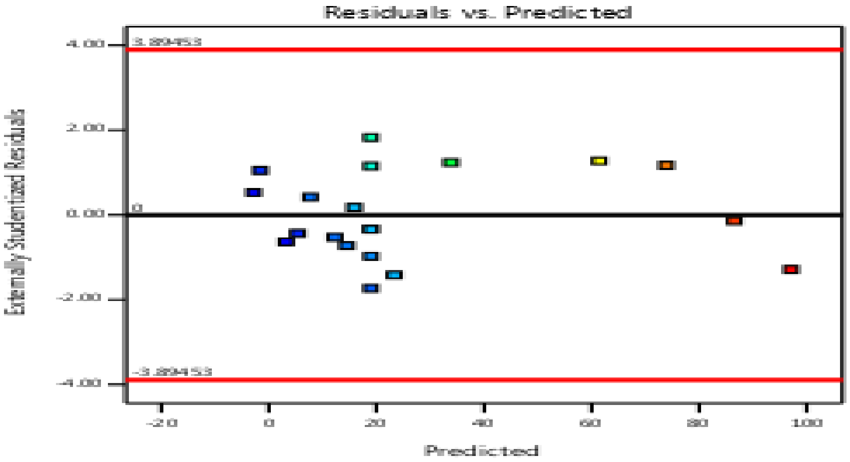

Figure 3: plot of residual Vs predicted values

Table 8. The experimental/actual values and the model-predicted values

Standard order	Actual value	Predicted value
1	0.00	-0.83
2	16.27	16.34
3	3.00	4.34
4	85.80	86.56
5	9.98	8.71
6	40.16	40.88
7	16.85	15.88
8	90.60	90.10
9	0.00	0.22
10	79.60	79.88
11	10.80	10.46
12	67.60	66.44
13	3.60	2.58
14	9.60	10.29
15	8.20	9.79
16	12.40	13.47
17	26.60	26.66
18	16.64	17.77
19	30.20	29.32
20	16.60	16.70

3.3.1 Two-Factor effects on biorefinery-SFCCR process efficiency

The production of biorefinery-based bio-aviation fuel from Jatropha oil (JO) using functionalized activated carbon (AC) catalysts through selective fluid catalytic conversion and recovery is a promising approach in the pursuit of sustainable aviation fuels. This study examines the interaction effects of various biorefinery-SFCCR variables on the percentage of bio-aviation fuel yield, providing insights into the optimal conditions for maximizing production efficiency. The interaction effects of the Short-Path Fluid Catalytic Conversion and Recovery (SFCCR) variables on the percentage bio-aviation fuel yield from Jatropha Oil using AC catalysts were examined through 3D surface response curves. These curves plotted the interactions between any two independent variables while maintaining the third variable at its central level. The resulting 3D plots (Figures 4-6) provide insights into the complex relationships between reaction parameters and bio-aviation fuel yield. The key variables investigated were reaction temperature, catalyst loading, and contact time.

The investigation into the two-factor effects on the SFCCR of bio-aviation fuel yield from Jatropha Oil using AC catalyst derived from rice husk through decarboxylation, in the absence of hydrogen addition, reveals notable interactions between reaction variables which indicates critical synergistic effects. Increasing reaction temperature and catalyst loading significantly improves bio-aviation fuel production, a trend consistent with findings in decarboxylation studies using Ni/AC catalysts for oleic acid conversion, where higher temperatures and catalyst loading optimized hydrocarbon yields without hydrogen donors (Zhang et al., 2018). This behavior is aligned with studies on decarboxylation over Ni-supported catalysts, where stearic acid conversion increased with higher temperatures and nickel loadings, maximizing at 370°C for 5 hours, with 80% selectivity to heptadecane (Wu et al., 2016). Similarly, the absence of external hydrogen in our method parallels findings from the decarboxylation of oleic acid, where in situ hydrogen transfer facilitated significant yields of heptadecane without hydrogen donors (Tan et al., 2020). In contrast to Ni-based catalysts, which showed more cracking at higher loadings, our AC-based method maintained robust biofuel yields without significant cracking. The decarboxylation without hydrogen addition is cost-effective and environmentally friendly, enhancing the sustainability of biofuel production. Moreover, the positive correlation between catalyst loading and fuel yield reinforces the catalyst's pivotal role in optimizing SFCCR rates.

Similarly, increasing contact time further enhances conversion rates, indicating a strong correlation between longer reaction times and higher yields, aligning with studies on Pt/MWCNT catalysts for microalgae oil decarboxylation (Yang et al., 2023). The highest yield in this study was recorded at 394.69°C and a catalyst loading of 4.67g, achieving a 90.91% fuel yield, which surpasses the 80% heptadecane selectivity reported in Ni/C systems at 370°C (Wu et al., 2016). This suggests the rice husk-derived AC catalyst provides an effective alternative for cost-effective decarboxylation, given its similar performance to metal-based catalysts, as supported by studies on continuous microfluidic decarboxylation systems (Li et al., 2023). The interaction effects between variables, such as temperature and catalyst loading, exhibit a synergistic effect, enhancing fluid catalytic conversion rates and biofuel recovery, a phenomenon observed across various decarboxylation processes (Su et al., 2015). Further exploration into the combined impact of these variables may offer optimized conditions for higher fuel yields with minimal hydrogen input.

The results demonstrated a strong and direct positive correlation between reaction temperature and the rate of fluid conversion and bio-aviation fuel recovery. The optimal temperature for maximum bio-aviation fuel yield from JO was found to be 394.69 °C using AC catalysts. As the reaction temperature increased, both the fluid conversion rate and bio-aviation fuel recovery improved significantly. This finding aligns with several studies in the literature, particularly those focusing on the catalytic cracking of vegetable oils for biofuel production. For instance, Zhao et al. (2015) reported optimal temperatures between 380-420°C for the catalytic cracking of soybean oil to produce aviation biofuels. Our results fall within this range, suggesting that despite the difference in feedstock, the temperature requirements for efficient cracking remain similar. However, it's worth noting that our process achieved high yields at a slightly lower temperature compared to some studies, which could be attributed to the efficiency of our AC catalyst.

The percentage of bio-aviation fuel yield showed a direct proportional relationship with catalyst loading. Increasing the catalyst dosage resulted in a higher rate of SFCCR. The maximum bio-aviation fuel yield from JO (90.91%) was recorded at a catalyst dosage of 4.67g of AC catalyst. This high yield is particularly noteworthy when compared to other studies in the field. For example, Wang et al. (2016) achieved a maximum jet fuel yield of 78% from camelina oil using a zeolite catalyst at similar temperatures but with higher catalyst loadings. Our higher yield with a lower catalyst loading suggests that our AC catalyst derived from rice husk may be more efficient for this process. This efficiency could be attributed to the unique surface properties and functional groups of the AC catalyst, which enhance its catalytic activity.

The SFCCR rate exhibited a direct proportional relationship with contact time. Both feed catalytic conversion and product recovery rates increased with longer contact times. The maximum percentage bio-aviation fuel yield from JO was recorded at 62.25 minutes. This optimal time is relatively short compared to some other studies in the literature, indicating a potentially more efficient process. For instance, Li et al. (2014) reported optimal contact times of 90-120 minutes for the catalytic cracking of waste cooking oil to produce aviation biofuels. Our shorter optimal time could lead to higher throughput and potentially lower energy costs in industrial applications. In comparison with other processes, our process utilizes decarboxylation in the absence of external hydrogen addition, employing a low-cost functionalized activated carbon catalyst derived from rice husk. This approach offers several advantages over traditional hydroprocessing methods used for bio-aviation fuel production. The production of bio-aviation fuel through decarboxylation using activated carbon catalysts has shown promising yields without the need for external hydrogen. For instance, research on Palm Fatty Acid Distillate (PFAD) demonstrated that using an activated carbon catalyst, a conversion rate of 77.07 % of free fatty acids into straight-chain hydrocarbons was achieved under optimized conditions, specifically with heptane as a solvent and an argon atmosphere (Wiethoff et al., 2019). Additionally, the integration of aldol condensation and hydrogenation processes over bifunctional catalysts, such as Ni/Mg–Al–O/AC, has been explored, yielding up to 81.1 % targeted alkanes, although this process typically involves hydrogenation (Shao et al., 2021). Furthermore, the catalytic hydrothermal decarboxylation of fatty acids in microalgae oil using multi-wall carbon nanotube-supported Pt catalysts achieved high selectivity for heptadecane, indicating the potential of various catalyst systems in enhancing biofuel yields (Yang R. et al., 2019). Overall, these studies highlight the effectiveness of activated carbon catalysts in bio-aviation fuel production through decarboxylation processes in the absence of external hydrogen addition.

This approach differs from some other studies in the literature. For example, Yang Z et al. (2019) used a hydrodeoxygenation process with external hydrogen addition to convert waste cooking oil into aviation fuel, achieving a yield of 85 %. The comparable yield (90.91 %) achieved in the present study without hydrogen addition represents a significant advantage in terms of process simplicity and cost-effectiveness. Hydroprocessing, as described by Gutiérrez-Antonio et al. (2017), typically requires high-pressure hydrogen and expensive noble metal catalysts. While it can achieve high yields (up to 99 % in some cases), the process is energy-intensive and has a higher carbon footprint due to the hydrogen requirement. Our process, in contrast, achieves comparable yields (90.91 %) without the need for external hydrogen, potentially offering a more sustainable and cost-effective alternative. The use of AC catalyst derived from rice husk also addresses sustainability concerns. As noted by Chatterjee et al. (2018), utilizing agricultural waste for catalyst production not only reduces costs but also contributes to waste valorization, aligning with circular economy principles.

Our AC catalyst shows promising performance compared to other catalysts reported in the literature. For example, Zhao et al. (2015) used HZSM-5 zeolite catalysts for aviation biofuel production from soybean oil, achieving yields of up to 85 %. Our higher yield (90.91 %) with an AC catalyst suggests that functionalized carbon-based catalysts could be competitive alternatives to traditional zeolites in this application. Moreover, the efficiency of our catalyst at lower loadings (4.67 g) compared to some studies using higher catalyst-to-oil ratios indicates potential economic benefits in large-scale applications. The findings of this study align with several recent investigations in the field of bio-aviation fuel production, while also presenting some unique aspects: In catalyst choice and performance, the use of low-cost functionalized activated carbon catalyst derived from rice husk in this study represents a sustainable and economically viable approach. This aligns with the growing trend of utilizing biomass-derived catalysts in biofuel production. For instance, Alsultan et al. (2021) demonstrated the effectiveness of activated carbon derived from waste rubber tires in biodiesel production, achieving a yield of 98.5 %. However, their study focused on biodiesel rather than bio-aviation fuel, highlighting the novelty of the current research.

The optimal temperature of 394.69 °C found in this study is comparable to other research in the field. Zhao et al. (2020) reported an optimal temperature range of 380-400 °C for the catalytic cracking of waste cooking oil to produce aviation fuel-like hydrocarbons. However, they used a different catalyst (Ni-MOF-74), which may account for slight variations in the optimal temperature. The optimal contact time of 62.25 minutes found in this study is relatively short compared to some other processes reported in the literature. For instance, Li et al. (2022) reported an optimal reaction time of 120 minutes for their bio-jet fuel production process using a Ni-based catalyst. The shorter reaction time in the current study could indicate higher efficiency and potential for improved throughput in industrial applications. The optimal catalyst loading of 4.67 g found in this study is within the range reported in similar studies. However, it's worth noting that the specific surface area and pore structure of the AC catalyst can significantly influence the optimal loading. Future studies could benefit from a detailed characterization of the catalyst properties to further optimize the process.

Our study demonstrates the potential of using low-cost, sustainable AC catalysts derived from agricultural waste for the production of bio-aviation fuel via decarboxylation. The high yields achieved without external hydrogen addition offer a promising pathway for more sustainable aviation fuel production. These findings contribute to the growing body of knowledge on sustainable aviation fuel production and offer insights into the development of more efficient and environmentally friendly catalytic processes. The high yield of 90.91 % achieved without external hydrogen addition indicates the efficiency of the decarboxylation process using AC catalysts, suggesting significant potential for economic viability in large-scale bio-aviation fuel production. The use of rice husk-derived AC catalysts aligns with circular economy principles, potentially reducing the overall environmental impact. The relatively short optimal contact time of 62.25 minutes suggests scalability potential, although further large-scale studies are needed. While the AC catalyst performs well, future research could explore optimization through different activation methods or precursors. Given the success of Jatropha oil, future studies could investigate the applicability of this process to other non-edible oil feedstocks, broadening the resource base for bio-aviation fuel production. In conclusion, this study demonstrates a promising approach to bio-aviation fuel production using a sustainable catalyst and an efficient decarboxylation process. Future research directions could include long-term catalyst stability studies, detailed product characterization, and techno-economic analyses to further assess the industrial viability of this process.

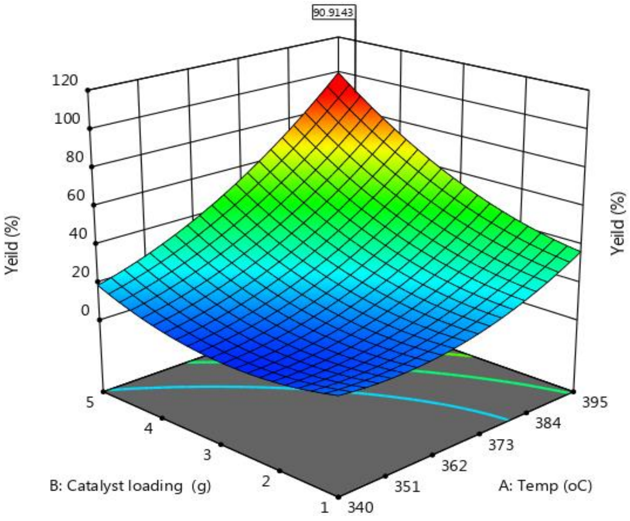

Figure 4: 3D plot of the effect of temperature and time on % bio-aviation fuel yield from JO using AC catalyst

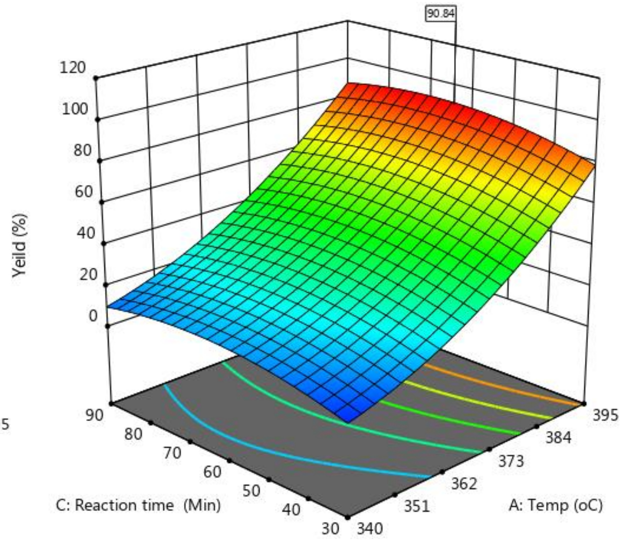

Figure 5: 3D plot of the effect of reaction temperature and catalyst loading on % bio-aviation fuel yield from JO using AC catalyst

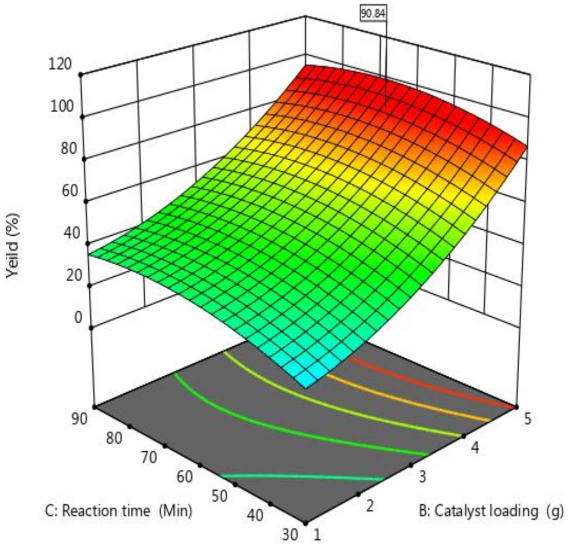

Figure 6: 3D plot of the effect of reaction time and catalyst loading on % bio-aviation fuel yield from JO using AC catalyst

3.3.2 Experimental-validation and numerical-optimization of biorefinery process

The numerical optimization and experimental validation of the biorefinery process for bio-aviation fuel (BAF) production via the solid-fluid catalytic conversion reaction (SFCCR) of Jatropha Oil (JO) using an activated carbon (AC) catalyst showed strong consistency between predicted and experimental results. The model, developed through response surface methodology (RSM), predicted a biofuel yield of 90.91 % under optimal conditions (394.69 °C, 4.67 g catalyst, and 62.25 minutes), as shown in Table 9, while the experimental yield was slightly lower at 88.60%. This small deviation confirms the reliability of the optimization process in accurately predicting outcomes for BAF production. This strong agreement validates the optimization approach, likely based on response surface methodology (RSM) or similar designs, which are widely used to fine-tune complex catalytic processes.

Compared to the literature, these results align well with other studies. For instance, Zhang et al. (2018) achieved a 90 % yield of heptadecane in the decarboxylation of oleic acid using a Ni/AC catalyst in the absence of hydrogen, similar to the hydrogen-free decarboxylation process in this study. The optimization of parameters like temperature and catalyst loading also follows trends seen in other works. For example, Yang et al. (2023) demonstrated the use of Pt/MWCNT catalysts for microalgae oil, achieving a 97% conversion with a similar temperature and catalyst optimization strategy, albeit with a different feedstock, external hydrogen addition and catalyst. However, these results were achieved with metal-based catalysts, which may not be as cost-effective as AC derived from rice husk catalyst.

The absence of external hydrogen addition in this study enhances its sustainability, given the cost and energy demands associated with hydrogenation. The absence of external hydrogen in this process, relying purely on decarboxylation, offers significant operational cost savings compared to hydrogenation-based methods, where hydrogen must be externally supplied. Optimizing the process without hydrogen addition, as demonstrated in this work, proves that high yields can still be achieved through careful control of variables like temperature, catalyst loading, and reaction time. The slight variation between predicted and experimental values may result from inherent process variability but demonstrates that the model is a reliable predictor of fuel yields under SFCCR conditions.

The use of low-cost AC catalysts derived from rice husk further supports the process's environmental and economic viability. Additionally, the comparison of oil types suggests that the feedstock plays a crucial role in determining the optimal process conditions and yield efficiency. While the AC catalyst here performs comparably to metal-based alternatives, the economic benefits of using biomass-derived catalysts highlight its potential for scaling.

Thus, this study's optimized biorefinery-SFCCR process offers a cost-effective and environmentally friendly alternative for biorefinery-based bio-aviation fuel production, validated through both predictive models and experimental trials. This suggests that future work could explore different types of bio-oils and further refine optimization parameters, enhancing scalability and cost-efficiency in biorefinery applications.

Table 9. The model predicted optimum conditions and experimental response values

	Optimum factors predicted			Model predicted value	Experimental value
Catalyst	Temperature (ºC)	Catalyst loading (g)	Time (mins)	Yield (%)	Yield (%)
AC	394.69	4.67	62.25	90.91	88.60

The optimized conversion temperature for Jatropha oil into bio-aviation fuel was determined to be 395 °C, yielding efficient conversion without excessive cracking of the product. Figures 9 and 10 illustrate the optimized product and conversion residue distribution, while Figures (7-8) and Table 10 provide detailed product composition under these conditions. The liquid phase yield was 93 %, consisting of 88.6 % bio-aviation fuel, 1.8 % biodiesel, 1.2 % gasoline, and 1.4 % water. Additionally, the gaseous product accounted for 1%, and the remaining 6 % comprised coke and residue. Notably, 5.7 % of the feedstock was lost as coke and semi-solid carbon-like material on the catalyst. This residue highlights the challenge of catalyst fouling in catalytic processes.

Further analysis reveals that this result aligns with the findings of Wang et al. (2020), who observed that higher temperatures lead to better biofuel yields but can also increase coke formation if excessive cracking occurs. This trade-off between maximizing yield and minimizing coke formation is a key consideration in optimizing biorefinery processes for biofuel production. Zhao et al. (2014) also demonstrated that temperature optimization is crucial, with their study on different vegetable oils showing optimal deoxygenation and hydrocarbon production around 300-320°C via hydrogenation. However, the bio-aviation fuel yield in this study surpasses typical results reported for other catalysts, such as zeolites, which have been shown to achieve similar yields at higher pressures and temperatures (Goh et al., 2021). While AC catalysts are more cost-effective and possess a higher surface area, they can accumulate coke over time, potentially deactivating the catalyst. In contrast, zeolites and bifunctional catalysts like Fe/AC, as reported by Lin et al. (2020), have shown greater resistance to coking, albeit at a higher cost. These studies highlight the need to balance cost, yield, and process efficiency for large-scale biofuel production.

In comparison to other studies, the biorefinery process in this work relies on decarboxylation without hydrogen addition, which contrasts with hydrogenation processes widely used in biofuel production. For example, Bala and Chidambaram (2016) observed that hydrogen addition in bio-aviation fuel production from algae oil improved yields by reducing the formation of coke through hydrodeoxygenation (HDO), where oxygen is removed as water rather than CO_2. Their process achieved a 98% liquid mass conversion using Ce-exchanged zeolite catalysts at 400°C. Similarly, Zhao et al. (2014) reported higher deoxygenation efficiency (99.29%) with Pd-based catalysts at 300°C, producing a high percentage of C_8-C_{16} hydrocarbons, which are critical for aviation fuel. However, these studies required hydrogen addition, whereas the current study demonstrates that significant yields can still be achieved via decarboxylation, though with slightly higher coke formation.

Coke formation is common in decarboxylation processes without hydrogen addition, as CO_2 is the main byproduct, resulting in carbon deposition on the catalyst surface. The relatively low coke yield in the current study (5.7%) suggests that the activated carbon catalyst facilitates efficient decarboxylation. However, it’s worth noting that further optimization could focus on reducing residue through improved catalyst design, as demonstrated by Goh et al. (2021), who utilized zeolite-based catalysts to achieve higher liquid yields and less coke formation in palm oil conversion under hydrogen-free conditions.

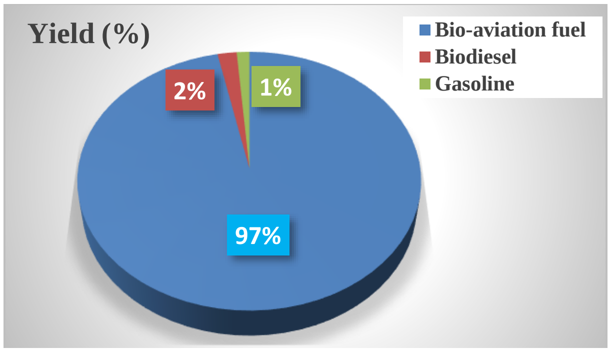

Figure 7: Biofuel yield under optimized conditions

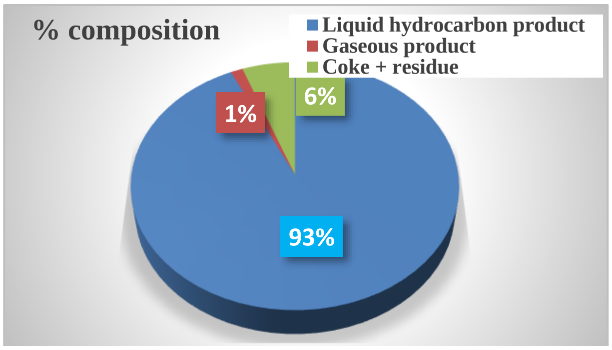

Figure 8: Solid, liquid and gaseous composition under optimized conditions

Table 10. Total product distribution under optimized conditions

Component	Composition (%)
Bio-aviation fuel	88.6
Biodiesel	1.8
Gasoline	1.2
Gaseous product	1.3
Coke + residue	5.7
Water	1.4

Fig. 9. Optimized bio-aviation fuel product

Fig.10. Conversion residue

3.4 Total Hydrocarbon Compound (THC) – Analysis

This section presents the result of the THC analysis of the synthesized biorefinery-based bio-aviation fuel from JO using AC catalysts. The hydrocarbon compositions of the produced bio-aviation fuel are shown in Figure 11 and Table 11. The analysis of Total Hydrocarbon Compounds (THC) in bio-aviation fuel synthesized from Jatropha Oil using AC catalysts reveals a hydrocarbon composition predominantly within the carbon range of C_9 to C_{16}. This composition aligns with the ASTM D1655-18a specifications for aviation turbine fuels, which are complex mixtures primarily composed of hydrocarbons, varying based on the feedstock and production methods employed (Arora & Mishra, 2023). Recent studies emphasize the importance of meeting these specifications to ensure performance and safety in aviation applications (Peters et al., 2023). Furthermore, advancements in biofuel production technologies, such as hydro-processed esters and fatty acids (HEFA) and alcohol-to-jet processes, have shown promising results in producing bio-aviation fuels that not only meet regulatory standards but also significantly reduce greenhouse gas emissions compared to conventional jet fuels (Tan et al., 2024a; Kameswari et al., 2023). This highlights the potential of biorefinery-based approaches in contributing to a more sustainable aviation sector while adhering to stringent fuel quality requirements. The hydrocarbon composition of bio-aviation fuel varies significantly based on the feedstock and production processes used. Bio-jet fuels typically consist of a mixture of paraffin (both iso and normal), cycloparaffins (naphthenes), and aromatics, with specific ratios influenced by the source material and processing methods employed. For instance, aviation fuel derived from rapeseed oil exhibits a hydrocarbon fraction primarily in the C_{15}–C_{18} range, with a notable reduction in aromatic compounds compared to conventional jet fuels, fulfilling ASTM D-7566 standards (Główka et al., 2023a). In contrast, biofuels produced from corn stover are rich in isoparaffins (50.4%) and have a lower oxygen content, indicating a different composition profile (Liu et al., 2023a). Additionally, the blending of bio-jet fuels with conventional fuels can enhance performance characteristics, as seen in the BIO50 blend, which demonstrates improved calorific value and lower emissions (Główka et al., 2023a; Adhikari, 2017). Overall, the diversity in feedstock and processing techniques leads to a wide range of hydrocarbon compositions in bio-aviation fuels.

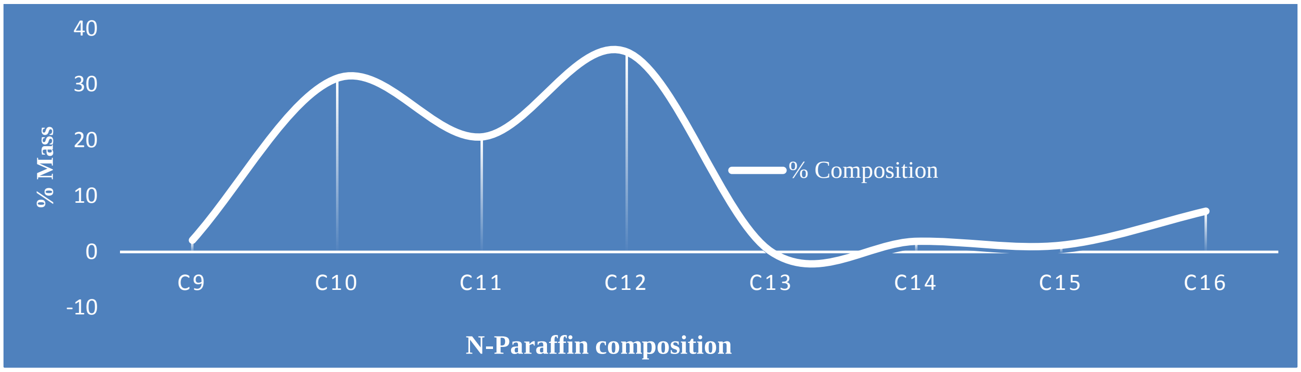

Figure 11: Hydrocarbon composition of bio-aviation fuel

Table 11. Total hydrocarbon compound

Carbon No.	Name
C9	Nonane
C10	Decane
C11	Undecane
C12	Dodecane
C13	Tridecane
C14	Tetradecane
C15	Pentadecane
C16	Hexadecane
C20	Eicosane
C26	Hexacosane
C27	Heptacosane
C34	Tetratriacontane
C38	Octatriacontane
C39	Nonatriacontane
Total (%)	100
Molecular weight (g/mol)	162.76

4.0. Conclusion

This study investigated a novel hydrogen-free biorefinery approach for the sustainable production of bio-aviation fuel. The primary focus of this research was to develop and optimize a single-step, heterogeneous fluid catalytic conversion and recovery (SFCCR) process for converting Jatropha seed oil (JO) into bio-aviation fuel using a low-cost, environmentally friendly catalyst derived from rice husk. The study hypothesized that this approach, by eliminating the need for external hydrogen and utilizing a sustainable catalyst, would offer a more efficient and cost-effective alternative to conventional biofuel production methods. The study successfully demonstrated the feasibility of this approach. A maximum bio-aviation fuel yield of 88.60% was achieved under optimized conditions, highlighting the potential of this process for high-value fuel production. Kinetic analysis revealed that the SFCCR process best fit a pseudo-second-order model, indicating a strong correlation between reaction rate and reactant concentration. The thermodynamic analysis further elucidated the process characteristics, confirming its spontaneous, endothermic, and irreversible nature. These findings provide crucial insights into the reaction mechanisms and process behavior, enabling more precise control and optimization of the SFCCR process.

The use of a low-cost, biomass-derived catalyst, coupled with the elimination of external hydrogen, significantly enhances the sustainability and economic viability of this biorefinery approach. This study demonstrates the potential of utilizing readily available and renewable resources to develop efficient and environmentally friendly biofuel production technologies. The findings contribute to the advancement of sustainable bio-aviation fuel production by offering a promising alternative to conventional hydrogen-based approaches. Future research directions should focus on further optimizing the catalyst formulation, exploring the use of different feedstocks, and investigating the long-term stability and reusability of the catalyst. Moreover, a comprehensive life cycle assessment (LCA) should be conducted to evaluate the environmental and economic impacts of this biorefinery approach across its entire lifecycle. The insights gained from this research can pave the way for the commercialization of sustainable bio-aviation fuels and contribute to the development of a more sustainable and environmentally friendly aviation industry.

Declaration of Competing Interest

The authors declare that they have no conflicts of interest.

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