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Original Paper

Enhanced efficiency in date seed biorefinery: The role of CTAB

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ABSTRACT

Date seeds are a viable biomass resource for pyrolysis due to their organic content; however, using them directly without pretreatment may lead to poor yields and product quality, especially in uncontrolled and uncatalyzed environments. Therefore, this research aims, for the first time, to use the cetyltrimethylammonium bromide surfactant (CTAB) as a novel treatment for date seeds and to investigate its effects on yield, characteristics, and the composition of the resulting pyrolysis products. The feedstock was pretreated with CTAB at different concentrations (1–2%) to modify surface properties and enhance biomass porosity for improved mass and heat transfer, as well as reaction efficiency. Pyrolysis experiments were carried out at moderate temperatures (300-400 °C) with different feedstock particle sizes under a nitrogen atmosphere. A bio-oil yield higher than 50 wt.% was obtained at pyrolysis temperatures higher than 350 °C. In contrast, higher biochar yields of more than 30 wt.% were obtained at the lower temperature (300 °C) and decreased as the temperature increased. Results also indicated that CTAB pretreatment, along with varying date seed particle sizes, had considerable effects on product yield and quality, with mitigation of secondary undesirable reactions. The products demonstrated notable characteristic features. This research presents an innovative solution for managing agricultural residues by converting them into energy and other useful resources, addressing both waste management and renewable energy strategies. The finding that date seed residues can serve as a resource for biofuel production and activated carbon manufacture aligns with circular economy concepts.

Keywords: *Biomass valorisation, CTAB pretreatment, Date seed biomass, Pyrolysis, Renewable energy*

1 INTRODUCTION

The rapid growth in population and industrial activities has led to a considerable increase in greenhouse gas emissions. This directly affects the environment, causing serious consequences such as accelerating global warming, rising sea levels, loss of biodiversity, and more frequent extreme weather events. As a consequence, it poses long-term risks and threats to both natural ecosystems and human societies [1, 2]. The growing need for environmentally sustainable biofuel sources as alternatives to conventional fossil-fuel energy, in response to the current global economy, makes biomass one of the most promising renewable energy options [3–5]. Moreover, the volume of solid waste has significantly increased, creating an urgent need for waste-management solutions.

Accordingly, numerous eco-friendly approaches have been proposed to mitigate these factors and to explore biofuel production from agricultural wastes. Among these approaches, and for many reasons such as affordability, simplicity, and flexibility, thermochemical methods have emerged as among the most effective techniques for biofuel production [6]. In particular, pyrolysis has attracted significant attention as a highly efficient and promising method for converting a wide range of biomass materials into valuable energy products. It involves the thermal decomposition of biomass at temperatures between 300–600 °C in an inert gas atmosphere (such as N2 or Ar) to produce three main products: biochar, bio-oil, and gaseous fuel [7].

In general, catalysts are used in the pyrolysis process, and the efficiency and quality of the products depend strongly on the catalyst type selected. Therefore, selecting cost-effective, robust catalytic materials is important for converting pyrolytic gases (particularly carbon dioxide) into valuable chemicals and biofuels [8]. Recently, there has been growing interest in developing 2D materials for renewable energy applications [9–11]. Research efforts have focused on tailoring the surface and electronic structures of 2D materials as promising catalysts for biomass conversion processes. These materials can demonstrate high efficiency, selectivity, and stability; therefore, they may play a vital role in producing high-value products from bio-waste materials. A series of metal- and metal oxide-based catalysts, such as Ni, Pt, Nb2O5, and other compounds, have been developed as efficient catalysts [12–14]. However, this field still needs further development.

Despite extensive studies on catalytic pyrolysis and the use of various biomass feedstocks, limited attention has been given to the role of surfactants, such as cetyltrimethylammonium bromide (CTAB), in modifying biomass properties prior to pyrolysis. Surfactants like CTAB may offer multiple benefits, including improving biomass porosity, altering surface chemistry, and possibly influencing the thermal degradation mechanism. These properties can enhance heat and mass transfer and may even provide catalytic-like effects during pyrolysis. However, the role of CTAB in this context remains largely underexplored, especially for agricultural wastes such as date seeds.

In this work, cetyltrimethylammonium bromide (CTAB) was employed not only as a modifying agent to alter the surface characteristics and porosity of date seed biomass but also as a potential catalytic additive. Its surfactant nature may facilitate better distribution of reactive sites and influence the decomposition environment. Although CTAB is not a conventional catalyst, its impact on product distribution, secondary reaction suppression, and thermal behavior during pyrolysis warrants investigation. To the best of our knowledge, no comprehensive study has been conducted on the effect of treating date seeds with cetyltrimethylammonium bromide (CTAB) prior to pyrolysis at moderate temperatures. Therefore, this research aims to investigate the impact of CTAB treatment on the yield and quality of pyrolysis products, including biochar, bio-oil, and pyrolytic gases.

2 MATERIALS AND METHODS

2.1 Preparation and size fractionation of date seeds

Date seeds (*Phoenix dactylifera L.*) were selected as the raw material due to their abundance in Iraq, especially in Anah City, Anbar Governorate, and their high organic content. After collection, the seeds were separated from the fruit tissue, soaked in distilled water for 24 h, scrubbed by hand, and rinsed again. Drying was conducted in two stages: sun-drying followed by oven-drying at 60 °C for 48 h until constant weight. The dried seeds were ground using a mechanical flour mill. Particle size distribution was determined by the mill type and sieve mesh sizes. To ensure consistency, the powder was sieved using 600 µm and 300 µm meshes. Additionally, some seeds were manually broken into four large pieces using an iron hammer. Four seed fractions were prepared and stored in sealed, labeled bags: (1) manually fragmented whole seeds, (2) particles >600 µm, (3) particles 300–600 µm, and (4) particles <300 µm. These size ranges were essential for evaluating the effects of surface area and morphology during processing.

2.2 Ctab solution preparation and blending process

In this study, a cationic surfactant, cetyltrimethylammonium bromide (C19H42BrN, CTAB), was employed as a surface-modifying agent. Different amounts of surfactant were dissolved in deionized water to prepare CTAB solutions at concentrations of 1%, 1.5%, and 2% (w/w relative to the weight of date seeds). To ensure complete dissolution and homogeneity, the solutions were continuously stirred for 30 minutes at room temperature.

After particle-size classification, date seed samples were mixed with CTAB in the Industrial Chemistry Laboratory at the College of Science, University of Anbar. The prepared CTAB solutions were mixed separately with each of the four particle-size fractions: whole fragmented seeds >600 µm, 300–600 µm, and <300 µm. Mixing was performed using an overhead mechanical mixer for

6 h per sample to ensure consistent interaction between CTAB and the biomass surface. After the blending stage, the samples were dried with heat to remove any remaining moisture and stabilize the materials for subsequent use.

2.3 Pyrolysis of date seed biomass

To examine the yield distribution of solid, liquid, and gaseous products, pyrolysis experiments were carried out using date seed biomass with and without CTAB surfactant treatment under controlled thermal conditions (as shown in Figure 1). For each experimental trial, 10 g of feedstock was precisely weighed and placed into a cylindrical crucible, which was then positioned at the center of the stainless-steel fixed-bed reactor. High-purity nitrogen gas (about 99% purity) was introduced into the reactor at a steady flow rate of 100 mL/min to maintain an oxygen-free environment during the procedure.

Once inert conditions were established, the reactor was heated at a controlled rate of 18 °C/min until it reached the target temperature (300 °C, 350 °C, or 400 °C), depending on the experimental trial. Upon reaching the desired final temperature, the system was held isothermally for 30 minutes to allow complete thermal decomposition of the biomass. During this residence time, the date seed material underwent pyrolysis, breaking down into volatile and non-volatile components. The evolved vapors were transported via a vapor decomposition line to a set of inclined glass condensers, where the condensable fractions were cooled and collected as bio-oil. Simultaneously, non-condensable gases that did not liquefy in the condenser were captured using specialized gas sampling bags for further analysis or venting. After the reactor was cooled to room temperature, the remaining solid residue (biochar) was carefully removed, weighed, and stored in moisture-proof containers. This step was essential for calculating the mass yield of char, which, along with the collected bio-oil and gas, provided a complete yield distribution for each pyrolysis temperature setting.

$$\text{Char Yield (\%)} = \frac{\text{Mass of char}}{\text{Initial biomass mass}} \times 100\% \quad (1)$$

$$\text{Oil Yield (\%)} = \frac{\text{Mass of condensed oil}}{\text{Initial biomass mass}} \times 100\% \quad (2)$$

$$\text{Gas Yield (\%)} = 100 - (\text{ Char Yield } + \text{ Oil Yield }) \quad (3)$$

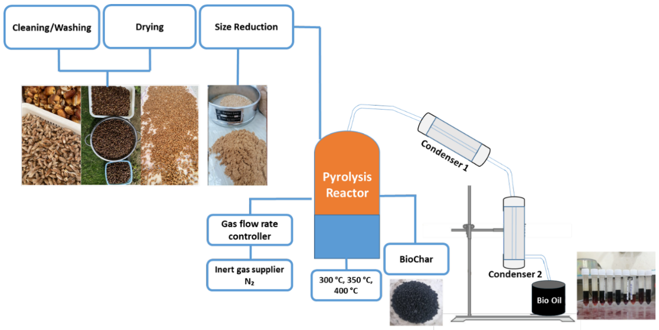

Fig. 1 Scheme of production of biochar and bio-oil from the pyrolysis of date seeds

2.4 Design of experiments

Design of experiments (DOE) is a statistical and mathematical technique used to examine and enhance the direct and indirect relationships between independent variables and system responses. It is an effective approach for reducing the number of experimental trials required for process optimization when the complexity of the system under study makes rigorous modeling impractical [15]. A full-factorial DOE was used to assess the effects of key variables on the distribution of pyrolysis products. This statistical method enables systematic investigation of the individual and combined effects of several factors on the yields of char, bio-oil, and gas. Three independent variables were selected for this investigation: date seed particle size, pyrolysis temperature, and CTAB concentration. To ensure thorough coverage of the experimental conditions, each factor was tested at multiple levels.

Four levels of CTAB concentration, the first factor, were tested: 0% (control), 1%, 1.5%, and 2% by weight relative to the biomass. This range was selected to examine the effects of increasing surfactant concentration on biomass decomposition and product distribution. The pyrolysis temperature, the second factor, was investigated at three temperatures: 300 °C, 350 °C, and 400 °C. Within the usual operating range for slow pyrolysis, these temperatures were selected to represent low, intermediate, and high pyrolytic conditions. Four size categories were used to assess the third factor, date seed particle size: whole seeds (fragmented into quarters), coarse particles (>600 µm), medium particles (300–600 µm), and fine particles (<300 µm). This factor considers how surface area and particle shape affect heat transfer and thermal-degradation behavior. Other factors, such as heating rate, pressure, and residence time, were not studied and were therefore kept constant. Forty-eight experiments were generated and randomized. Table 1 summarizes the experimental factors and their corresponding levels.

Table 1 Levels of experimental factors utilized in the full factorial design

Independent variables	**Levels**
CTAB concentration	0% (control), 1%, 1.5%, 2%
Pyrolysis temperature	300°C, 350°C, 400°C
Date seed particle size	Whole seeds, > 600μ m, 300 – 600μ m, < 300μ m

To ascertain the statistical significance of each independent variable and their interactions, and to eliminate variables that were not significant at an alpha level of 0.05, analysis of variance (ANOVA) was conducted. Factorial plots were also used to examine how key variables and their interactions affect process responses.

2.5 Analysis of oil and gas products

Gas chromatography-mass spectrometry (GC–MS) analyses were performed to determine the chemical composition of the bio-oil fraction. Chromatogram peaks were compared with the National Institute of Standards and Technology (NIST) mass-spectral library to accurately identify the compounds.

To determine the composition of the gas fraction produced from the pyrolysis of untreated and CTAB-modified date seeds (300–600 µm), a gas chromatograph was used. After completing the gas analysis, the gas compositions were normalized to exclude oxygen and nitrogen that were not produced during the pyrolysis reaction but were most likely introduced during feedstock loading into the reactor and/or during gas sampling.

3 RESULTS AND DISCUSSION

3.1 Statistical analysis of pyrolysis products

The experiments were performed using a full factorial design to determine the influence of CTAB concentration, pyrolysis temperature, and date seed particle size on product distribution in the form of gas, bio-oil, and char. Analysis of variance (ANOVA) was used to examine product yields obtained from 48 experimental trials, in addition to some replications. Main effects and interaction effects were found to be significant at the 95 percent confidence level (alpha = 0.05). A backward stepwise elimination regression was used to develop the quadratic model for the product-yield responses. This technique begins with all candidate factors in the model (i.e., the full model) and then removes the least significant variable at each step based on a Significance Level to Stay (SLS) criterion [16]. The results are interpreted based on heat and mass transfer, the thermal-decomposition nature of the biomass, and the effect of CTAB as a surface-active agent. To visualize trends and identify conditions that promote the formation of specific pyrolysis fractions, main- and interaction-effect plots were used.

3.2 Effect of process variables on char yield

The influence of pyrolysis process parameters on char yield was investigated using a full factorial design involving three factors: pyrolysis temperature, CTAB concentration, and date seed particle size. Analysis of variance (ANOVA; Table 2) revealed that all three main effects had a statistically significant effect on char production (p-values < 0.05). Moreover, the two-way interactions between temperature and CTAB concentration with the feedstock condition were also statistically significant. This indicates that these variables can affect char yield both independently and synergistically. In contrast, no three-way interaction terms were statistically significant.

Table 2 ANOVA results for the full factorial design for the char yield

Source of variance	**Degree of freedom**	**Adj. Sum of squares**	**Adj. Mean square**	**F-value**	**P-value**
Model	23	20.7524	0.90228	1207.24	0
Linear	8	20.4601	2.55752	3421.93	0
Temperature	2	12.6594	6.3297	8469.08	0
CTAB Concentration	3	3.5343	1.17811	1576.3	0
Feedstock Condition	3	3.6486	1.2162	1627.27	0
2-Way Interactions	15	0.1446	0.00964	12.9	0
Temperature x Feedstock Condition	6	0.1281	0.02135	28.56	0
CTAB Concentration × Feedstock Condition	9	0.0158	0.00176	2.35	0.043
Error	26	0.0194	0.00075		
Total	49	20.7718			

Among the studied factors, pyrolysis temperature emerged as the most dominant parameter influencing char yield. As shown in the main effects plot (Figure 2), increasing the temperature from 300 °C to 400 °C resulted in a pronounced decrease in char yield, from approximately 3.2 g to 1.8 g. This trend is consistent with established pyrolysis behaviour: increasing thermal energy enhances the decomposition of biomass polymers into volatiles and gases, thereby minimizing solid residues. At lower temperatures, thermal degradation is less intense, and more solid carbonaceous material is retained as char.

CTAB concentration was also strongly and inversely correlated with char yield. As CTAB concentration increased to 1%, 1.5%, and 2%, char yield decreased consistently from approximately 2.8 g to approximately

2.1 g at 2%. This decrease can be attributed to surfactants altering the surface properties of biomass [17]. Because CTAB is a cationic surfactant, it may promote heat penetration and potentially influence decomposition through catalytic-like effects by interacting with lignin, cellulose, and hemicellulose [18]. Such interactions could also increase the production of volatiles and condensable vapors, potentially at the expense of char.

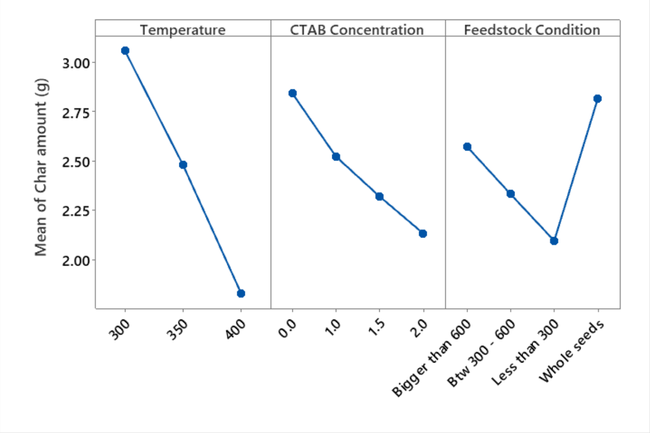

Fig. 2 The main effects plot of char yield from the pyrolysis of CTAB-treated date seeds. Factors include particle size (whole, >600 µm, 300-600 µm, <300 µm), CTAB concentration (1%, 1.5%, 2%), and pyrolysis temperature (300-400°C)

Particle size (feedstock condition) also significantly influenced char production. Fine particles (<300 µm) produced the lowest char yield, whereas larger particles (>600 µm) and whole seeds yielded higher amounts (approximately 2.6–2.7 g). This behavior is primarily governed by heat-transfer constraints [19, 20]. Smaller particles have a greater surface-area-to-volume ratio, which increases the rate of heat absorption and accelerates devolatilization. As a result, a greater portion of the biomass is converted into vapor-phase products. Conversely, larger particles and whole seeds, because of their bulk and lower effective thermal conductivity, can undergo incomplete decomposition, leaving more solid residue behind.

In addition to the individual effects, significant two-way interactions were observed, indicating that the level of one factor influences the effect of another factor on char yield. The interaction between temperature and feedstock condition (Figure 3, bottom-left plot) was significant (p-value = 0). In general, char yield decreases as temperature increases for all feedstock conditions; however, the magnitude of this decrease depends on particle size. For example, as the temperature increases from 300 °C to 400 °C, the char yield from whole seeds drops less sharply than the char yield from particles >600 µm. This suggests that the thermal decomposition of larger or intact particles is less sensitive to temperature changes within the studied range, likely due to internal heat- and mass-transfer limitations that reduce the effectiveness of external temperature increases [19, 20]. In contrast, smaller particles have a larger surface area and heat up more rapidly, resulting in a greater decrease in char yield as temperature increases because their decomposition more readily follows the applied thermal energy.

The interaction between CTAB concentration and feedstock condition (Figure 3, bottom-right plot) was also significant (p-value = 0.043). This interaction plot shows that the effect of CTAB concentration on char yield varies with particle size. Increasing CTAB concentration generally reduces char yield across all feedstock conditions, but the extent of the decrease differs among size fractions. For example, the char yield from whole seeds appears to change less with increasing CTAB concentration than that of particles >600 µm or 300–600 µm. This may indicate that CTAB's surface-modifying or catalytic-like effects are more pronounced in particles with greater exposed surface area (such as the >600 µm or 300–600 µm categories), which can facilitate surfactant accessibility and interaction with the biomass structure, thereby promoting devolatilization and reducing char formation. Conversely, CTAB may have limited penetration and distribution within intact or minimally fragmented seeds, resulting in a smaller impact on pyrolysis behavior and char yield.

Overall, the results indicate that pyrolysis temperature is the most important factor governing char yield, followed by particle size and CTAB concentration. These results are consistent with established pyrolysis mechanisms and suggest that CTAB can act as a useful modifying agent for shifting product distributions.

3.3 Effect of process variables on oil yield

The effects of all three pyrolysis parameters studied herein on bio-oil yield were investigated using the full factorial design. The ANOVA results for bio-oil yield (Table 3) indicate that all three main effects, temperature, CTAB concentration, and date seed particle size (feedstock condition), had a statistically significant impact on bio-oil production, as reflected by p-values < 0.05. Furthermore, two of the three two-way interactions, namely temperature × CTAB concentration and temperature × feedstock condition, were also statistically significant, implying that the combined effects of these factors are important for understanding bio-oil yield. In contrast, the CTAB concentration × feedstock condition interaction was not significant for bio-oil yield (unlike for char yield). No three-way interaction terms were statistically significant.

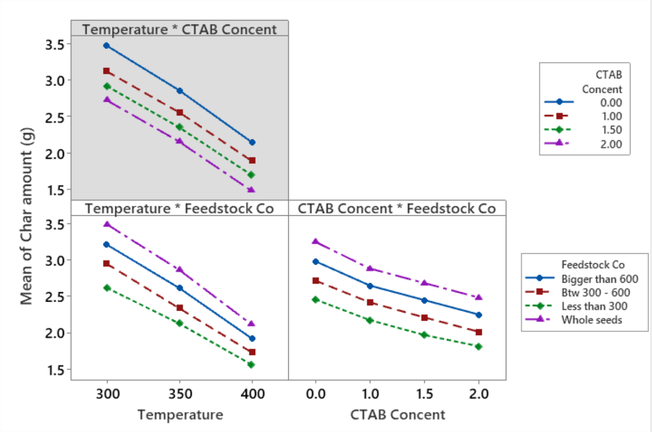

Fig. 3 The interaction effects plot of char yield from the pyrolysis of CTAB-treated date seeds. Factors include particle size (whole, >600 µm, 300-600 µm, <300 µm), CTAB concentration (1%, 1.5%, 2%), and pyrolysis temperature (300-400°C)

The pyrolysis temperature showed a clear trend in the main effects plot for bio-oil yield (Figure 4). Bio-oil yield increased from about 4.1 g at 300 °C to a peak of about 5.1 g at 350 °C and then declined slightly to about 4.9 g at 400 °C. This pattern is common in biomass pyrolysis, which typically exhibits an optimal temperature range for maximizing bio-oil production. At lower temperatures (300 °C), thermal energy may be insufficient to fully depolymerize biomass components, resulting in lower yields of volatile and condensable organic compounds that form bio-oil. As the temperature increases to 350 °C, more effective thermal degradation increases the liquid-product yield, consistent with general pyrolysis principles. At higher temperatures (e.g., 400 °C), secondary reactions such as cracking, polymerization, and gasification of primary pyrolysis products become more prominent, thereby decreasing bio-oil yield and increasing gas production [21–23].

CTAB concentration also had a significant effect on bio-oil yield (Figure 4). Bio-oil yield increased gradually from about 4.2 g to about 5.1 g as CTAB concentration increased from 0% to 2%.

Table 3 ANOVA results for the full factorial design for the oil yield

Source of variance	**Degree of freedom**	**Adj. Sum of squares**	**Adj. Mean square**	**F-value**	**P-value**
Model	20	18.5767	0.92883	798.52	0
Linear	8	17.5379	2.19224	1884.67	0
Temperature	2	8.7957	4.39785	3780.85	0
CTAB Concentration	3	5.2906	1.76352	1516.1	0
Feedstock Condition	3	3.2369	1.07896	927.59	0
2-Way Interactions	12	1.2945	0.10788	92.74	0
Temperature x CTAB Concentration	6	0.072	0.012	10.32	0
Temperature × Feedstock Condition	6	1.2274	0.20456	175.86	0
Error	29	0.0337	0.00116		
Total	49	18.6104			

This positive correlation suggests that CTAB may enhance bio-oil formation by promoting the conversion of biomass-derived macromolecular fragments into smaller condensable molecules, potentially through catalytic-like effects or by modifying biomass structure. Because CTAB is cationic, it may interact with acidic functional groups or influence re-polymerization reactions, thereby promoting bond scission or altering reaction pathways to favor liquid products over char or gas.

Regarding feedstock condition (particle size), the main effects plot (Figure 4) shows that particles <300 µm and 300–600 µm (fine and medium fractions) yielded the highest amounts of bio-oil, about 5.0 g and 4.9 g, respectively. In contrast, bio-oil yields from whole seeds and particles >600 µm (coarse fractions) were lower, at about 4.4 g and 4.6 g, respectively. Smaller particles have a higher surface-area-to-volume ratio, which can promote liquid-product formation by facilitating faster heat penetration and volatile release. Larger particles and whole seeds may impose internal heat-transfer limitations that increase the residence time of volatiles, raising the likelihood of secondary cracking reactions and re-polymerization into char or non-condensable gases, thereby reducing bio-oil yield.

The interaction between temperature and CTAB concentration (Figure 5, top-left plot) was highly significant (p-value = 0). The plot shows that although bio-oil yield typically peaks at 350 °C and increases with CTAB concentration, the magnitude of CTAB's effect depends on temperature. The difference in bio-oil yield between low and high CTAB concentrations is less pronounced at 300 °C than at 350 °C. For example, at 300 °C, yields increased from about 3.7 g (0% CTAB) to 4.5 g (2% CTAB), whereas at 350 °C the range increased from about 4.6 g (0% CTAB) to 5.4 g (2% CTAB). This suggests that CTAB's beneficial impact on bio-oil formation is more pronounced and synergistic at the optimal temperature. Although CTAB continues to increase yield at 400 °C, overall yields begin to decrease, indicating that the positive effects of CTAB are not entirely offset by the negative effects of secondary reactions at higher temperatures. Overall, this interaction indicates that CTAB is most effective at temperatures that already favor liquid-product formation, rather than at very low or very high temperatures where other limiting factors predominate.

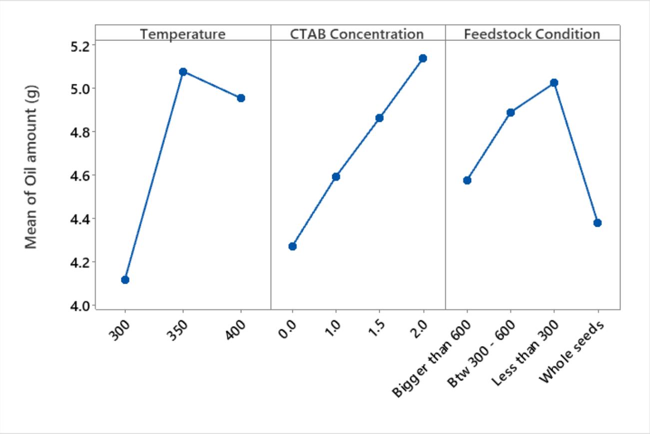

Fig. 4 The main effects plot of oil yield from the pyrolysis of CTAB-treated date seeds. Factors include particle size (whole, >600 µm, 300-600 µm, <300 µm), CTAB concentration (1%, 1.5%, 2%), and pyrolysis temperature (300-400°C)

Additionally, the interaction between temperature and feedstock condition (Figure 5, bottom-left plot) was highly significant (p-value = 0). This interaction indicates slight variation in the optimal temperature for bio-oil yield depending on particle size. Although sensitivity to temperature change differs among size fractions, 350 °C generally appears to be the peak for most feedstock conditions. Particles <300 µm and 300–600 µm exhibit a distinct peak at 350 °C and a noticeable drop at 400 °C. As discussed above, smaller particles are more sensitive to temperature variations, leading to increased secondary degradation at higher temperatures and efficient volatile release under optimal conditions. In contrast, the 350 °C peak is less pronounced for whole seeds and particles >600 µm, and the decrease at 400 °C is less evident or may even show a slight increase for whole seeds. This may be due to slower heat transfer in larger particles; at 350 °C, their interiors may not have reached optimal pyrolysis conditions.

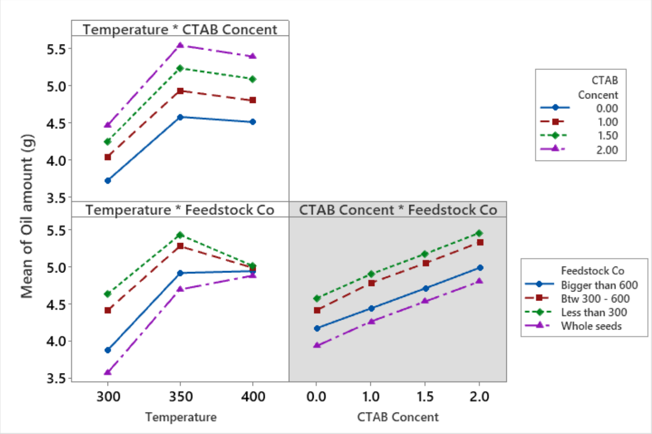

Fig. 5 The interaction effects plot of oil yield from the pyrolysis of CTAB-treated date seeds. Factors include particle size (whole, >600 µm, 300-600 µm, <300 µm), CTAB concentration (1%, 1.5%, 2%), and pyrolysis temperature (300-400°C)

At 400 °C, continued heat penetration may allow additional devolatilization, partially offsetting the effects of secondary reactions that are more apparent in smaller particles. This suggests that, to overcome heat-transfer constraints and achieve high bio-oil yields from larger particles, higher temperatures or longer residence times may be required.

Overall, both individual factors and their combined effects should be evaluated to maximize bio-oil yield. The most economical conditions appear to involve higher CTAB concentration, smaller particle sizes, and an optimal temperature near 350 °C. The best results are achieved by fine-tuning these parameters while accounting for their interactions.

3.4 Gas composition analysis for date seed pyrolysis

Studying the non-condensable gas products provides important information about the thermochemical processes occurring during pyrolysis of date seed cores, both untreated and CTAB-treated. The results show that both temperature and the presence of CTAB have a clear and consistent effect on the distribution of gaseous products, as shown in Figure 6.

The gas composition of untreated date seed cores followed trends that are consistent with typical pyrolysis behavior of lignocellulosic biomass. As pyrolysis temperature increased from 300 °C to 400 °C, the relative amount of carbon dioxide (CO2) decreased noticeably from 40% to 23%. Although the overall gas yield likely increases, the decrease in CO2 concentration indicates that decomposition pathways shift with temperature. At higher temperatures, thermal degradation pathways favor more extensive bond scission and secondary cracking reactions, leading to increased formation of lighter hydrocarbons and hydrogen, thereby reducing the proportional contribution of CO2 from decarboxylation. In contrast, hydrogen (H2) and methane (CH4) increased consistently and substantially with temperature. This increase in energy-dense gases is attributed to faster breakdown of the biomass structure and primary pyrolysis volatiles at higher temperatures. Additionally, the proportion of C2–C4 hydrocarbons increased steadily from 4% to 12%, further supporting more frequent cracking reactions.

Between 300 °C and 350 °C, the percentage of carbon monoxide (CO) increased slightly (from 36% to 37%), indicating stronger decarbonylation. However, it then decreased to 32% at 400 °C. This non-monotonic behavior suggests that, although CO formation pathways remain active, CO may be consumed in secondary reactions (e.g., methanation or the Boudouard reaction) at the highest temperature, or its net formation may decline as H2 and CH4 are produced in larger amounts [24–31].

The introduction of CTAB as a modifying agent exerted a notable influence on gas composition, as shown in Figure 6. A lower relative percentage of CO2 in CTAB-modified samples was a consistent finding at all temperatures examined (e.g., 33% at 300 °C down to 18% at 400 °C, compared to 40% and 23% for untreated biomass, respectively). This suggests that CTAB may reduce the CO2 fraction, either by inhibiting specific decarboxylation reactions or, more likely, by promoting alternative decomposition pathways that favor the formation of other gaseous species. Evidence for CTAB activity is also reflected by the higher proportions of H2 and CH4 observed in the modified samples. At 400 °C, for example, H2 increased to 17% compared with 5% for untreated biomass, and CH4 increased to 24% compared with 18% for untreated biomass. This increase in hydrogen and methane supports the role of CTAB in promoting cracking reactions that enhance scission of C–H and C–C bonds in the biomass matrix and increase volatile-product formation [32]. The CTAB-modified samples also showed higher CO proportions than untreated biomass at 300 °C (40%) and 350 °C (42%). However, the CO percentage decreased to 29% at 400 °C, similar to the untreated samples, indicating a complex balance between formation and consumption pathways at the highest temperature. While the C2–C4 hydrocarbon trends for both feedstocks were generally similar and increased with temperature, CTAB showed a slight increase at 350 °C (7% vs. 6%).

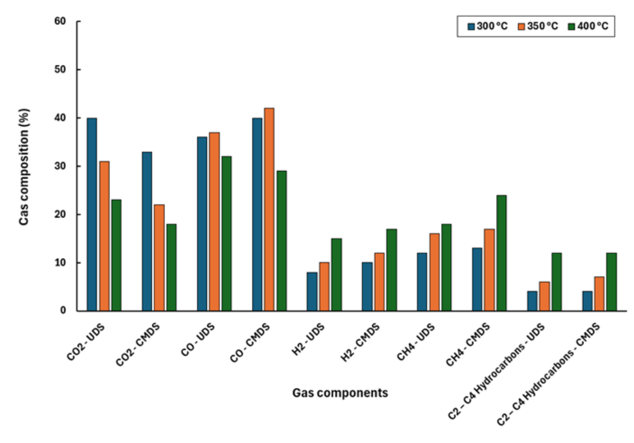

Fig. 6 The dispersion of gaseous products at different temperatures (300, 350, and 400 °C), CTAB concentration of 1.5%, and date seeds particle size of 300–600 µm. UDS refers to untreated date seeds, while CMDS refers to CTAB-modified date seeds

Overall, gas analysis indicates that the proportion of energy-rich H2 and light hydrocarbons increases with rising pyrolysis temperature, consistent with more intensive thermal cracking. Notably, CTAB appears to further shift the gas composition by reducing CO2 and promoting the formation of H2 and CH4. These findings demonstrate the potential of CTAB to improve the quality of the gaseous product stream during pyrolysis for energy applications and are consistent with the proposed mechanism of CTAB interaction with biomass.

3.5 Bio-oil composition analysis for date seed pyrolysis

Bio-oils produced from the pyrolysis of both feedstocks, the untreated and CTAB-modified date seed biomass (300–600 µm), at 400 °C, were analyzed for their compositions in detail. As shown in Figure 7, the bio-oil produced from untreated date seed contained about 13% water, 7% carboxylic acids, and 18% phenolic compounds. Also, approximately 13% and 10% of the total composition were alkanes and aromatic hydrocarbons, respectively, whereas oxygenated compounds, including acids, ketones, and furans, made up around 20% of the bio-oil. This implies that the deoxygenation processes were not fully completed under these conditions. Nevertheless, the bio-oil profile changed significantly, likely due to biomass modification by CTAB. Notably, the hydrocarbon fractions increased considerably, while the water and acid contents decreased to 7% and 4%, respectively. Aromatics increased to 17%, while alkanes and alkenes reached 21% and 13%, respectively. The percentage of unknown or heavy tar-like compounds, referred to as "Others," on the other hand, dropped markedly from 16% in the untreated sample to just 3% after biomass treatment with CTAB. These changes in composition imply that CTAB overall promotes more efficient deoxygenation and prevents polymeric residues from forming during pyrolysis.

The results clearly demonstrate that CTAB plays a catalytic role in enhancing cracking and deoxygenation reactions during pyrolysis. The reduction in water and acid content is consistent with CTAB's ability to break down the biomass structure, facilitate the release of bound water, and catalyze the decarboxylation of carboxylic acids, such as the conversion of palmitic acid to alkanes and carbon dioxide [33]. The higher radical-driven cleavage of long-chain lipids, known to occur during surfactant-based pyrolysis of lignocellulosic wastes, is indicated by a notable increase in alkanes from 13% to 21% [30, 34, 35]. Despite these developments, the ester level remained approximately constant at 1%, suggesting that the applied process conditions, including temperature, residence time, and surfactant concentration, may have inhibited transesterification. The higher content of phenols (18–21%) and aromatics (10–17%) in the CTAB-modified bio-oil might relate to increased lignin depolymerization, particularly through cleavage of β-O-4 ether linkages, as well as hypothetical cycloaddition mechanisms such as Diels–Alder reactions with intermediates oxidized to an alkene [35–38]. The surfactant may reduce tar formation partially by minimizing repolymerization of thermally formed reactive intermediates, as indicated by the almost complete absence of the "Others" fraction in CTAB-treated samples. These findings agree with earlier works, which have indicated that CTAB can increase porosity and accessibility to thermally labile sites and allow more selective cracking reactions [39, 40].

To verify the GC–MS results for the bio-oil composition chart (Figure 7) before and after CTAB treatment of date seeds, FTIR analysis was conducted for the produced bio-oil in both cases (Figure 8). The FTIR spectra for both bio-oils show a broad band around 3425 cm-1, characteristic of O–H stretching vibrations, indicating the presence of hydroxyl groups from water, alcohols, phenols, or carboxylic acids. However, the band corresponding to the DSO spectrum (black line) is broader and more intense than that of DSO-CTAB (red line). This suggests a higher content of O–H-containing compounds (water) in the DSO sample, consistent with the bio-oil composition analysis, which showed DSO had a higher water content.

Both spectra also show peaks around 2923–2850 cm-1, attributed to C–H stretching vibrations of aliphatic compounds (methyl and methylene groups), suggesting the presence of alkanes and other saturated hydrocarbon chains. The intensity of the DSO-CTAB peak appears relatively strong, which may correlate with the higher alkane content observed in the bio-oil composition analysis. Furthermore, a prominent peak was observed around 1700 cm-1, corresponding to C=O stretching vibrations of carbonyl groups, indicating the presence of aldehydes, ketones, carboxylic acids, and esters [41]. This peak appears slightly more intense in the DSO-CTAB spectrum than in the DSO spectrum, supporting an increase in ketones and possibly other carbonyl-containing compounds (such as some esters or specific aldehydes) in the CTAB-treated sample, as indicated by the bio-oil composition results.

Stretching vibrations of C=C in aromatic rings or conjugated alkenes were detected through peaks around 1600 cm-1, which were more defined for DSO-CTAB [42]. This supports the previous finding of higher aromatic content in the CTAB-treated bio-oil. The peaks at 1460 cm-1 and 1380 cm-1 are typically assigned to asymmetric and symmetric CH2 and CH3 bending, confirming the presence of aliphatic chains. Additionally, bands in the 1300–1000 cm-1 region are often related to C–O stretching vibrations of alcohols, phenols, ethers, and carboxylic acids, as well as C–C stretching vibrations [43]. An obvious difference between the two spectra suggests variations in the types and quantities of oxygenated compounds. The DSO-CTAB spectrum shows more pronounced peaks in certain areas within this region than DSO, which may reflect the observed shift in oxygenated compounds.

Overall, assessment of the DSO-CTAB spectrum indicates that the produced bio-oil has a higher proportion of hydrocarbons (alkanes, alkenes, and aromatics) and carbonyl-containing compounds (ketones). It also has a lower proportion of highly oxygenated compounds and water, consistent with the intended quality improvement from CTAB pretreatment.

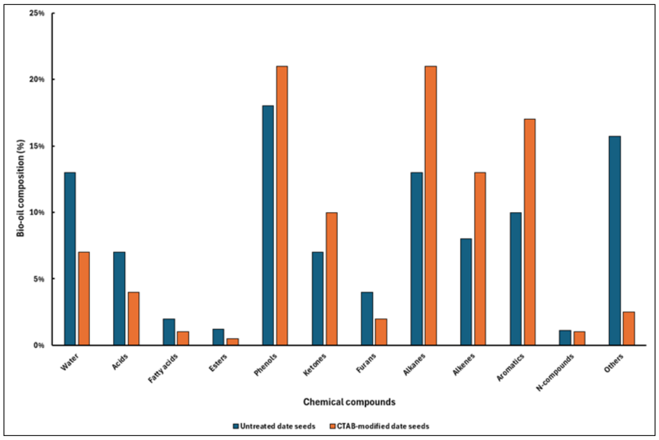

Fig. 7 The dispersion of bio-oil products at a pyrolytic temperature of 400 °C, CTAB concentration of 1.5%, and date seeds particle size of 300-600 µm

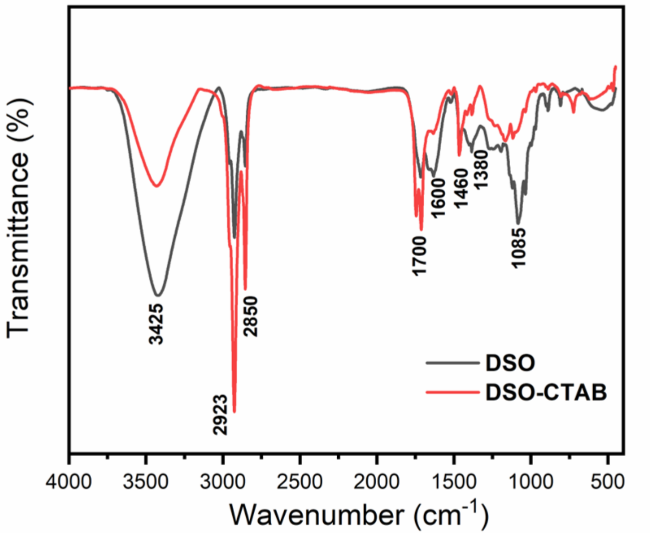

Fig. 8 FTIR of bio-oil products at a pyrolytic temperature of 400 °C, CTAB concentration of 1.5%, and date seeds particle size of 300-600 µm

4 CONCLUSION

This research successfully examined the valorization of date seed waste via pyrolysis after CTAB surfactant treatment at different concentrations, with a particular focus on biofuel and biochar production. Analysis of variance revealed that all three main factors had a statistically significant effect on char production, with pyrolysis temperature having the greatest impact, followed by date seed particle size and CTAB concentration. Similarly, for bio-oil production, all three main effects were also statistically significant, with pyrolysis temperature again being the most influential factor, followed by CTAB concentration and particle size. In addition, several two-way interaction effects were statistically significant, indicating that these variables can influence char and oil yields both independently and synergistically. However, no three-way interaction terms were statistically significant.

CTAB demonstrated multiple benefits in this study, including enhanced biomass porosity, modified surface chemistry, and potential influence on thermal degradation pathways. These effects contributed to improved heat and mass transfer and may have introduced catalytic-like behavior during pyrolysis. As a result, CTAB use led to increased bio-oil yields (>51 wt.%) and an overall improvement in pyrolysis efficiency. The generated bio-oil exhibited promising characteristics as a renewable fuel and had a favorable composition for energy applications. The findings also demonstrated the potential of CTAB to improve the quality of the gaseous product stream during pyrolysis for various energy-related uses. Overall, this work offers a sustainable model for transforming agricultural waste into useful materials, contributing to the circular economy while advancing sustainability through effective waste management and renewable energy.

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Data availability

N/A

DECLARATIONS

Conflict of interest

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

Consent to publish

N/A

Ethical approval

N/A

Abbreviations

CTAB, Cetyltrimethylammonium bromide; DOE, Design of experiments; ANOVA, Analysis of variance; NIST, National Institute of Standards and Technology; SLS, Significance level to stay; UDS, Untreated date seeds; CMDS, CTAB-modified date seeds; DSO, date seed oil.

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