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effect of CaO nanocatalyst on bio-oil production from algae and date seeds via microwave-assisted co-pyrolysis

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Abstract

One of the most effective ways of managing solid waste is microwave-assisted pyrolysis. This research used MW-assisted catalytic co-pyrolysis to extract essential oils from algae powder (AP) and date seed (DS). Graphite and a CaO nanocatalyst were utilized. As for the feedstock, it was a 1:1 mixture of AP and DS. The char content, oil production, and gas generation of co-pyrolysis yields varied between 18.8 wt% and 24.31 wt%, 43.08 wt%, and 55.295 wt%, and 25.905% to 32.60 wt%, respectively. The effect of the CaO nanocatalyst on product yields, feedstock conversion, and heating rates was analyzed. Product yields, average heating rates, and conversion factors were among the metrics studied to determine the synergistic effects and pyrolysis index, which represent the effect of materials composition when mixed to improve the thermal decomposition products and the efficiency of the process. More oil and char were produced due to the synergy that occurred during co-pyrolysis. The bio-oil obtained from algae powder (AP) co-pyrolysis and date seed (DS) was analyzed using GC-MS. The catalyst allowed for the synthesis of aliphatic compounds, aromatic compounds, amides, and alkenes by co-pyrolysis synergy. The significance of this work lies in its demonstration of an efficient and sustainable method for converting algae and date seeds into valuable bio-oil using catalytic microwave-assisted pyrolysis, highlighting the increased yield, product quality, and process efficiency through synergistic interactions.

Keywords: Nanocatalyst; algae powder; date seed; co-pyrolysis; synergy effect; bio-oil

1. Introduction

Sustainable and realistic solid waste management is essential for extracting valuable materials from biomass waste feedstocks. Typical organic solvents used in chemical labs and factories to pre-treat lignocellulosic biomass threaten human health, the environment, and safety [1]. Cellulose (32–47%), hemicellulose (19–27%), and lignin (5–24%) make up the bulk of lignocellulosic leftovers such as rice straw and tea trash [2]. The two most common types of organic polymers that can be recycled are cellulose and lignin. All lignocellulosic biomass residue is structurally composed of these components and hemicellulose [3]. Lignocellulosic materials may provide sustainable fuels and feedstock chemicals within the biorefining framework [4]. With concerns about fossil fuel depletion and environmental limits, biodiesel has emerged as a viable renewable fuel option to replace mineral diesel from fossil fuels. Enzymatic, heterogeneous, and homogeneous catalysts expedite the transesterification reaction, the primary step in biodiesel synthesis. Heterogeneous catalysts are more favourable and cost-effective than homogeneous catalysts, according to Khan et al. (2021). Many heterogeneous catalysts have been created using different sources to make the production process more cost-effective. Following the optimal performance of these catalysts and chemical processes, the study has shifted to explore alternative approaches, such as utilizing non-traditional means like microwave, ultrasonic, plasma heating, etc., to further improve the process's overall efficiency. Research on microwave-supported heterogeneously catalyzed biodiesel production has been the aim of this brief review.

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Methods for synthesizing heterogeneous catalysts, a transesterification reaction mediated by microwaves and solid catalysts, the unique thermal effects of microwaves, and parametric optimization in microwave heating are all covered. Heterogeneously catalyzed transesterification reactions can be significantly sped up utilizing microwave technology (reduction of reaction durations from 5-60 min) while keeping or increasing catalytic activity (>90%), according to the review [5]. Zandjou et al. (2024) explore state-of-the-art research on improving biodiesel production using catalysts and nanocatalysts based on biochar. Because of the increasing demand for renewable energy, biodiesel has emerged as a leading contender to replace fossil fuels. To enhance several steps in biodiesel production, our investigation centers on biochar's revolutionary role as a functional catalyst and its metamorphosis into nanocatalysts. This chapter delves into various biochar-based catalyst production methods, such as coprecipitation, pyrolysis, and impregnation. These catalysts greatly improve crucial processes in biodiesel synthesis, transesterification, and esterification. In addition to outlining the framework for novel developments, the article also discusses this rapidly expanding sector's difficulties and potential rewards. One intriguing path is using functional catalysts and nanocatalysts based on biochar. These have the potential to significantly improve the energy landscape by promoting the sustainable production of biodiesel [6]. For the most part, lignocellulosic biomass makes up agro-industrial waste. Several technologies have been created to turn these by-products into useful items. Pyrolysis is one of these processes: the thermal breakdown of organic compounds. Saving time, increasing heating efficiency, and promoting more accurate process control are some of the advantages of microwave-assisted pyrolysis (MAP) over conventional pyrolysis. A study conducted by Pimenta et al. (2023) investigated the liquid by-product of microwave-assisted pyrolysis (MAP) of brewer's wasted grain (BSG), the primary by-product of the brewing industry's waste. The investigation focused on the distribution of products and hydrocarbon concentration in the liquid product as a function of temperature, moisture content, and catalyst % (calcium oxide). Despite a very high liquid output of 71.8% at a BSG moisture content of 14%, the hydrocarbon yield was just 21.60%, which is not very promising. An optimization study was conducted to get the best bio-oil yield and quality. A temperature of 570 °C and a catalyst/biomass ratio of 12.17% were the ideal conditions. Due to the presence of aromatic hydrocarbons, which are organic molecules of great importance to the industry, the optimal liquid product composition results are encouraged [7]. According to a study by Zhang et al. (2024), a nitrogen-rich porous carbon with a wide range of pore sizes was created by combining kapok wood (KW) with Chlorella vulgaris (CS) in a two-step co-pyrolysis process. This method uncovered two nitrogen-doping methods for CS, which might be used as a sustainable nitrogen source. When KW and CS are mixed at a 3:7 ratio, the resulting porous carbon K3C7PC has a pore volume of 3.44 cm3/g and the largest specific surface area (SSA) of 2909.78 m2/g. If you look at the weight loss curves, you'll see that KW biochar keeps some of the nitrogenous molecules that CS makes. When 70% CS is combined with KW, the specific capacitance of K3C7PC reaches 380 F/g, in contrast to the 253.8 F/g obtained from KWPC through pyrolysis, according to the three-electrode test. Furthermore, with a power density of 125 W/kg, the symmetric supercapacitors of K3C7PC achieve an energy density of 8.09 Wh/kg, and their capacitance retention rate remains 98.49% even after 10,000 cycles. This job can easily outline directions for the co-pyrolysis of lignocellulosic and algal biomass to produce nitrogen-rich porous carbon [8]. According to Torres-Sciancalepore et al. (2024), the kinetics parameters and products were examined concerning the mixing factor concerning the co-pyrolysis of two rosehip wastes and the subsequent co-gasification with CO_2 of the residual biochar. As the hemicelluloses, cellulose, lignin, and $CaCO_3$ in the ashes decompose, six distinct processes are linked to this slow pyrolysis (heating rates of 5, 10, and 20 °C/min), according to thermogravimetric research. Activation energies of 84.68-223.42, 230.11-270.85, 187.58-303.37, and 400.11-421.71 kJ/mol for hemicellulose, cellulose, lignin, and $CaCO_3$ breakdown, respectively. The gas and tar studies revealed that the blend, which included 25% seed waste and 75% husk waste, generated the highest concentration of hydrogen (5.639 mmol/g biomass). In contrast, the blend containing 25% husk waste and 25% seed waste created the highest concentration of carbon monoxide (3.642 mmol/g biomass). It was heated with carbon dioxide to test how reactive the biochar made from the mixtures and pure wastes were to gasification. Incorporating husk waste into the mixture enhances the biochar's reactivity, primarily because of its increased ash concentration [9]. Bhoi et al. (2020) detailed catalyst developments that aim to improve hydrocarbon compounds in bio-oil produced through catalytic pyrolysis of biomass. Further, it has skimmed the surface of what other operational factors like temperature, biomass type, heating rate, vapours residence time, carrier gas, and hydrogen donor can do to affect bio-oil yield and characteristics. There was a significant relationship between the bio-oil yield and quality, the type of catalysts used, and the temperature. According to the TGA-DTA study, the central biomass pyrolysis zone for high bio-oil yield is between 400 and 600 °C. Pyrolysis of biomass was shown to occur at an average temperature of 500 °C in pilot, semi-pilot, and large-scale units. Metal oxide catalysts, catalysts based on zeolite, and catalysts supported by transition and noble metals are some of the newer, more sophisticated catalysts developed to improve bio-oil by removing unwanted chemicals and increasing hydrocarbon output. Although non-noble metal catalysts are more widely used and less expensive, noble metal catalysts can create bio-oil with a lower concentration of oxygenated molecules [10]. According to Yönet et al. (2024), using recycled polyethylene trash as a catalyst, the seed shell biomass of Mediterranean pine trees has the potential to produce hydrogen and methane gasses. Polyethylene materials' densities, viscosities, and degassing points were initially calculated in the research. At a temperature of 600°C, the pyrolysis was performed at a rate of 50°C/min. A gas chromatography apparatus was used to examine the gases that were extracted. The final step of the experiments involved examining the microstructures and observing the solid remains under an optical microscope. The findings indicated that a combination of biomass from

Mediterranean pine seed shells and low-density polyethylene might potentially generate gasses such as methane and hydrogen. The M8 catalyst, with its extremely high density (0.950 gr/cm^3) and exceptionally low viscosity (0.45 gr/10 min), achieved the best results regarding methane and hydrogen gas production. The pyrolysis trials yielded gases consisting of 38.44% CH_4, 19.50% CO_2, and 42.06% H_2 from the biomass of Mediterranean pine seed shells. In addition, DEFRA values and CO_2 emission values of biomass were compared. The study proved that the seed shells of Mediterranean pine trees can be used as a biomass source and could substitute fossil fuels in internal combustion engines since they can be converted into hydrogen and methane through the pyrolysis process [11]. The rationale for using calcium oxide as a catalyst is due to its catalytic cracking properties, cost-effectiveness, and previous success in improving thermal cracking. The selection of algae and date seeds was based on their rich cellulose and oil content, their availability in Iraq as a country with abundant palm cultivation, and their sustainability benefits. The Novelty of our research is that, to our knowledge, this is the first time that a mixture of date seeds and algae has been used in oil production by microwave-assisted thermal decomposition. The effect of the nano-assisting factor on oil production has been studied; as gases are reduced, oil production is increased, and its properties are improved.

This study investigates how using CaO nanocatalyst influences the co-pyrolysis of date seed and algae with MW assistance to generate oil, gas, and char. Results will be assessed according to pyrolysis index, yields, composition, heating rate profile, average heating rate, high heating value, energy consumption, processing time, and heating rate profile.

2. Materials and Methods

2.1. Materials

The date seed (DS) and algal powder (AP) were dried in a hot air oven set at 100 °C in this experiment. A particle size of 150 µm was determined after it was passed through laboratory sieves. They were sealed in plastic bags to keep the dried AP and DS away from the air. A susceptor made of graphite powder with a particle size of 100 µm was utilized to transform microwave radiation into heat energy. For catalytic MW-assisted pyrolysis, 1 g of commercial CaO nanocatalyst was mixed with feedstock, and susceptors were contained in a round-bottomed borosilicate glass flask reactor. Ceramic wool was the thermal insulation muffle with a shallow cylindrical shape, holding the borosilicate flask in place. Additional reinforcement for the insulation muffle was provided by wrapping it with Teflon® tapes [12,13].

Fig. 1 shows groups of very small, granular particles that nanoscale calcium oxide (CaO). These particles are between 20 nm and 50 nm in size. The particles are loosely grouped into bigger clusters that look like sponges. This is normal for nano-materials since they have a lot of surface energy, which makes them stick together. Even though the clusters are stuck together, you can still see that they are porous, which is great for catalytic uses since it lets gases or pyrolysis vapours get inside and interact with the surfaces inside. The rough and uneven texture of the surface shows that it has a lot of surface area. A high surface area in catalysis suggests more active areas where chemical reactions can happen. This structure helps absorb pyrolysis vapours and turn them into useful things like alkanes, aromatics, and alkenes [12,13].

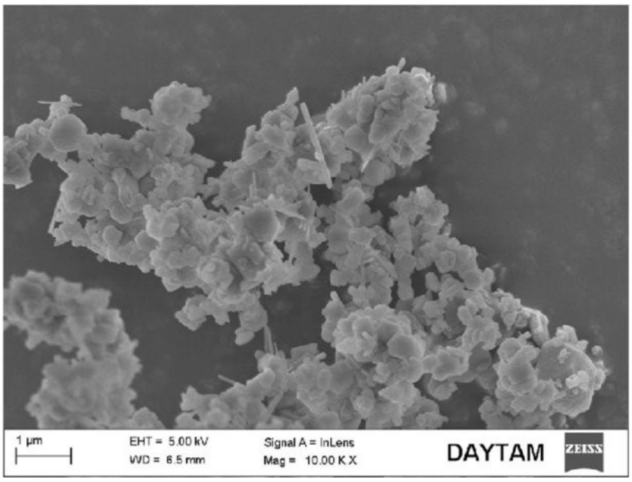

Fig. 1. CaO nanoparticles image by scanning electron microscopy

2.2. Feedstock pre-treatment

AP and DS were pre-treated using thermal and mechanical approaches. For thermal pre-treatment, the AP and DS were kept in an electric hot air oven at 80 °C for 6 hrs to remove moisture. Date seeds were ground in an electric grinder to increase the surface area [13].

2.3. Experimental methodology

This study used a modified multimode microwave oven to perform MAP experiments. Microwave ovens in the domestic pulse setting are often used for quick heating. The microwave radiation at a typical frequency of 2.45 GHz is equivalent to a wavelength of around 12.24 cm. However, the electromagnetic field has an irregular distribution within the oven cavity. An utterly round hole was machine-drilled into the upper surface of the oven's cavity. It was carved out of this space to accommodate the gas purging pipe, temperature sensor, and vapour collector. The combination of feedstock and susceptor was placed in a 500 mL round-bottom flask. So that the susceptor particles could disperse evenly throughout the feedstock, the two were mixed well in each experiment. A contact-type temperature sensor (K-type thermocouple) was inserted inside the borosilicate flask to monitor the feedstock temperature during pyrolysis. The sensor was kept in a metallic tube with a hollow cylindrical shape to reduce the impact of microwave interference. A digital temperature indicator was connected to the thermocouple. A gas collection and vapour condensation mechanism was attached to the borosilicate flask. Nitrogen gas was purge-gassed at a rate of 50 mL/min for 10 minutes before each experiment, after maintaining the feedstock and susceptor in the oven cavity in the borosilicate flask, further to exclude any atmospheric oxygen from the feedstock combination. The top of the flask was attached to a system that collected oil and measured temperature; ceramic wool served as insulation. The diagram of the experimental setup is explained in Fig. 2. After closing the door, we used the controls on the panel to adjust the microwave's power and time. After the pyrolysis temperature hit 650 °C, the microwaves were turned off in each experiment, which involved recording the temperature every 30 seconds. After the temperature dropped to room temperature, the borosilicate flask was removed from the oven by opening the front door. To determine the char yield, it weighed the flask; to determine the oil yield, it measured the condensers and the flasks used for collecting the oil. The feedstock was combined with 10 g of graphite for every experiment to reach the necessary pyrolysis temperature. The feedstock quantity was 20 g in the four experiments conducted for MAP and MACP of AP and DS. Three separate, non-consecutive repetitions of each experiment were carried out [13,14].

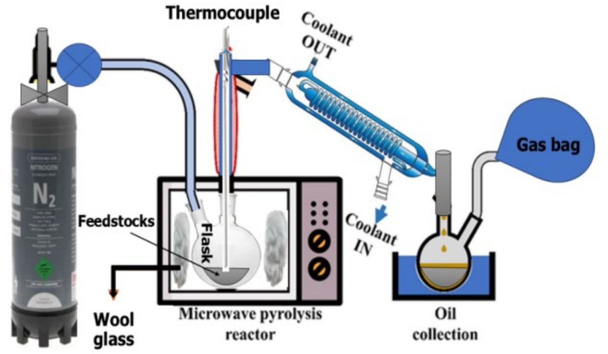

Fig. 2. Diagram of the experimental setup

To ensure homogeneous heating in MAP, microwave absorbers (graphite as a susceptor) are commonly added to the feedstock sample. These materials are good at absorbing microwave radiation and turning it into heat, which is then passed on to the remainder of the sample through conduction, which helps heat it evenly. Making sure that the size and substance of the particles are the same helps keep localized heating disparities to a minimum. Keep glass wool in the microwave cavities of multimode applicators to spread the microwave field more uniformly and keep the heat inside the flask content. Flask location substantially impacts heating behavior due to the spatial variance in the electromagnetic field within the cavity. Putting the flask in the middle of the microwave's standing wave pattern in a multimode microwave can help focus the waves evenly [24].

2.4. GC/MS evaluation of oil production

GC-MS, Gas chromatography, and mass spectrometry (Agilent 7890, 5975C) were used to examine the molecular makeup of the MAP oil sample. The sample injector was kept at a temperature of 220 °C, and 0.25 µL of the oil sample was injected into it for this study. The gas chromatography (GC) oven was brought up to temperature from room temperature to 350 °C in 30 minutes, employing a heating rate that is not isothermal of 5 °C/min. The carrier gas utilized was high-quality helium gas flowing at a rate of 2.0 mL min^{-1}. The compounds were separated using a conventional Rxi-5Sil MS column, which had the following dimensions: 30 m length, 0.25 mm inner diameter, and 0.25 µm film thickness. The chemical composition of the oil was determined by analyzing its mass spectra using a mass spectrometer. Maintaining an isothermal temperature of 220 °C for the ion source and 175 °C for the detectors was done. A source of ions within the MS had an electron ionization potential of 70 eV. To scan most of the relevant compounds in the 50–500 Da m/z range, a typical threshold of 100 was selected. Compounds were evaluated when the spectra had a match factor of more than 80% compared to the NIST collection. The bio-oil compounds' chromatogram and their complete inventory are available in the supplementary materials. An investigation was conducted on the chemicals, and a reaction mechanism was proposed based on the results [13-17].

2.5. Product yield and microwave energy consumption calculations

The apparatus for conducting experiments on microwave-assisted pyrolysis consists of multiple parts. The primary parts are empty and filled glass flasks, condensers, elbow joints, and adopter joints. The yield of the three-phase co-pyrolysis products—gas, oil, and char—was evaluated by weighing each part before and after each pyrolysis experiment. A round bottom flask, a condenser, a multiple adopter joint, and an elbow joint had their weight variations (in g) estimated before and after the pyrolysis experiment. The yield weight of the oil can be determined using the formula (1) [13,17]:

$$A_{\text{oil}} = (A_{\text{wight of Condenser after exp.}} - A_{\text{wight of Condenser before exp.}}) + (A_{\text{wight of elbow joint after exp.}} - A_{\text{wight of elbow joint before exp.}}) + (A_{\text{wight of adopter joint after exp.}} - A_{\text{wight of adopter joint before exp.}}) + (A_{\text{wight of collecter flask after exp.}} - A_{\text{wight of collecter flask before exp.}}) \quad (1)$$

Eq. (2) provides the formula for calculating the char yield weight (g):

$$A_{\text{char}} = (A_{\text{Round bottom flask after exp.}} - A_{\text{Round bottom flask before exp.}}) \quad (2)$$

In order to find the gas yield, it was used the formula in Eq. (3) to subtract the feedstock weight (AP: DS) from the oil plus char yield weight in (g):

$$A_{\text{gas}} = 100 - (A_{\text{oil}} + A_{\text{char}}) \quad (3)$$

To find the gas, bio-oil, and char yield, respectively, utilize Eq. (4), (5), and (6) in that sequence:

$$\text{Char yield(wt.\%)} = (\text{char in (g)} / \text{feedstock in (g)}) \times 100 \quad (4)$$

$$\text{Oil yield(wt.\%)} = (\text{Oil in (g)} / \text{feedstock in (g)}) \times 100 \quad (5)$$

$$\text{Gas yield(wt.\%)} = 100 - ((\text{Char yield (wt.\%)} + \text{oil yield(wt.\%)} \quad (6)$$

To estimate microwave energy consumption, we can use Eq. (7):

$$Microwaveenergy = \text{Microwave power } (W) \ x \ Total\ pyrolysis\ time \text{ (min)} \quad (7)$$

2.6. Synergy effect of feedstock and CaO nanocatalyst

A synergistic effect occurs during pyrolysis when two or more biomass types work together to produce an output. Pyrolysis causes the value to be greater than or equal to the predicted value based on the weighted average of the feedstock. The ratio of feedstocks used can affect the synergistic effects. This could result from chemical reactions involving carbon and hydrogen molecules in the biomass mixture. To find out if the co-pyrolysis of biomass mixtures has a synergistic impact, one can compare the theoretical and experimental values of the parameters. Equations (8 and 9) allowed us to determine the degree of interaction between different biomass mixtures during co-pyrolysis, also called the synergistic effect; equation (8) can be rewritten as [13,17, 25,26]:

$$\Delta X = X_{EXP} - X_{CAL} \tag{8}$$

To determine XCAL, the following equation (9) was used:

$$X_{CAL} = A1B1 + A2B2 \tag{9}$$

B1 and B2 stand for the mass fractions of the feedstocks in the mixture, and A1 and A2 stand for the weight percentages of feedstocks 1 and 2, respectively. A negative synergistic impact is shown when $\Delta X > 0$; from equations, we can recognize an increase in yield. If the $\Delta X < 0$, it indicates that the synergistic effect is a positive one, and there is a decrease in yield.

The catalytic impact of the CaO nanocatalyst during microwave-assisted co-pyrolysis leads to the following synergistic effects: (1) Basic Surface of CaO: CaO is very basic, which makes it easier to break C–O, C–C, and C–N bonds in biomass parts. This makes deoxygenation easier by using decarboxylation and decarbonylation processes. (2) Microwave Absorption: CaO absorbs microwave radiation better than biomass alone because it is a microwave susceptor. This makes local heating better and speeds up thermal cracking reactions. (3) Deoxygenation Pathways: CaO helps get rid of oxygen by turning it into CO and CO_2. Carboxylic acids and phenols undergo catalytic decarboxylation and dehydration, respectively, resulting in aliphatic and aromatic hydrocarbons. (4) Cracking and Aromatization: Long-chain fatty acids and triglycerides are broken down into shorter hydrocarbons, while intermediates like olefins and dienes turn into aromatic compounds when they are catalyzed. (5) Suppression of Nitrogen and Sulphur Compounds: CaO absorbs acidic by-products (such as NH_3 and H_2S), which stops nitrogenous and sulphurous aromatics from forming in the final oil. Formulas (10-13) can explain the Hypothetical Reaction Pathways [25,26]:

Deoxygenation represents by formula (10):

$$\text{R-COOH (Fatty acid)} \rightarrow \text{R-H (Alkane)} + CO_2 \text{ (Decarboxylation)} \tag{10}$$

Cracking can be represented by formula (11):

$$\text{R-}CH_2\text{-}CH_2\text{-R'} \rightarrow \text{R-}CH_3 + CH_2\text{=CH-R' } (\beta\text{-scission}) \tag{11}$$

Aromatization can be represented by formula (12):

$$C_6H_{12} \text{ (Cyclohexane intermediate)} \rightarrow C_6H_6 \text{ (Benzene)} + 3H_2 \tag{12}$$

Phenol Conversion can be represented by formula (13):

$$\text{Phenol} \rightarrow \text{Benzene} + \text{CO (Deoxygenation)} \tag{13}$$

2.7. pyrolysis index (PI)

Utilizing the pyrolysis index (PI) allows for optimizing the pyrolysis process and investigating sustainability limits. Principle variables (PI) are primarily determined by the following: residence time, conversion, high heating value, MW power consumption, and ingredient amount. The value of PI can range from nil to infinity. Eq. (14) will be used to determine the PI in co-pyrolysis [17].

$$\text{PI} = X \,.\, C \,.\, Q / \text{P} \,.\, \text{R} \tag{14}$$

The variables X, C, Q, P, and R represent feedstock conversion percentage, heating value, quantity, power consumption, and residence duration, respectively.

3. Results and discussion

3.1. Microwave-assisted pyrolysis of AP and DS

A microwave-assisted pyrolysis reactor was used to subject AP and DS to individual pyrolysis. Each experiment used the same 20 g feedstock, 10 g graphite susceptor, and 450 W operating microwave power. In order to achieve the most particular spectra due to pyrolysis, the heating rate is an important variable to control. Hence, the data on temperature vs time that has been collected in pyrolysis experiments should be taken into account. For every trial, the mean heating rates were calculated. The pyrolysis temperature of 650 °C is reached in 24 minutes due to the average heating rate of 31.2 °C/min in AP pyrolysis. Due to the average heating rate of 27.27 °C/min, DS pyrolysis takes 18 minutes to achieve the pyrolysis temperature of 515 °C. Table 1 details the results of pyrolysis on raw AP, which showed an oil output of 49.2 wt%, char of 10.5 wt%, and gas conversion of 40.2 wt%. Conversely, bio-oil makes up 39.16 wt% of DS yields, gas 42.85 wt%, and char 17.99 wt%. It is suggested that feedstock selection, processing method intensification, and product output optimization be investigated to enhance the MAP oil's properties. The two most important parameters to tune are the pyrolysis temperature and the MW power. Fig. 3 shows the variance in individual pyrolysis product yields and CO pyrolysis product yields with blend ratios (10 g:10 g) of AP: DS with and without a CaO Nano catalyst used [13,17].

Table 1. Experimental details and product yields

feedstock	Char (wt%)	Oil (wt%)	Gas wt%	Conv. (wt.%)	AHR °C/min	Time min	Temp. °C	HHV MJ/Kg	Power KJ
algae	10.5	49.2	40.2	89.4	31.2	24	650	31.2	648
Date seed	17.99	39.16	42.85	82.01	27.27	18	515	37.2	486
Algae + date seed	18.8	55.295	25.905	81.2	26.45	20	555	35.6	540
Algae + date seed +CaO Nanocatalyst	24.314	43.08	32.60	75.68	22	24	555	40.3	648

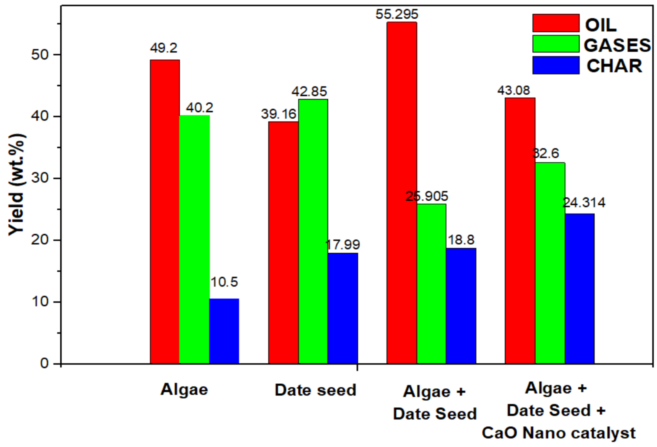

Fig. 3. Individual pyrolysis product yields and Co-pyrolysis product yields with mixture ratios (10g:10g) of AP: DS with and without CaO Nanocatalyst

The mixture of algae powder and date seeds resulted in oil production of 55.29% by weight, as shown in Fig. 3. This suggests that the two feedstock components worked together synergistically. On the other hand, adding a calcium oxide nanocatalyst increased gas and coal production and decreased oil production to 43.08 wt%. This indicates that secondary cracking is enhanced by the catalyst, leading to a shift in product distribution towards gas rather than oil. This lines up with the study findings by Yi et al. (2019) and Li et al. (2021) [21,23].

3.2. Microwave-assisted catalytic and non-catalytic co-pyrolysis of AP and DS

Researchers conducted MW-assisted catalytic co-pyrolysis studies to study the synergistic impact of AP and DS. 450 W of running microwave power, a 10:10 ratio of AP to DS, 10 grams of graphite susceptor, and 1 gram of CaO nanocatalyst. In every set, you'll find three experiments. With and without the CaO nanocatalyst in MW, the AP to DS blending ratio was tested in each experiment. The typical heating rates to reach the 555 ◦C pyrolysis temperature ranged from 26.45 to 22 ºC/min, as shown in the studies. The results of the co-pyrolysis of raw AP and DS are shown in Table 1. The process yielded 55.295 wt% oil, 18.8 wt% char, and 25.905 wt% gases. In contrast, bio-oil (43.08 wt%), gas (32.60%), and char (24.314%) make up the yields of DS catalytic co-pyrolysis and AP catalytic co-pyrolysis, respectively. (Refer to Fig. 3 Show how the yields of the pyrolysis product change depending on the AP: DS blend, with or without using a CaO nanocatalyst [14-17].

3.3. Average heating rate

The heating rate of algae in the microwave was 31.2 °C/min, which was greater than that of date seeds. The chemical makeup and high thermal conductivity of algae powder are probably to blame for this. Algae high in lipids or other compounds may heat up more rapidly when exposed to microwave radiation. Contrarily, red algae had a higher heating rate (27.27 °C/min) when subjected to microwave heating than date seeds. Compared to date seeds rich in oil, those that contain more lignin or cellulose are less sensitive to microwave heating. This makes them less efficient in absorbing microwave energy, so they will heat up more slowly. The simultaneous pyrolysis of algae and uncatalyzed date seeds using microwave-assisted pyrolysis, using both source materials in co-pyrolysis, decreased the thermal breakdown rate to 26.45 °C/min when microwaved [17-20].

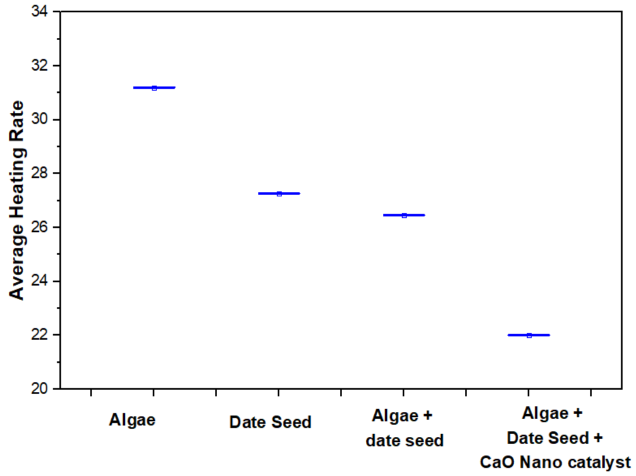

Fig. 4. The average heating rate of MW- assisted pyrolysis and co-pyrolysis of AP and DS

One possible explanation is that the composition of raw materials becomes more heterogeneous when mixed, making it more difficult for them to absorb microwave radiation uniformly. The total thermal decomposition rate may be lower if materials with various heating rates are combined, such as date seeds, which are rich in lignin, and high-fat red pepper seeds. Another possibility is that the combination will have a thermal storage effect, rendering the heating process slower due to the absorption and dissipation of energy by one material type relative to another. Fig. 4 shows that the AHR rate drops to 22 °C/min when the CaO Nano catalyst is added because of its catalytic capabilities [17-20]. Fig. 4 illustrates that the CaO Nano catalyst reduced the AHR; a Higher heating rate promotes faster thermal decomposition, which enhances oil production. When a nanocatalyst is present in the mixture, the heating rate is reduced, and the reaction time is prolonged due to increased secondary reactions such as cracking and char formation, resulting in more char and gas formation. This matches the findings of Guo et al. (2020) [22].

3.4. The synergy of co-pyrolysis of algae powder (AP) and date seed (DS)

Synergy happens once the combined effects of two or more substances are more significant than the total of their separate effects, or vice versa. The carbon and hydrogen molecules that make up the two materials could undergo chemical reactions, leading to this. When pyrolyzing a mixture of two different materials, it is crucial to determine the synergistic influence. When particles combine in either a positive or negative way, it's called a synergistic effect. The feedstock selection process, pyrolysis operating parameters, and the combined impact of pyrolysis on the yields of three-phase products are highly correlated. Regarding the samples under study, the calculated and actual results for AP and DS pyrolysis show that these processes yield the highest product. Test results were obtained by co-pyrolyzing AP: DS with and without a CaO nanocatalyst. The theoretical values were calculated by conducting separate pyrolysis experiments on AP and DS with a CaO Nanocatalyst. Mathematical studies were performed to ascertain the catalytic co-pyrolysis of AP: DS and the synergic effects between them. Each feedstock mixture's weight determines its pyrolytic yield, conversion, and average heating parameters. Synergistic impacts on product yield parameters are shown in **Fig. 5** and **6**. There will be a synergistic impact if the gas yield variables in theory and experiment differ. These synergistic effects are quantified in **Table 2** and vary with feedstock (AP: DS) with and without a CaO Nanocatalyst. Both positive and negative values are made possible by the synergistic effect. With 1 g of CaO nanocatalyst and co-pyrolysis feedstock (AP: DS), the gas yield synergistic effect values reveal a negative synergy of (-8.92 wt%). The char yield has the lowest positive synergistic effect (10.07 wt%). In contrast, the oil yield has the most negative effect (-1.1 wt%), as shown in **Fig. 5**. However, as shown in **Fig. 6**, the uncatalyzed co-pyrolysis had a negative synergistic effect on gas yield of 15.61 weight percent and a positive effect on oil yield of 11.11 weight percent and char yield of 4.56% [13,17]. **Fig. 5** and **6** show that algae and date seed synergy enhances oil production due to complementary decomposition pathways. Meanwhile, with the nanocatalyst, the reaction shifts towards increased gas and char formation due to deoxygenation and secondary cracking, reducing overall oil yield. This matches with our previous study, Hamzah et al. (2023) [17].

The positive synergy of gas yield (−15.61%) greatly increases gas creation. It is probably because the volatiles are cracking more easily, and the heavier molecules are turning into gas more easily. Algae's nitrogen/lipid composition might boost gas-phase reactions. The negative synergy of the oil yield (+11.11%) is a decrease in the oil yield. Possible suppression from competitive reactions that make gases that don't condense. Thermal degradation of volatile substances before condensation. Char Yield (+4.56%); Decrease in char yield. This means that the feedstock is more completely volatilized, which may seem nice, but it is actually wicked synergy (the yield is less than planned).

Table 2. Analysis of synergy effects in process parameters

Feedstock	Synergy effect in char yield	Synergy effect on oil yield	Synergy effect in gas yield
Algae + date seed	4.56	11.11	-15.61
Algae + date seed +CaO Nanocatalyst	10.07	-1.1	-8.92

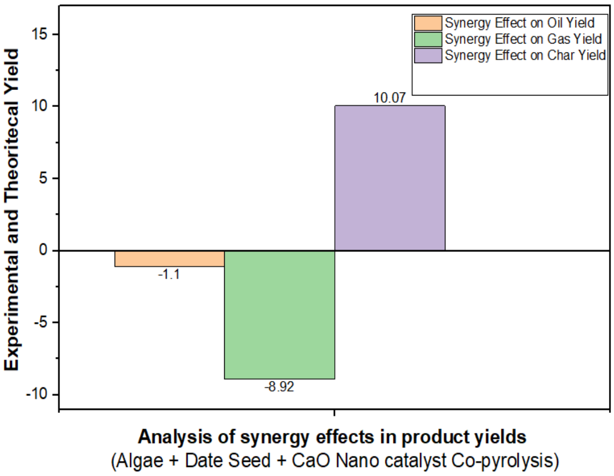

Fig. 5. Synergy effect of catalyzed co-pyrolysis of algae and date seed

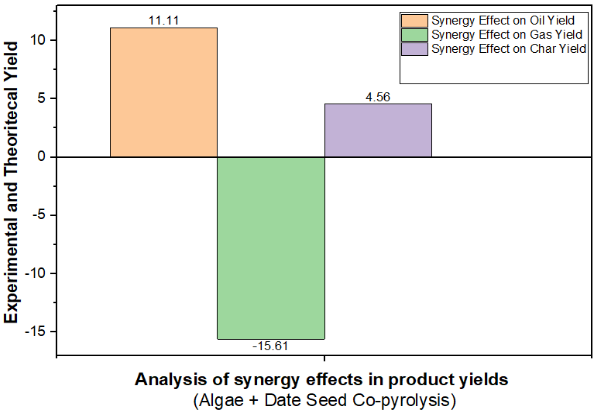

Fig. 6. Synergy effect of uncatalyzed co-pyrolysis of algae and date seed

The positive synergy of oil yield (−1.1%) means that the oil yield increased slightly. CaO may help catalytic cracking and deoxygenation, enhancing oil quality and quantity. Gas Yield (8.92%): Gas formation improved. CaO helps in decarboxylation, decarbonylation, and the release of light gases. It may also help change condensable into permanent gases. The Negative Synergy of Char Yield (+10.07%): There was less char formation. This could be because catalytic cracking leaves less carbon behind. But according to your convention, this is a bad synergy. **Table 3** represents the significant chemical and thermal interactions that are involved.

Table 3. Important chemical and thermal interactions involved

Type of Interaction	Description
Hydrogen transfer	Algae's lipid content facilitates oil production in uncatalyzed runs.
CaO-Catalytic cracking	CaO breaks up lengthy chains but can break too much, lowering the amount of condensable oils.
Gas foraging	(CaO) absorbs CO_2 → forms $CaCO_3$ → ostensible gas yield reduction.
Char upgrade	CaO helps secondary reactions and carbon fixation happen on its surface.
Thermal synergy	The different decomposition temperatures of AP and DS make co-pyrolysis more efficient at using heat.

3.5. Composition of oil yield from AP and DS

The oil extracted from date seeds and algae using microwave co-pyrolysis includes various chemicals such as hydrocarbons, oxygenates, nitrogenous ones, sulfate-containing ones, and more. Lipid and protein breakdown produce hydrocarbons, such as aromatics and alkanes, which predominate. In the process of breaking down carbohydrates, oxidized substances such as acids and phenols are produced. Because algae are rich in proteins, they produce nitrogenous compounds like pyridines and indoles, while sulfurous chemicals reflect the naturally occurring sulfur in algae biomass. Fatty acids like palmitic and oleic acids suggest that algae and seeds contribute lipids. It shows how bio-oil could be used as a sustainable biofuel or chemical feedstock [13,17,26]. Table 4 shows the GC-MS Identified Compounds – Without CaO Nanocatalyst, and Table 5 shows GC-MS Identified Compounds of co-pyrolyzed oil – With CaO Nanocatalyst.

Table 4. GC-MS identified compounds of Co-pyrolyzed oil – without CaO Nanocatalyst

Compound Name	Retention Time (min)	Molecular weight (g/mol)	Relative Abundance (%)
Toluene	4.21	92.14	3.4
Phenol	5.85	94.11	5.1
2-Methylphenol (o-Cresol)	6.33	108.14	2.8
Indole	9.2	117.15	2.1
Pyridine	4.6	79.1	2.2
Benzeneacetonitrile	12.33	131.16	1.7
Dibenzothiophene	13.87	184.26	1.3
Palmitic acid	16.1	256.42	7.3
Oleic acid	18.22	282.46	6.8
2,4-Dimethylphenol	6.77	122.17	2.3

As a basic nanocatalyst, CaO promotes deoxygenation, decarboxylation, and aromatization, resulting in an increase in hydrocarbons and a decrease in oxygenates and nitrogenous chemicals. The lack of pyridine and indole in the catalyzed oil means that the fuel is of better quality and has less nitrogen, which helps cut down on NOx emissions. Because CaO makes cracking and deoxygenation happen more, there are more alkanes and aromatics (such as heptadecane and naphthalene). Table 6 shows the Compounds Exclusive to Catalyzed vs. Uncatalyzed Oil.

Table 5. GC-MS identified compounds of Co-pyrolyzed oil – with CaO Nanocatalyst

S.N.	Name of Compound	Retention Time (min)	Molecular weight (g/mol)	Relative Abundance (%)
1.	Toluene	4.21	92.14	3.9
2.	Phenol	5.85	94.11	3.2
3.	2-Methylphenol (o-Cresol)	6.33	108.14	1.9
4.	Naphthalene	10.45	128.17	4.6
5.	Benzofuran	7.12	118.13	1.9
6.	Hexadecane	19.04	226.44	3.9
7.	Methyl palmitate	17.88	270.46	2.5
8.	Heptadecane	21.9	240.45	2.9
9.	Palmitic acid	16.1	256.42	6.0
10.	Oleic acid	18.22	282.46	5.4
11.	2,4-Dimethylphenol	6.77	122.17	1.7

Table 6. Compounds exclusive to catalyzed vs. uncatalyzed oil

Catalyzed Oil	Uncatalyzed Oil
Naphthalene	Indole
Benzofuran	Pyridine
Hexadecane	Benzeneacetonitrile
Heptadecane	Dibenzothiophene
Methyl palmitate	-

Table 7. Key compound groups and their potential use

Group / Compound	Possible Application
Phenols	Used in medicines, adhesives, and resins. But their high polarity makes fuel less stable.
Alkanes (e.g., hexadecane, heptadecane)	They are great for transportation fuels (diesel-range) since they have a lot of energy. It is stable and burns cleanly.
Aromatics (e.g., toluene, naphthalene)	It can be used in octane boosters or petrochemicals, but too much can make soot and poisonous.
Fatty Acids (palmitic, oleic)	Be used to make biodiesel or directly as bio-lubricants and surfactants.
Esters (methyl palmitate)	It is good for biodiesel applications since it has a low viscosity and good ignition properties.
Nitrogenous Compounds (e.g., indole, pyridine)	Make oil poor because they release NOx and are unstable. It may need to be upgraded or taken away.
Oxygenates (e.g., cresols, benzofuran)	Moderate fuel value, however, is an issue because it is corrosive and doesn't heat up very well. Good for chemical feedstocks.

When algae and date seeds are co-pyrolyzed with CaO nanocatalyst, the result is a higher output of hydrocarbons and esters, which makes the oil more like gasoline, lowering the amount of nitrogen and sulphur compounds, which makes emissions and stability better. Better deoxygenation means fewer acids and phenols. Table 7. Showed the Key Compound Groups and Their Potential Use.

3.6. Pyrolysis index (PI) for AP and DS

We can optimize the pyrolysis process and find the sustainability limitations using the pyrolysis index (PI). The primary factors that establish the principle variables (PI) are the following: amount of ingredients, residence duration, conversion, high heating value, and MW power usage. PI can take on values between zero and infinity. Fig. 7 shows the PI values of 40.82 and 37.32 for co-pyrolysis of algae powder (AP) and date seed (DS) with a 10:10 mixing ratio, with and without a CaO nanocatalyst. Table 8 shows that the individual pyrolysis PI values for algae powder (AP) are 48.1 and for Date seed (DS) 67.43. Co-pyrolysis enhances the decomposition efficiency through the synergistic effect of the raw materials, resulting in an intermediate PI. The low PI observed with the CaO nanocatalyst suggests that the catalyst affects the reaction kinetics by promoting secondary reactions such as cracking and deoxygenation, which slows the overall pyrolysis rate. The decrease in PI with the nanocatalyst indicates a shift toward char and gas formation and a slower decomposition process. This matches the study findings of Li et al. (2021) [23,27-30].

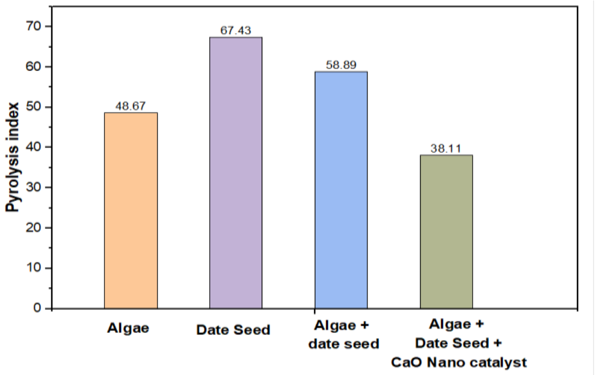

Fig. 7. Pyrolysis index of AP and DS

Table 8. Experimental pyrolysis index (PI)

Feedstock	Pyrolysis index (PI)
Algae	48.67
Date seed	67.43
Algae + date seed	58.89
Algae + date seed +CaO Nano-catalyst	38.11

4. Conclusions

In this investigation, AP and DS were catalytically co-pyrolyzed with the help of a 450 W microwave. It was used to investigate the effects of the CaO nanocatalyst on energy consumption, synergy, and product yields. Pyrolytic yields, average heating rates, and conversion factor percentages were studied concerning the co-pyrolysis synergistic effect. The typical heating rates (22-31.2 °C/min) were affected by the blend ratio (10:10 g), catalyst, and the kind of feedstock (AP: DS). While uncatalyzed co-pyrolysis yielded the most oil at 55.295% by weight, employing a CaO nanocatalyst resulted in the highest char yield at 24.314 wt% and gases at 32.60%. Combined pyrolysis of AP and DS has far-reaching effects on product yields, energy requirements, and synergy. The study's key findings indicated that AP and DS, when combined in the proposed MW-assisted catalytic co-pyrolysis process, could be a good substitute for conventional ways of expanding, recycling, and decomposing hydrocarbon molecules into lighter hydrocarbon molecules and valuable gas and liquid by-products. Significant discoveries point to algae as the optimal feedstock for bio-oil synthesis due to their high oil yield (49.2%), low char formation, and other desirable properties. Its low MW energy consumption makes it an attractive fuel for efficient pyrolysis processes. Although date seeds increased oil yield, combining algae and date seeds decreased solid waste. The increased HHV of the feedstock's bio-oil opens the door to potential new applications of concentrated energy. Although it generated the least gas, the blend of date seeds and algae produced the greatest bio-oil at 55.295%. Combining oil output with gas generation can lead to a biofuel production compromise using this mix. Oil yielded by the date seed and algal powder mixture was 55.29 percent by weight. This points to a synergistic effect between the two feedstock components. However, gas and coal output increased, and oil output decreased to 43.08 wt% when a calcium oxide nanocatalyst was added. This suggests that the catalyst improves secondary cracking, which causes the product distribution to change from oil to gas. The CaO Nano catalyst decreased oil output and increased gas generation during pyrolysis by decreasing energy. A realistic way to optimize biofuel production is to use catalysts to improve the bio-oil's quality, as demonstrated by the improved HHV of the bio-oil. Co-pyrolysis produces an intermediate PI by maximizing the decomposition efficiency via the synergistic action of the source ingredients. Because of its effect on secondary reactions, including cracking and deoxygenation, the CaO nanocatalyst reduces the total pyrolysis rate, as indicated by the low PI. Decomposition is slowed, and the drop in PI with the nanocatalyst shows a shift towards char and gas production. Important in the real world, this research shows that algae could be a respectable sustainable biofuel source because of their high bio-oil yield and minimal char production. Biofuel production on a larger scale may benefit from its high energy content and rapid conversion rate. Date seed, an agricultural by-product, appears to be a promising biofuel source. It may be used in some industrial contexts due to its high energy content and malleability. Utilizing a nanocatalyst in conjunction with date seed and algae provides an opportunity to enhance bio-oil quality while increasing efficiency. Making more sustainable and energy-dense fuels from biomass waste could be a step towards a more circular economy. The goal of future studies should be to optimize the catalyst so that we can increase oil yield while reducing energy consumption. Studies should focus on increasing the pyrolysis process's capacity to handle large amounts of feedstock to ensure consistent energy yields at larger scales. Positive Interactions: Researching more feedstock combinations could lead to optimized pyrolysis results and overall biofuel generation. Before deciding whether or not to employ these feedstocks in commercial biofuel production, it is important to do life cycle assessments to determine their financial and ecological effects. These assessments will pave the way for future work in this study area by providing vital information on the items' characteristics and possible uses.

Declaration of Competing Interest

No authors' relationships or financial conflicts of interest were considered to impact this study.

Data availability

The data that has been used is confidential.

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