Applied Science and Engineering Progress, Vol. 18, No. 1, 2025, 7454

Research Article

The Potential Significance of Microwave-Assisted Catalytic Pyrolysis for Valuable Bio-Products Driven from *Albizia* Tree

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Received: 4 January 2024; Revised: 6 April 2024; Accepted: 3 July 2024;

Abstract

The objective of this study is to investigate the feasibility of Na_2CO_3 and ZSM-5 as catalysts in the microwave pyrolysis of Albizia branches. An evaluation was conducted to determine the influence of power applied, experimental time, particle size, and catalysis type and ratio on the quality and quantity of pyrolysis products. Established methods such as GC-MS, FTIR, HHV, SEM, EDX, and BET were used to characterize the properties of bio-oil and biochar produced. The results demonstrated that using both catalyst types led to a substantial enhancement in biogas production. The improvement ranged from 5% to 41% with Na_2CO_3 and reached 45% with ZSM-5. At a lower power level of 300 W, the bio-oil yield augmented from 28% to 40% and 53% when using ZSM-5 and Na_2CO_3, respectively. The GC-MS analysis revealed that the utilizing of catalysts enhanced the levels of aromatic compounds, esters, and alcohols in bio-oil, along with an increase in the higher heating value (HHV) from 19.5 MJ/kg to 22 MJ/kg and 24.2 MJ/kg using Na_2CO_3 and ZSM-5, respectively. Moreover, the biochar's surface area and pore volume experienced a considerable rise, going from 0.5512 m^2/g and 0.00011 cm^3/g to a higher value of 115.2073 m^2/g and 0.0774 cm^3/g when treated with Na_2CO_3. The data indicated that both catalyst types enhanced the generation of CH_4, and CO_2 was lower with ZSM-5. The utilization of catalysts improves the quality of the biofuel produced and promotes the efficiency of the process in terms of energy consumption and processing time.

Keywords: Albizia branches, Biochar, Bio-oil, Catalytic microwave pyrolysis, Na_2CO_3, ZSM-5

1 Introduction

The need for energy sources that rely on fossil fuels has increased due to the growing population and technological advancements [1]. However, burning these fuels has environmental detrimental repercussions, including declining air and water quality, health issues, and price instability. These problems are especially troublesome in underdeveloped nations, as they raise the rates of neonatal and maternal death and lower life expectancy [2].

On the other hand, renewable energy sources like solar radiation, wind, biomass, water, and geothermal are becoming more popular due to their limitless availability, insignificant greenhouse gas emissions, and cost-effectiveness [3]. As a promising substitute, biomass—an abundant renewable resource with carbon as its primary component—shows a significant agreement of promise by 2050, it intends to provide up to 27% of the global energy needed for transportation. It has resources that could produce heat and transfer it into solid, liquid, or gaseous states. Biomass is a renewable energy source since its processing and combustion release less carbon dioxide into the atmosphere [4].

Diverse energy sources could emanate from biomass residues via mechanical, thermochemical, and biological processes [5]. Pyrolysis is a thermochemical conversion process widely explored for producing liquid fuel from solid biomass feedstock. During this process, large biomass molecules collapse into a gaseous form in conditions of absence of oxygen. The solid charcoal remains after the process is completed [6], [7]. Biomass is converted into biogas, biochar, and bio-oil through pyrolysis and refining. Biochar, a solid structure with the finest grains, is advantageous for many environmental applications, including carbon sequestration, energy storage electrodes, and soil amendment and modification [8]. Bio-oil is a dense liquid that contains over 300 oxygenated components, and it has become a promising alternative fuel for various applications such as engines, furnaces, petrol additives, and chemical solvents. Moreover, bio-oil is employed to produce pigments, surfactants, polyurethanes, plastics, and synthetic fibers [9], [10].

The pyrolysis process, an energy-to-heat conversion process, can be categorized as slow, fast, and flash [11]. Microwave pyrolysis is a process that involves heating feedstock particles using microwave radiation. Then, the heat is transferred out of the feedstock, resulting in heat loss. The feedstock material has low thermal conductivity, which causes a temperature gradient. This gradient forces the volatile components to diffuse from the core to the surface at a lower temperature [12], [13].

Catalysts are often used in microwave pyrolysis to increase the reaction rate or the potential temperature of biomass, leading to advanced production of bio-oil, biochar, and biogas [14]. Many types of catalysts can be used in this process, such as zeolite, carbonates and metal oxides, clays, and carbon-based substances biochar as catalysts. These vari eties improve the heat assimilation of biomass and result in superior combustible products [15]. Zeolite is widely recognized as an agent that reduces oxygen molecules while producing light aromatic compounds [16]. In addition, metal oxides and carbonate are frequently employed owing to their influence on gaseous substances [17]. By reducing the proportion of heavy compound fractions in bio-oil, natural and pillared clays, such as bentonite, may increase bio-oil yield [18]. Activated carbon, a substance characterized by its chemical inertness and high surface porosity, is regarded as a cost-effective substitute for traditional catalyst supports owing to its cost-effectiveness or cost-free generation from biomass and refuse materials [19].

Several pyrolysis processes were used to convert the Albizia plant, including flash pyrolysis [4] and fixed bed pyrolysis [20] to produce biogas, bio-oil, and biochar; the bio-oil produced was less than 50%, and the char was less than 40% for the two processes. The features of these two separate pyrolysis processes were almost comparable, based on the physical and chemical requirements. These comprised the low calorific value of the biochar and bio-oil, the absence of surface area and particle size in the two systems, the abundance of functional groups in the liquid fuel, and the different proportions of alcohols, aldehydes, and ketones in the fuel.

However, microwave technology was not employed in the production of the three distinct categories of biomass derived from this plant. In the current research, albizia branches were catalytically pyrolyzed using two types of catalysts, ZSM-5 and Na_2CO_3, using microwave technology. Several variables were investigated to examine the quantity and quality of the gaseous, liquid, and solid bio-products after the addition of the catalyst. These variables comprised the duration of the experiment, the power level employed, the catalyst proportion, and the particle size. Additionally, the chemical and physical properties of the products were characterized.

2 Materials and Method

2.1 *Material*

Albizia trees are a prevalent plant species found within the University of Baghdad in Baghdad, Iraq. Branches were gathered from this location and then dried at 100 °C for a day using an oven dryer. After drying, the branches were crushed using a grinder, and the resulting particles were separated into two size groups (1 mm – 500 µm and less than 500 µm). Two types of catalysts were used in this study: Na_2CO_3 (purity 99.9%), its hygroscopic colorless crystals or white crystalline powder or granules (New Delhi-110002 (INDIA)). The other one is ZSM-5 (purity 98%) with a surface area of 352 m^2/g and a ratio of Al / Si equal to 30.

2.2 *Material preparation*

Zeolite (ZSM-5) and sodium carbonate (Na_2CO_3) in concentrations of 10% and 5% were combined with 10 and 5 g of the raw material to prepare experimental samples. The catalysts were shaped as fine particles by being compressed with a force of up to 10 tons to make them into larger particles that could be easily removed from the biochar.

2.3 *Method*

The same experimental setup used in the previous study [21], was used to conduct the experiments. A customized microwave oven (24 L, Samsung, China) with seven power settings (100, 200, 300, 450, 600, 700, and 800 W) was utilized. The pyrolysis reactor was made of a cylindrical Pyrex glass vessel with a height of 17 cm and a diameter of 5 cm. The reactor was coupled to an outlet tube that sent the pyrolysis gases to a condensation unit made up of a three-glass cylinder kept at –15°C and an intake tube for injecting inert N_2 gas (98% purity). A K-type thermocouple was installed in a third tube to track the temperature inside the reactor. A BIOGAS 5000 gas analyzer was used to examine the non-condensed gases before they were released into the atmosphere. The obtained products, bio-oil, biochar, and bio-gas, were collected and weighed using the equation below:

$$\mathrm{Y(o,c,)} = \frac{\mathrm{W_{o,c,}}}{\mathrm{W_{Biomass}}} * 100$$

where $\mathrm{W_{Biomass}}$ is the weight biomass before pyrolysis (g) and $\mathrm{W_{o,c}}$ is the weight of bio-oil and biochar obtained from the pyrolysis process (g).

The reactor was first filled with varied volumes of feedstock (5, 10 g), with a catalyst ratio between 5% and 10%. Biomass particle sizes range from 1 mm-500 µm and 500 µm. To establish an oxygen-free atmosphere, inert N_2 gas was added into the system at a flow rate of 1 L/min for 15 min before the experiment began. After that, the microwave was turned on at a certain power level.

2.4 *Products analysis*

The physical and chemical properties of the resulting bio-oil were identified to understand their characteristics and potential applications. Fixed standards methods were used to determine the physical attributes of bio-oil, such as viscosity, acidity, calorific value, and density. The viscometer (Cap 2000, USA) device was used to measure viscosity, and a pH meter (Starter 2000, USA) was utilized to determine the acidity of the bio-oil; density was determined by measuring the weight of a known volume. The bomb calorimeter (CAL3K-AP, South Africa) was used to calculate the samples' heating value.

Fourier transform infrared spectroscopy (FTIR) (Tensor 27, Germany) was used to identify a sample's functional groups and chemical bonds. At the same time, gas chromatography-mass spectrometry (GC-MS) Agelint (7820A, USA) is used to detect chemical compounds that are presented in bio-oil. There is the provision of an HP-5ms capillary column in the system. Helium (99.999% purity) is used as a carrier gas. The bio-oil sample was prepared by diluting it with hexane, and the volume of the injected sample was 1 µL. The temperature of the oven was initially set at 50 °C for 3.5 min in the system program, then it was raised by 4 °C /min to 180 °C and held for 5 min. The injected and detector temperatures were maintained at 250 °C and 230 °C, respectively.

The specific surface area of biochar was determined based on Brunauer–Emme t–Teller (BET); the scanning electron microscopy (SEM) of biochar was carried out by a Hitachi S3000N VP-SEM with EDX.

3 Results and Discussion

3.1 *Effect of catalyst on the product yield*

3.1.1 Effect of power level

It is feasible to observe that the experiment's duration time and microwave pyrolysis temperature are both influenced by the catalyst's presence. The heat transfer mechanism inside the microwave begins with a transition of heating from the magnetron to the catalyst by convection and then from the catalyst to the biomass by conduction, which could increase the ability of the feedstock to absorb the microwave radiation [22]. This mechanism accelerates the reaction and reaches the end using less duration than without a catalyst. Furthermore, after stabilizing, a long reaction time may lead to a second reaction that produces an undesirable product. Generally, each type of adsorbent or catalyst has a unique influence on product production. Figure 1 below shows that utilizing 450 W of power level and particle size of 1–500 µm during 20 min. The results demonstrated a fair augmentation in bio-gas production, where it boosted from 5% without catalyst to 45% using ZSM-5 and reached 41% with Na_2CO_3, indicating a significant improvement in bio-gas production. On the other hand, bio-oil dropped from 55% without a catalyst to 25% and 34% when ZSM-5 and Na_2CO_3 were used, respectively. Furthermore, the biochar production was reduced from 40% without a catalyst to 30% with ZSM-5 and 25% when Na_2CO_3 was adopted. These differences in biofuel production occur due to the catalyst's impact on the heat's ability to absorb the biomass and increase the rate of temperature. With a ratio of 10% catalyst to biomass, it tends to improve and create a high percentage of gases due to the significant temperature rise. In contrast, biomass pyrolysis without using the catalyst and under the same conditions leads to a high percentage production of bio-oil and biochar. These results could be attributed to the biomass used in this study seeming to have a good microwave radiation absorber, and the addition of catalyst at this ratio led to a significant increase in temperatures, which resulted in a reduction in biochar and bio-oil fuels and a notable improvement in gaseous fuels.

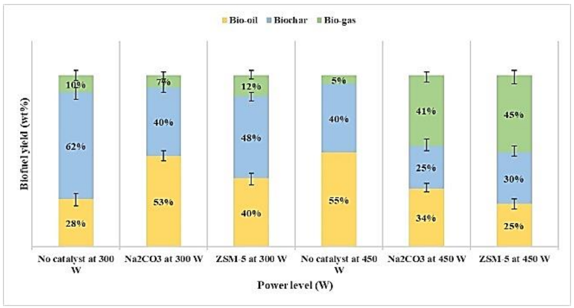

Figure 1: Effect of power levels on biofuel production.

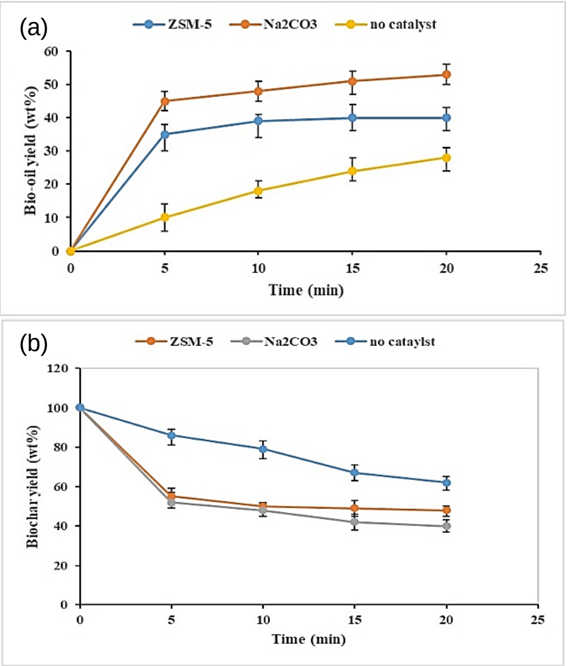

Figure 2: Effect of time on (a) bio-oil and (b) biochar production.

Moreover, the difference in the power level utilized and the catalyst used affected the bio-products. It can also be noticed from Figure 1 that by switching the power level from 450 W to 300 W using a ZSM-5 catalyst, the bio-oil percentage rose from 25% to 40% and from 34% to 53% with Na_2CO_3. The same response appeared with biochar. When the power dropped from 450 W to 300 W, the percentage augmented from 30% and 25% to 48% and 40% by using ZSM-5, Na_2CO_3, respectively, while the gas production was decreased by a percentage of 33% and 34% when ZSM-5 and Na_2CO_3 were used. These results are in line with the previous study [5], which pointed out that adding a catalyst leads to reducing the power requirement for the production of bio-oil and biochar due to enhancing the final temperature.

Additionally, Figure 1 compares the yield of bio-oil produced with and without using the catalyst at the power level of 300 W. It could noticed that there is a high enhancement in the final yield of bio-oil. For instance, using 300 W with both types of catalysts goes towards enhancing the bio-oil; for the same condition, the percentage of bio-oil was 28% without using a catalyst as investigated in the previous study [21]. This percentage rose to 40% while using ZSM-5 and reached to 53% with Na_2CO_3. The biochar product had a reflected response on the ratio where it was 62% without catalyst and reduced to 40% and 48% when Na_2CO_3 and ZSM-5 were utilized, respectively. The gas product was reduced from 10% without a catalyst to 7% with Na_2CO_3 and raised to 12% with ZSM-5 due to temperature rising.

The sort of fuel produced is considerably dependent on the power level used. Biogas, which can be utilized in direct combustion operations, is produced at higher temperatures using higher power. Compared to bio-oil, which is employed as a fuel, a basis for pharmaceuticals, or an ingredient in industrial processes, is produced at medium temperatures using lower power. Low power is used to generate solid biofuels, which are used in place of fuel, plant fertilizers, water filtration and purification materials, etc.

3.1.2 Effect of experimental time

Time is a crucial economic factor in the biofuel production process. Utilization of a catalyst reduces energy consumption and the time required to complete the biomass conversion process. According to Figure 2, it was discovered by repeating a few experiments that the standard deviation was within 5%. Figure 2(a) shows that the yield of bio-oil is strongly affected in the first few minutes and then increases insignificantly when the time is increased to 20 min. When using ZSM-5 as a catalyst, the percentage of bio-oil produced was 35% at 5 min and increased slightly to reach a maximum value of 40% at the end of 20 min. Similarly, when Na_2CO_3 was used as a catalyst, 48% of bio-oil was produced at 10 min and reached 53% at 20 min. However, the increase of bio-oil without a catalyst was gradual, starting from 10% at 5 min and reaching 28% at the final minute.

Likewise, it is feasible to produce nearly the same quantity of biochar when using a catalyst with a lower period than that without a catalyst and with a higher quality obtained. As shown in Figure 2(b), biochar production without any addition reached 62% during 20 min, while 55% and 52% can be produced in 5 min using ZSM-5 and Na_2CO_3, respectively. Bu *et al.* [23], Mohamed *et al.* [5], also found that a higher temperature was reached within the first few minutes with the higher biofuel production.

During the initial phase of the thermal analysis, the temperature reaches its highest level due to the catalyst maximizing microwave thermal absorption. This absorption may be produced by moisture residues present in the raw material. After that, the temperature starts to stabilize, and there may be a slight increase in the ultimate yield, which is barely noticeable in the final bio-oil product.

The reaction mechanism of a catalyst in pyrolysis involves a series of steps, including adsorption, activation, cracking, deoxygenation, reforming, and catalysis of specific reactions. The catalyst's nature and the specific biomass feedstock influence the chemical transformations during the thermal decomposition of biomass. Adsorption is the initial step, followed by adsorbing species activation, which can compose the breaking of specific chemical bonds within the biomass molecules. Cracking and deoxygenation reactions are crucial for producing gases like methane and hydrogen while improving reactions to transform hydrocarbons into hydrogen-rich gases. Acid-base catalysis can be facilitated by catalysts with acidic or basic sites, influencing the distribution of hydrogen within the products [24].

3.1.3 Effect of particle size

The other parameter that seemed to affect the proportions of the products is the biomass particle size. Figure 3 shows the effect of the two-particle sizes 1 mm- 500 µm and less than 500 µm at a power level of 300 W on the production of biofuels and also with an error percent within 5%. We observed from both Figures 3(a) and (b) that the desirability of the three types of resulting fuel is similar when using both types of catalysts, provided the size of the particles used decreases. Specifically, we noticed that the bio-oil decreased from 40% to 32% and from 53% to 36% when using Na_2CO_3 and zeolite, respectively. On the other hand, biochar dropped from 48% to 41% when using Na_2CO_3 and from 40% to 32% when using zeolite. This decrease is due to an increase in the surface area between the resulting molecules caused by a reduction in their size. This, in turn, leads to an increase in reaction temperatures, which explains the increase in the proportion of gases produced in both types. As we learned earlier, an increase in reaction temperatures tends to produce gases, which is what happened in this case.

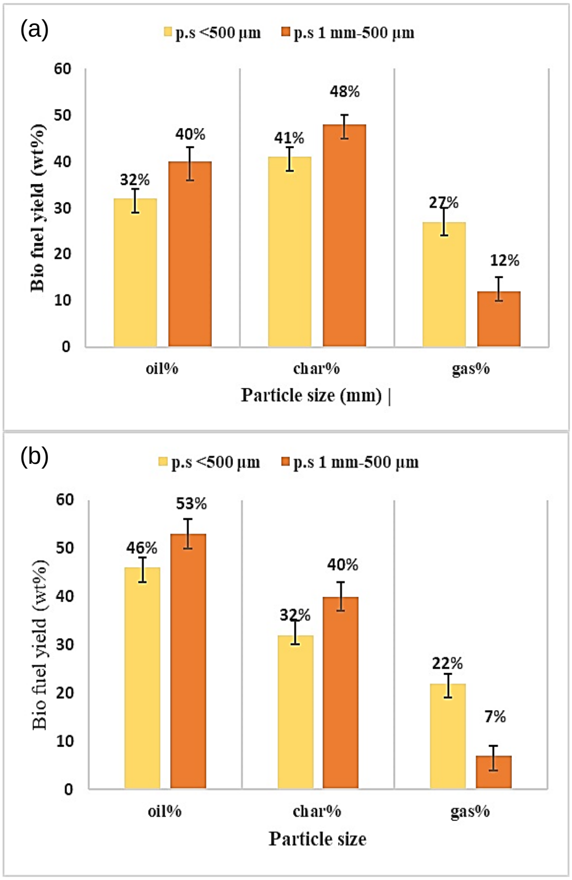

Figure 3: Effect of particle size on biofuel yield using (a) ZSM-5 and (b) Na_2CO_3.

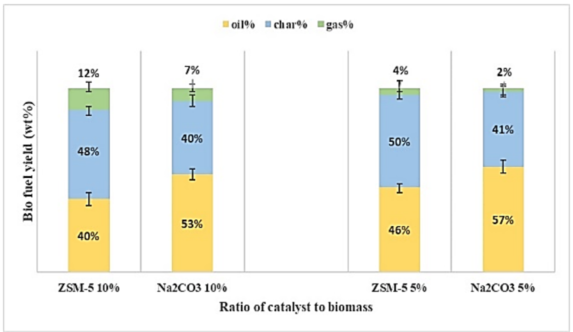

Figure 4: Effect of catalyst to biomass ratio on biofuel using 300W.

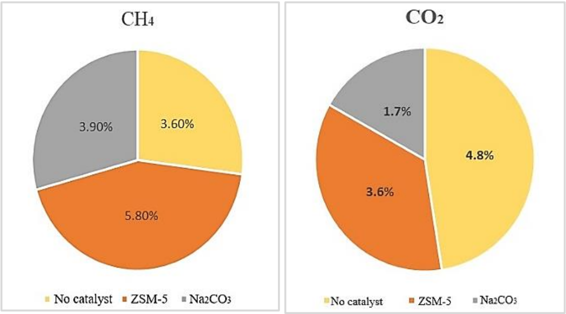

Figure 5: Bio-gas concentration during the pyrolysis process.

3.1.4 *Effect of catalyst to biomass ratio*

The last studied parameter was the ratio of catalyst to biomass to show the effect of using a catalyst on bioproducts. A clear improvement in the production of bio-oil and biochar fuels (Figure 4) has been observed when the catalyst-to-biomass ratio is reduced. It has been indicated that the catalyst-to-biomass ratio reduction from 10% to 5% when ZSM-5 and Na_2CO_3 are employed increases the bio-oil yield by 6% and 4%, respectively. Also, there was a slight increase in the production of biochar, as it is shown that when using ZSM-5, the yield increased from 48% to 50%, and when Na_2CO_3 was applied, the production increased from 40% to 41%. On the other hand, gas products were reduced by 8% when ZSM-5 was used and by 5% when Na_2CO_3 was applied. Similar results were reported by Liu *et al.* [25], and Seo *et al.* [26], due to the fact that increasing the catalyst-to-biomass ratio causes the biomass to absorb higher temperatures, which aids in the formation of gaseous and the reduction of bio-oil and biochar. Thus, lowering the catalyst-to-biomass ratio is optimal for bio-oil and biochar production.

3.1.5 Bio-gas production

Pyrolysis produces several gases, including methane and carbon dioxide, based on the catalyst utilized. One of the significant chemical gases that contribute to energy production is methane. Regarding carbon dioxide, contemporary energy production techniques aim to minimize its creation as much as possible. It is one of the greenhouse gasses that contribute to global warming. Figure 5 shows that 3.6% of CH_4 was generated without a catalyst at different experimental conditions. It is raised to 3.9% and 5.8% while using Na_2CO_3 and ZSM-5. At the same time, CO_2 reached its maximum value of 4.8% without using a catalyst, and then it dropped to 3.6% and 1.7% with ZSM-5 and Na_2CO_3, respectively.

Catalysts are designed to focus on desired products based on their properties, such as strength, Brønsted and Lewis acid distribution, porosity, and metal addition. Factors like pore size, distribution, specific surface area, and phase structure also play a role in catalytic pyrolysis. Large-pore zeolites promote heavy hydrocarbon formation, while medium-pore zeolites promote lighter products. Pore size is crucial in catalytic pyrolysis, as narrow pores allow products to diffuse, while larger pores facilitate secondary reactions. The form of the catalyst also affects product distribution, with powder-form ZY catalysts promoting olefins and pellet-form catalysts promoting paraffins and naphthalenes [27], [28]. The current results demonstrated that ZSM-5 and Na_2CO_3 catalysts play a crucial role in biomass pyrolysis. ZSM-5 is known for its catalytic cracking ability, which selectively breaks down large biomass molecules into smaller hydrocarbons, promoting the formation of light gases like methane and ethane. It also favors the production of aromatic hydrocarbons, leading to the formation of benzene, toluene, and xylene. Furthermore, it facilitates deoxygenation reactions, reducing oxygen content in biomass and producing gases like carbon monoxide and carbon dioxide. Its catalytic activity is temperature-sensitive, affecting gas distribution. Na_2CO_3, on the other hand, promotes dehydration and decarboxylation, contributing to the production of gases like carbon dioxide and water vapor. Its basicity influences gasification reactions, favoring the production of gases like carbon monoxide and hydrogen. The choice between these catalysts depends on the desired product spectrum and pyrolysis process goals [29].

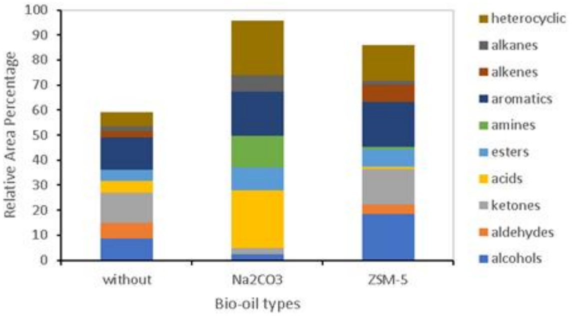

Figure 6: Difference between chemical composition of bio-oil.

3.2 *Effect of catalyst on bio-oil characteristics*

3.2.1 Physical analysis

Using catalysts in microwave pyrolysis can improve the bio-oil produced quality by enhancing its physical properties. Catalysts can help remove oxygen from the bio-oil through a deoxygenation reaction, which leads to increased stability, higher heating value, and improved energy density. The density of bio-oil has a direct impact on bio-oil usage as biofuel in engines. Consequently, its measurement is critical [30], [31]. The presence of carboxylic acids in bio-oils, such as acetic, formic, and oleic acids, suggests high acidity, which can cause corrosion and other problems when used as a fuel and chemical feedstock. The catalytic process may inhibit the devolatilization of hemicellulose in the feedstock to form organic volatile molecules in the liquid product, resulting in less acid generation [32]. Using a catalyst also can improve the formation of a lighter aromatic compound and lead to a decrease in the viscosity of the resulting bio-oil, this could be attributed to the fact that catalytic processes accelerate pyrolysis reactions when adsorbents are used, increasing the proportion of lighter chemicals in bio-oils as shown by Mahmoud Fodah *et al.* [33]. In addition, using a catalyst_could also reduce the content of oxygen elements, which enhanced the calorific value of the bio-oil [34].

Table 1 shows the effect of adding a catalyst on the main properties of bio-oil produced through the microwave pyrolysis process. It is clear via the explanations of the oil's assets that using ZSM-5 gives the lowest viscosity and density value, as well as the highest pH value and calorific value. This is due to the amount of content produced by zeolite, which are light, volatile materials, low in oxygen, and with a low acid content.

Table 1: Physical properties of the bio-oil with and without catalyst.

Type of Bio-oil	**Viscosity (cSt)**	**Density (kg/m^3)**	**pH**	**HHV (MJ/kg)**
Without catalyst	4.8	1045	5	19.5
Na_2CO_3	3.1	1033.15	4.8	22.0
ZSM-5	2.8	1029.8	5.9	24.2

3.2.2 Chemical analysis of bio-oil

GC-MS (Gas chromatography-mass spectrometry) of Bio-oil. The GC mass analysis for the bio-oil obtained with and without catalyst was characterized to identify and analyze the components in the mixture. Utilization of a Na_2CO_3 catalyst in the pyrolysis process resulted in a different composition of the bio-oil compared to the one produced without a catalyst. The most abundant compound found in the bio-oil with Na_2CO_3 catalyst is Mequinol, the monomethyl ether of hydroquinone (Area% 8.52), followed by Phenol, 2,6-dimethoxy- (Area% 6.62), and N-Propionylimidazole (Area% 6.35). Mequinol is also found by Lei *et al.* [35], and Saravana Sathiya Prabhahar *et al.* [36], which is a possible pharmaceutical component being tested for use in the treatment of melasma. Other compounds such as n-hexadecanoic acid (Area% 3.22), Hexadecanoic acid, methyl ester (Area% 2.98), and 1,2-Cyclopentanedione, 3-methyl- (Area% 2.63) are also present in significant amounts. The total amount of active ingredients in the bio-oil is without a catalyst was 59.21%; however, this level rose to 95.73% when Na_2CO_3 used as a catalyst. It can be seen that the bio-oil produced using Na_2CO_3 has an acidic nature than that without a catalyst (Figure 6). Also, the percentage of aromatics increased by about 5%. When the Maillard reaction between sugars and amino acid radicals occurs at high temperatures, the proportion of heterocyclic compounds rose to 21.79%, which is also larger than that without catalysts, such as furans, pyrans, and pyridines. Also, when compared to bio-oil without catalyst, esters have a greater percentage (9.12%).

The presence of the catalyst can significantly influence the formation and distribution of different compounds in the bio-oil, leading to a higher yield of phenolic compounds. The higher yield of phenolic compounds in bio-oil produced with a Na_2CO_3 catalyst is a notable result, as phenolic compounds have various applications in the chemical and pharmaceutical industries. For instance, phenolic compounds can be used as antioxidants, preservatives, and intermediates in the synthesis of various chemicals [37].

Moreover, in the case of using ZSM-5 catalyst, the occurrence of some classes has increased. This could be due to the catalytic properties of ZSM-5, which is known for its high selectivity towards producing aromatics in petroleum refining. The most abounded component in this case was furfuryl alcohol at a percentage of 14.9%. Furfuryl alcohol is an essential intermediate for the manufacture of lysine, ascorbic acid, and numerous lubricants, producing resins [38]. The total active ingredients were 85.91%. Furthermore, the quantities or area of certain compounds changed significantly. For instance, “2-Cyclopenten-1-one” appears in a higher amount with the ZSM-5 catalyst, and several compounds are only present with the catalyst (such as “3-Fluorophenylhydrazine hydrochloride”, “Ascorbic acid, 2,6-palmitate”, and “6-Dodecanylcyclohexane”). The catalyst seems to promote particular reactions and thus changes the product distribution. This type of catalyst could increase alcohol, aromatics, and esters components, therefore reducing the acidity, which makes the bio-oil highly preferable due to its properties of higher heating value and lower pH value.

The potential use of this bio-oil can vary depending on its composition. For example, bio-oil rich in phenolic and aromatic compounds can be used as a chemical feedstock [39], whereas bio-oil rich in hydrocarbons can be directly used as a fuel or upgraded for use as a biofuel. The presence of certain high-value chemicals, like 2,6-Dimethoxyphenol, also suggests potential for pharmaceutical and cosmetic applications.

FTIR spectroscopy is a valuable technique for identifying functional groups and molecular structures in organic compounds. According to Figure 7 below, the primary functional groups are the same in all types of oil, depending on their density. For instance, the absorbance peaks of O-H stretching between 3000 cm^{-1} and 3500 cm^{-1}, which denotes the presence of alcohols, phenols, and water, is high when ZSM-5 is used as a catalyst. This indicates that the addition of ZSM-5 to the biomass during pyrolysis resulted in increasing in the alcohol and aromatics compounds, which is remarkably consisted with the GC-MS results. However, when the absorbance peaks of C≡C stretching appeared between 2000 cm^{-1} and 2500 cm^{-1}, the variation is almost perceptible, indicating that all types contain relatively similar concentrations of functional groups of alkyne and nitrogen-containing compounds in the bio-oil. C-H bending indicated the presence of aromatic compounds visible at wavelength 1650 cm^{-1} and 2000 cm^{-1} for all types, with the most abounded in ZSM-5 bio-oil, which deals with the GC-MS analysis. N-O stretching and C-H bending reveal the presence of nitro-compound, alkane, and aldehyde between 1300 cm^{-1} and 1600 cm^{-1} vibration with the most percent noticeable while using Na_2CO_3, as shown in the GC-MS analysis. The last vibration between 1000 cm^{-1} and 1300 cm^{-1} is shown in nested proportions with all three types of catalyst, which is indicated by the convergent presence of phenols, esters, amine, and fluoro compounds. FT-IR spectrums suggested that the bio-oil gained from pyrolysis was mostly composed of aromatic compounds.

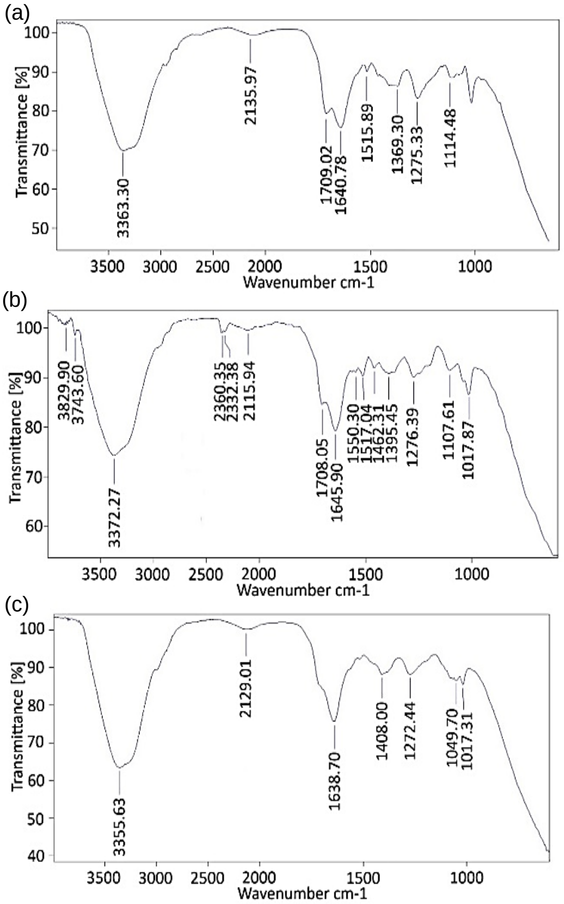

Figure 7: FTIR of the three types of bio-oil a) no catalysts b) with ZSM-5 C) with Na_2CO_3.

4 Biochar Analysis

4.1 *Physical analysis of biochar*

BET (Brunauer-Emmett-Teller) surface area and pore volume analysis and HHV (Higher heating value). The surface area and pore volume of the biochar from microwave pyrolysis given in Table 2 are significantly influenced by the type of catalyst used. Without using a catalyst, the surface area of the biochar was 0.5512 m^2/g, and its pore volume was 0.00011 cm^2/g. This indicates a minimal porosity in the biochar, which could reduce its potential applications, such as for carbon sequestration and soil amendment. The feedstock is one of the important parameters that affect the surface area and pore volume. Softwood, *Caragana korshinskii*, and different biochars were studied by many researchers and each of them had a different value of surface area and pore volume [40]. Also, another researcher found the heating temperature can affect the surface area and pore volume of the biochar and showed that increasing pyrolysis temperature can increase this value [41], [42].

Table 2: surface area and pore volume of biochar before and after adding catalyst.

Biochar Types	Surface Area (m^2/g)	Pore Volume (cm^3/g)
Without catalyst	0.5512	0.00011
With Na_2CO_3	115.2073	0.0774
With ZSM-5	45.0667	0.0433

The utilization of Na_2CO_3 as a catalyst significantly increased the surface area and pore volume to 115.2073 m^2/g and 0.0774 cm^3/g, respectively, which promoted the development of a porous structure in the biochar, attributed to the higher reaction temperature, and enhanced the surface area and pore volume.

ZSM-5 catalyst produced biochar with a convergent surface area of 45.0667 m^2/g and pore volumes of 0.0433 cm^3/g. These results indicate the influence of these catalysts in promoting porosity in the biochar. In microwave-assisted pyrolysis, moisture is evaporated from the particle's interior before the organic components are released into the gas stream. In addition to quickly sweeping volatiles out of the pores and forming preferred pathways in the biochar, the steam from vaporized water also improves the porosity of the material. These findings suggest that the type of catalyst used in microwave pyrolysis can significantly affect the surface area and pore volume of the resultant biochar, thus impacting its properties and potential applications [33], [43].

Examining the calorific value of fuel is critical since it reveals the qualities of the fuel as well as the intended deployment. The higher the calorific value, the more it can be utilized as missile fuel or a substitute for fossil fuels like coal. Increasing carbon content and reducing oxygen content positively impacted the heating value of biochar. It is examined that biofuel without catalysts had a calorific value of 23.5 MJ/kg, while it increased to 27 MJ/kg when zeolite was used and reached 31 MJ/kg when Na_2CO_3 was used. This deals with other researchers who found the same response of increasing HHV with increasing carbon and reducing oxygen content [44].

In general, SEM images provide insights into the physical structure and morphology of biochar produced via microwave pyrolysis. It may be noticed that several differences between the surfaces of biochar by examining the illustration. Thus, Figure 8(a) below shows the morphology of the biochar surface without the use of a catalyst and implies that the surface is a type of cube structure, which is practically homogenous smooth, with a proportion of the lengthy cracks that separate the cube molecules, reflecting the lower surface area and pore volume recorded in the Brunauer-Emmett-Teller (BET) analysis. However, biochar particles without catalysts might still show some degree of porosity [42], [45].

Figure 8(b) demonstrates that pyrolysis inherently induces the creation of pores in the charred material while using ZSM-5 as a catalyst, so there is a presence of various-sized pore pores along, these pores are typically formed by the release of volatile components from the biomass during the pyrolysis process [46], [47], with a few atypically-shaped spherical particles that are fixed to a zigzag surface. The biochar surface area increased noticeably from 0.5512 m^2/g to 45.0667 m^2/g due to these properties.

Using Na_2CO_3 in Figure 8(c) depicts the distribution of spherical particles of various sizes in a large number indicated by a fragile, porous, wavy surface with very small pores, which is one of the most essential qualities that resulted in an increase in surface area from 0.5512 m^2/g to 115.2073 m^2/g.

The size and distribution of these pores can vary depending on the feedstock and the specific pyrolysis conditions (e.g., temperature, heating rate). If the feedstock comprises a lignocellulosic material, one might observe remnants of the plant's cellular structure, which could appear as larger, irregular voids in the SEM images [46].

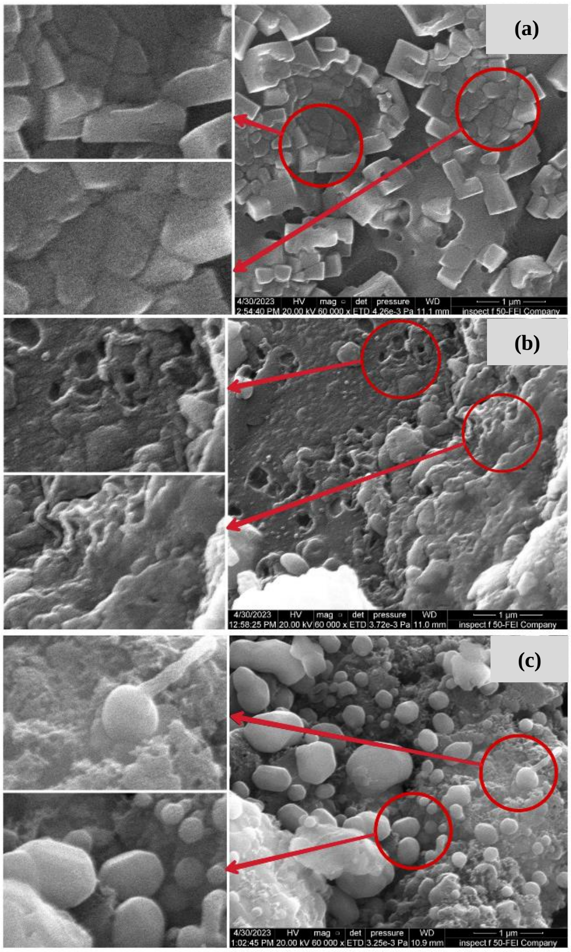

Figure 8: SEM micrography a) biochar without catalyst, b) biochar with ZSM-5, c) biochar with Na_2CO_3.

The size and distribution of these pores can vary depending on the feedstock and the specific pyrolysis conditions (e.g., temperature, heating rate). If the feedstock comprises a lignocellulosic material, one might observe remnants of the plant's cellular structure, which could appear as larger, irregular voids in the SEM images [46].

While these comments are generalizations and assumptions based on typical results seen in biochar SEM images, it's important to note that the specific appearance of biochar can vary greatly depending on the pyrolysis process and catalyst used. In general, using any type of catalyst can improve the surface area and pore volume of the resulting biochar depending on the reaction that occurs during the pyrolysis reaction.

Table 3: EDX analysis of biochar (element concentration).

Element	Without Catalyst		ZSM-5		Na_2CO_3	
	Atomic %	Wt %	Atomic %	Wt %	Atomic %	Wt %
C	60.3	51.0	64.5	52.0	80.3	68.4
O	36.5	41.1	25.6	27.5	13.3	15.1
Mg	0.4	0.7	0.4	0.7	1.0	1.7
Al	0.1	0.2	2.2	4.0	0.2	0.4
Si	0.1	0.2	4.0	7.5	0	0
P	0.1	0.2	0.3	0.7	0.3	0.6
S	0.1	0.2	0.1	0.3	0.5	1.3
Cl	0.5	1.3	0	0	2.2	6.0
K	1.2	3.2	1.3	3.5	2.3	6.5
Ca	0.7	1.9	1.5	3.9	0	0

According to the EDX analysis, the minerals attached to the sample contain elements, such as carbon, oxygen, magnesium, silicon, and aluminum, along with small amounts of chlorine, potassium, calcium, phosphorus, and silicon as shown in Table 3. Carbon and oxygen are the dominant elements, with carbon accounting for approximately 60.3% of the atomic composition and 51.0% of the weight. This is expected since carbon is the primary component of biomass and remains a significant part of the biochar after the pyrolysis process, especially when produced through microwave pyrolysis without the use of a catalyst. Oxygen is the second-most dominant element, accounting for approximately 36.5 atomic % and 41.1 weight %. Oxygen is inherent to the biomass structure and is also present in large quantities in the resulting biochar. One of the purposes of using catalysts in pyrolysis processes is to improve the chemical composition of solid fuels, where they enhance carbon content and reduce oxygen percent [48]. As shown below, using ZSM-5 increased Carbon content, which is at 64.5 atomic % and 52.0 weight %, and decreased Oxygen content to 25.6 atomic % (27.5 weight %).

Carbon content has highly increased significantly compared to both the biochar produced without a catalyst and with a catalyst. It now accounts for approximately 80.3 atomic % and 68.4 weight %. This significant enhancement in carbon content might be attributed to the catalytic effects of Na_2CO_3, promoting the carbonization process and resulting in higher carbon content in the biochar. The Oxygen content has significantly decreased to 13.3 atomic % (15.1 weight %), the lowest among the three samples. This again suggests the effectiveness of Na_2CO_3 as a catalyst in promoting the release of oxygen-containing functional groups during pyrolysis.

The carbon content, combined with appealing properties such as porous structure and high specific surface area, makes biochar an ideal candidate for a variety of applications such as water treatment and soil amendment, where materials with high carbon content and a large surface area (with high adsorption capacities) are required [49].

Other elements, such as Magnesium (Mg), Aluminum (Al), Silicon (Si), Phosphorous (P), and Sulfur (S), are present in trace amounts. These elements are likely part of the biomass feedstock's mineral matter that persists in the biochar after pyrolysis. Chlorine (Cl), Calcium (Ca), and Potassium (K) are present in slightly higher amounts compared to other minerals. These elements might also originate from the mineral matter in the biomass.

The presence of these minerals in the biochar can have implications for its potential uses. For instance, biochar with a high mineral content can be beneficial for soil amendment as it can slowly release these minerals into the soil, enriching its nutrient content. Although Biochar’s mineral elements concentration depends on the feedstock, chicken manure-derived biochar contains high Ca and K, crucial for soil quality. In some cases, inorganic fertilizer can be applied to provide the required elements and also as an adsorbent to purify air and water contaminants. Understanding the effects of feedstock type on biochar composition is essential [49], [50]. Moreover, the high carbon content indicates potential uses of this biochar in carbon sequestration and as a fuel source [51].

4.2 *Chemical analysis of biochar*

The chemical compatibility of the prepared biochar materials was evaluated using FTIR spectroscopy measurements. Generally, Figure 9 shows that the fundamental functional groups of the biochar are about the same, with some drop or increase between one form and the other, and that the intensity of the appearance of the functional group is predominantly determined by the catalyst used. For example, O-H stretching between (3200–3550 cm^{-1}) indicated that Carboxylic acid or water presence appeared highly when the biochar was pure and with Na_2CO_3 and less with ZSM-5, while the clear absorption peaks at 2920.23 cm^{-1} and 2850.79 cm^{-1} correspond to C-H stretching vibration appeared with the pure biochar only. C=C and C=O stretching (1600–1700 cm^{-1}) and C=C stretch (1400–1600 cm^{-1}) indicated the presence of aromatic and benzene rings, which were found with ZSM-5 and Na_2CO_3 biochar more than biochar without catalyst. Furthermore, C-O (1000–1300 cm^{-1}) vibration indicated the aromatic, alcohol, phenol, and aliphatic (Aryl-alkyl ethers), which were mostly found with ZSM-5 biochar and lower concentration with Na_2CO_3 and pure biochar. Alkene, aromatic, and peroxide appeared with the peaks of =C-H bending between (675–1000 cm^{-1}) vibration, which improved by using the catalyst and more highly found with the two types of catalysts than without the catalyst.

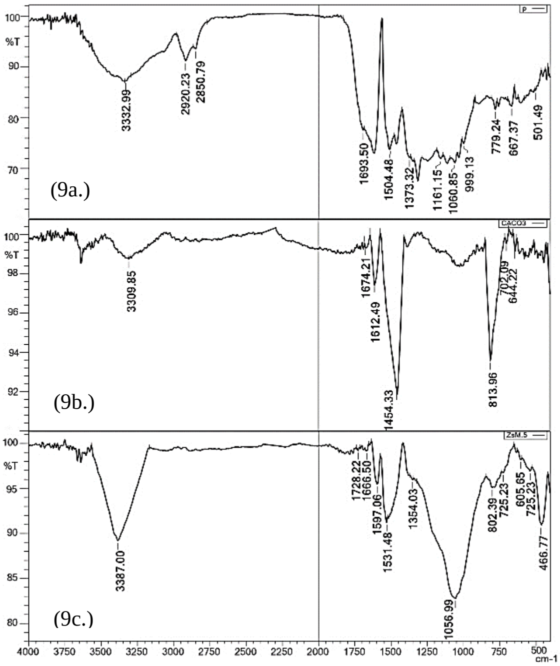

Figure 9: FTIR of biochar before and after adding catalyst (a) no catalysts, (b) with Na_2CO_3, (c) with ZSM-5.

5 Conclusions

This study aims to investigate the potential of catalytic microwave pyrolysis of Albizia branches using Zeolite (ZSM-5) and Na_2CO_3 as catalysts to produce biofuel. It focuses on distinguishing the differences that occur when different catalysts have been applied to the pyrolysis process by examining numerous factors, such as power levels, duration time, particle size, and catalyst/biomass ratio. The significant role of catalysts in gas yield enhancement has been remarkably detected, using Na_2CO_3 and ZSM-5 catalysts led to an observed increase in gas yield from 5% to 41% and 45%, respectively. The power level factor exhibited a counter effect on the bio-oil yield. By decreasing the power level from 450 W to 300 W, a maximum value of bio-oil yield was achieved at 53%

and 42% for Na_2CO_3 and ZSM-5, respectively. Likewise, the catalyst/biomass ratio has a similar influence as the power level effect on the bio-oil and biochar yield. Compared to an ordinary pyrolysis process that achieves the paramount amount of biofuel in 20 min, catalytic pyrolysis could achieve this target in just 5 min. More valuable components, such as aromatics, aliphatic chemicals, and esters, could be obtained in the bio-oil generated by catalytic pyrolysis. As a result of ZSM-5 catalyst utilization, a bio-oil with high alcohol content has been produced and exhibits a high suitability for use as fuel. Moreover, an increase in the higher heating value (HHV) of the bio-oil from 19.5 MJ/kg to 22 and 24.2 MJ/kg when Na_2CO_3 and ZSM-5 have been utilized, respectively. The significant effect of Na_2CO_3 addition on the biochar was unveiled by increasing the surface area from 0.5512 m^2/g to 115.2073 m^2/g. Furthermore, an increase from 0.00011 cm^3/g to 0.0774 cm^3/g in pore volume was observed with the same catalyst. Consequentially, the applicability of biochar in adsorption, soil amendment, and pollutant removal will show high efficiency. An increase in HHV from 23.5 MJ/kg to 27 and 31 MJ/kg is attributed to the addition of Na_2CO_3 and ZSM-5 catalysts, respectively, resulting in the generation of a biochar that is more suitable to use as a fuel. The advantages of using catalysts have been emphasized in many aspects, such as increasing the generation of a considerable CH_4 gas. While simultaneously reducing CO_2 emissions that contribute to global warming. In conclusion, the determination of bio-oil and biochar composition produced from the pyrolysis process is greatly affected by the catalyst type. More research is required to optimize the catalytic pyrolysis process for each catalyst type to assess the applicability of the generating bio-oil.

Author Contribution

M.F.A.: Data curation, formal analysis, funding acquisition, writing an original draft; A.M.A.: research design, reviewing and editing, methodology, project administration. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

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