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The effect of methanol additive on the formation of palm oil biodiesel deposit in hot surface deposit test

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ABSTRACT

Deposit formation remains a critical challenge in the utilization of palm oil biodiesel due to its high viscosity, low volatility, and dominance of saturated fatty acid methyl esters (FAME). This study investigates the effect of methanol addition on deposit formation behavior of palm oil biodiesel using a Hot Surface Deposit Test (HSDT), with a focus on linking molecular composition, thermophysical properties, and evaporation-driven deposit mechanisms. Biodiesel methanol blends with methanol contents ranging from 5% to 25% were characterized using GCMS, density, viscosity, and heating value measurements. Deposit formation was evaluated under hot surface temperatures between 230 °C and 290 °C. GCMS results revealed that methanol addition systematically shifted the FAME composition from saturated methyl esters toward unsaturated species, particularly methyl oleate and methyl linoleate. This compositional change was accompanied by a significant reduction in density up to 2.3% and viscosity over 30%, enhancing droplet atomization and evaporation characteristics. The heating value of the blends decreased with increasing methanol content, leading to reduced thermal cracking intensity during droplet–surface interaction. HSDT results demonstrated a substantial reduction in deposit area with increasing methanol fraction and surface temperature, indicating a transition from a liquid-film-dominated to an evaporation-dominated deposit formation regime. The findings highlight that deposit mitigation in palm oil biodiesel can be effectively achieved through fuel formulation strategies that enhance evaporation kinetics rather than relying solely on antioxidant additives or engine hardware modifications. Methanol is shown to function as an evaporation-enhancing additive that suppresses deposit formation by synergistically modifying molecular composition, physical properties, and thermal behavior of biodiesel.

Keywords: palm oil biodiesel, methanol additive, deposit formation, hot surface deposit test, evaporation kinetics, thermophysical properties.

INTRODUCTION

Palm oil biodiesel, has been widely developed as a sustainable alternative fuel for diesel engines due to its renewable and biodegradable nature. Biodiesel has its potential to reduce greenhouse gas emissions compared to conventional fossil fuels [1–3]. The abundant availability of feedstock and the existence of an established supply chain further position palm oil biodiesel as a strategic renewable fuel option in tropical countries [4]. However, the use of pure biodiesel (B100) still faces significant technical challenges, particularly regarding deposit formation in injection systems and hot engine surfaces, which can reduce performance, combustion efficiency, and the lifespan of engine components [5–7].

Deposit formation in the use of biodiesel is generally associated with high viscosity, low volatility, and the dominance of saturated fatty acid methyl esters (FAME), which promotes the formation of a liquid film on hot surfaces before thermal and oxidative degradation occurs [8,9]. Several studies have reported that palm oil biodiesel has a higher tendency to form deposits compared to conventional diesel due to its relatively high methyl palmitate and methyl stearate content [10,11]. This deposit has the potential to disrupt the injector spray pattern, increase particulate emissions, and accelerate fouling in the fuel system [12]. Deposit formation is initiated by incomplete droplet evaporation and prolonged liquid-phase residence time, which enables oxidation, polymerization, and carbon residue formation on heated surfaces.

Various approaches have been proposed to address the issue of biodiesel deposits, including the addition of antioxidants, modification of injector design, and optimization of engine operating conditions [13–15]. The use of antioxidants has been proven to improve the oxidative stability of biodiesel and suppress degradation during storage, but their effectiveness against thermal deposits on hot surfaces is still limited [16]. Additionally, hardware-based approaches often require high costs and are not always compatible with existing diesel engines, making them less flexible for widespread implementation.

Recent research has expanded toward fuel formulation strategies using additives that directly modify droplet behavior and fuel volatility. Comprehensive reviews highlight that biodiesel compatibility and deposit control increasingly depend on additives capable of altering thermophysical and interfacial properties rather than solely improving oxidation stability [17,18]. Studies on nano-additives demonstrate potential in enhancing heat transfer and combustion characteristics, but issues related to suspension stability, agglomeration, and long-term reliability remain unresolved [19,20]. In contrast, short-chain oxygenated additives such as alcohols provide a more direct pathway to deposit mitigation by increasing volatility and reducing viscosity, thereby promoting faster droplet evaporation [21]

In recent years, attention has begun to focus on the use of short-chain alcohols as biodiesel additives to improve physical properties and combustion characteristics. Methanol, as an oxygenated fuel with high volatility and low viscosity, has been reported to reduce biodiesel viscosity, improve atomization, and accelerate the combustion process [22,23]. Additionally, the increased fuel oxygen content due to the addition of methanol has the potential to reduce soot and particulate formation during combustion [24]. However, most biodiesel–methanol research focuses on engine performance and emissions, while the fundamental mechanism of deposit formation during droplet–surface interaction has rarely been isolated and examined [25]. Existing deposit studies predominantly address oxidation during storage or long-term injector fouling without explicitly linking droplet evaporation kinetics to hot surface deposit growth

Deposit formation in diesel engines originates from droplet interaction with heated walls, where evaporation rate, rheological properties, and surface temperature play decisive roles [26]. The hot surface deposit test (HSDT) provides a controlled platform to study this interaction independently of full combustion, enabling direct observation of evaporation-driven deposit mechanisms [27,28]. Despite its relevance, integrated studies connecting FAME molecular composition, thermophysical properties (density, viscosity, calorific value), and evaporation kinetics remain scarce. Experimental validation of how unsaturated FAME dominance influences hot surface deposit behavior is still limited, particularly within alcohol-modified biodiesel systems.

Therefore, a clear research gap exists in understanding how methanol addition alters palm oil biodiesel deposit formation through coupled changes in molecular structure, thermophysical behavior, and droplet evaporation dynamics. Addressing this gap is essential for developing fuel formulation strategies that suppress deposits without requiring major engine modifications. The present study investigates methanol-induced deposit mitigation using a Hot Surface Deposit Test framework combined with GC–MS analysis and thermophysical characterization. The key novelty lies in demonstrating that biodiesel deposit control can be achieved through evaporation kinetics engineering driven by molecular and thermophysical optimization, establishing a paradigm shift from oxidation-based mitigation toward evaporation-dominated strategies.

MATERIALS AND METHODS

Palm oil biodiesel (B100) was used as the base fuel in this study, while methanol (purity ≥99.8%) was used as an additive to investigate its effect on fuel properties and deposit formation behavior. The biodiesel-methanol mixtures were prepared with methanol volume fractions of 5%, 10%, 15%, 20%, and 25%, each denoted as B100M5, B100M10, B100M15, B100M20, and B100M25, respectively. Each mixture was homogenized using a magnetic stirrer at room temperature for approximately 15 minutes to ensure phase uniformity before testing. Chemical composition analysis was performed using gas chromatography-mass spectrometry (GC-MS) to identify and quantify the dominant fatty acid methyl ester (FAME) components, with relative composition determined thru peak area normalization. The effect of adding methanol on thermophysical properties was evaluated by measuring density, kinematic viscosity, and calorific value. Density was measured at room temperature using a calibrated digital density meter, while kinematic viscosity was determined according to ASTM D445 procedures. The calorific value of each fuel mixture was measured using an oxygen bomb calorimeter following standard calorimetry methods.

The hot surface deposit test (HSDT) was conducted to investigate droplet–surface interaction and deposit formation behavior of biodiesel methanol blends under controlled thermal conditions. As illustrated in Figure 1, a fixed-volume fuel droplet (5 ± 2 μL) was dispensed using a horizontally positioned micro syringe to ensure precise control of droplet size and injection repeatability. The micro syringe configuration minimized gravitational acceleration effects and enabled consistent droplet impingement conditions on the heated surface. The associated uncertainty in droplet volume was estimated based on syringe calibration and repeatability tests. The droplet was released toward a flat metallic plate heated to a predetermined temperature ranging from 230 °C to 290 °C, representing typical diesel engine wall temperature conditions. Surface temperature was continuously monitored using a calibrated K-type thermocouple with an uncertainty of ± 1.5 °C, embedded near the droplet impact zone to ensure thermal stability throughout the experiment. Temperature fluctuations during each experiment were maintained within ±2 °C to ensure stable thermal boundary conditions. The heated metallic plate provided a well-defined boundary for evaluating evaporation and deposit formation without the influence of combustion. Each experimental condition was repeated three times to ensure reproducibility, and the reported deposit area represents the average value. The standard deviation was calculated to evaluate experimental variability, which was found to be within ±5% for all test conditions

A camera positioned above the heated surface was employed to capture top-view images of the droplet impact, spreading, evaporation, and residue formation processes. This configuration allowed direct observation of droplet dynamics, including liquid film formation, evaporation rate, and the evolution of solid deposits on the surface. The use of top view imaging ensured accurate visualization of the deposit area and minimized

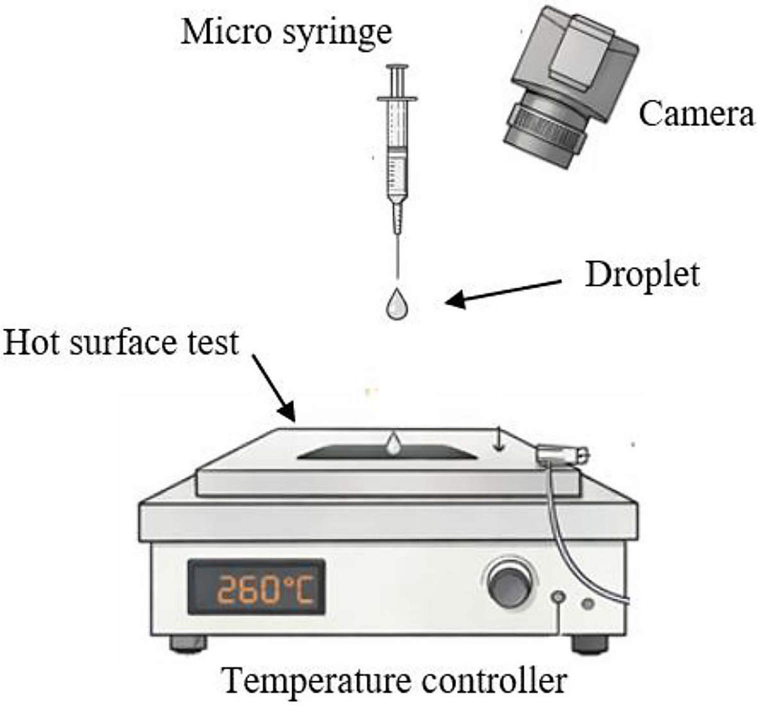


Figure 1. Schematic of hot surface test experiment

optical distortion. After each droplet–surface interaction, the surface was allowed to cool naturally, and the resulting deposit was documented for quantitative analysis. The resulting images were analyzed using image processing techniques implemented in MATLAB. First, each image was converted into grayscale to simplify intensity-based analysis. A thresholding method was then applied to distinguish the deposit region from the background, followed by binary segmentation to isolate the deposit area. Subsequently, a pixel-to-length calibration was performed using a reference scale to determine the actual deposit area quantitatively. The uncertainty in the deposit area measurement was estimated to be within ±3%, primarily attributed to limitations in image resolution and sensitivity to threshold selections

By isolating the droplet evaporation and surface interaction phenomena, the HSDT enabled direct evaluation of evaporation-controlled deposit formation mechanisms independent of full combustion processes

RESULTS AND DISCUSSION

Chemical separation techniques are employed in the analysis of chemicals in a solution by means of GCMS (gas chromatography and mass spectroscopy). A chromatographic column is used to separate the mixture's constituent chemicals. Variations in the solubility values of the competing compounds in the flowing solvent and their absorption into the stationary phase cause the separation mechanism between multiple compounds (Figure 2).

The GCMS test results show that the compounds in the biodiesel and methanol mixture consist of more than 80 compounds. To simplify analysis, the dominant compounds from GCMS data in a mixture of biodiesel and methanol are shown in Table 1.

Table 1 shows that the addition of methanol to palm oil biodiesel significantly affects the distribution of major fatty acid methyl ester (FAME) compounds. The fuel blend notation used in this study follows the format B100Mx, where B100 represents pure biodiesel and Mx denotes the percentage of methanol (by volume) added to the biodiesel. For example, B100M5 corresponds to a blend of 95% biodiesel and 5% methanol, while B100M25 represents 75% biodiesel and 25% methanol. The four dominant compounds identified, namely methyl palmitate ($C_{17}H_{34}O_2$), methyl linoleate ($C_{19}H_{34}O_2$), methyl oleate ($C_{19}H_{36}O_2$), and methyl stearate ($C_{19}H_{38}O_2$), undergo a systematic change in relative fraction as the methanol content increases from 5% to 25%. It was observed that the fraction of methyl palmitate, as a medium-chain saturated FAME, consistently decreased from 51.07% in B100M5 to approximately 38.5% in B100M25. This decrease indicates that the addition of methanol tends to inhibit the dominance of saturated compounds, which are thermodynamically less volatile and more thermally stable. In the context of deposit formation, methyl palmitate is known as one of the main precursors of carbon deposits due to its tendency to form solid residues during prolonged heating.

Conversely, the methyl oleate fraction showed a significant increase, from 38.28% in B100M5 to 48.57% in B100M25. The dominance of these unsaturated compounds indicates that methanol plays a role in shifting the FAME composition equilibrium toward structures with double bonds,

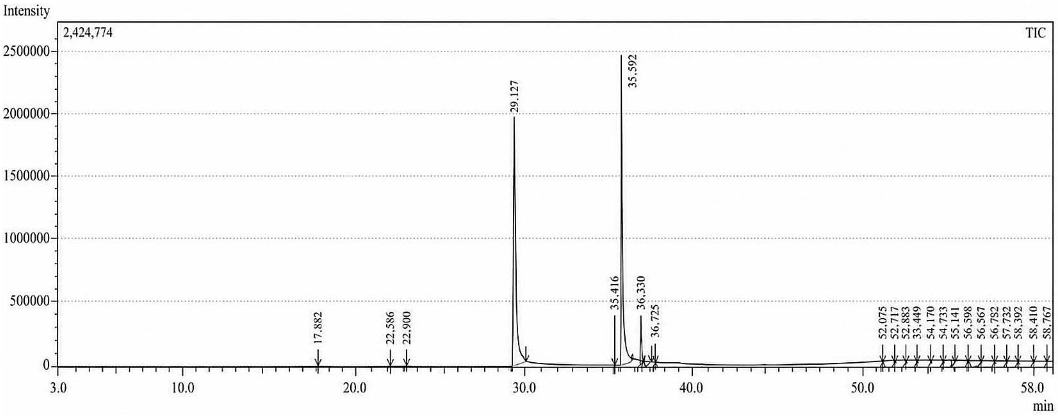


Figure 2. Chromatogram for the B100M5 mixture

Table 1. GCMS Analysis for dominant compounds of methanol-palm oil biodiesel mixture

Compounds	Chemical formula	Compositions (%)				
		B100M5	B100M10	B100M15	B100M20	B100M25
Methyl palmitate	$C_{17}H_{34}O_2$	51.07	46.14	40.53	38.28	38.52
Methyl linoleate	$C_{19}H_{34}O_2$	3.78	4.19	4.95	5.10	5.05
Methyl oleate	$C_{19}H_{36}O_2$	38.28	42.21	46.78	47.88	48.57
Methyl stearate	$C_{19}H_{38}O_2$	4.65	5.14	6.67	7.22	6.75
Other		2.22	2.32	1.07	1.52	1.11

which have weaker intermolecular forces and higher volatility. This condition is highly relevant to the droplet evaporation mechanism and directly contributes to the reduction of deposit formation on hot surfaces. A gradual increase was also observed in methyl linoleate, although in a relatively small fraction. This increase remains significant mechanistically because compounds with two double bonds have lower oxidative stability but faster evaporation rates, thus shortening the liquid residence time on the hot surface. This has a direct implication on the reduction of liquid film precursor formation, which is the initial stage of deposit formation.

Meanwhile, methyl stearate, although a long-chain saturated FAME, showed an increase up to a methanol content of 20% before slightly decreasing at B100M25. This pattern indicates competition between the subsequent esterification process and the diluting effect of methanol at high concentrations. Nevertheless, the contribution of methyl stearate to the total composition remained far smaller than that of methyl palmitate and methyl oleate, making its impact on deposit characteristics relatively limited.

The change in FAME distribution due to the addition of methanol is a key finding because deposit formation is highly sensitive to the ratio of saturated and unsaturated FAME. Saturated FAME tends to undergo partial thermal decomposition and polymerization on hot surfaces, while unsaturated FAME is more volatile and fragments more easily before forming solid residues. With the increasing fraction of methyl oleate and methyl linoleate, the biodiesel-methanol mixture shows a tendency to shift from a condensation-based deposit formation regime toward an evaporation-dominant regime. The GC-MS results not only describe the changes in chemical composition but also provide a strong mechanistic foundation for explaining the deposit reduction phenomenon observed in hot surface testing. This approach enhances the novelty of the research by directly linking the molecular composition of the fuel to deposit behavior, an aspect that is still rarely discussed comprehensively in the biodiesel-alcohol literature.

The density graph in Figure 3 shows that adding methanol to palm oil biodiesel results in a consistent and systematic decreasing trend in density as the methanol fraction increases. The density of pure biodiesel (B100) was recorded at 0.864 g/cm^3, then gradually decreased to 0.844 g/cm^3 in the B100M25 mixture. This decrease is equivalent to a density reduction of approximately 2.3% compared to B100, and about 5% compared to B30. This phenomenon is primarily caused by the intrinsic density difference between methanol and biodiesel, where methanol has a significantly lower density (~0.79 g/cm^3). However, these results cannot be explained solely as a linear mixing effect. Density changes are also closely related to modifications in the molecular structure of biodiesel, as indicated by previous GC–MS results.

The decrease in biodiesel-methanol density is consistent with the increasing fraction of unsaturated FAME, particularly methyl oleate and methyl linoleate. Unsaturated FAME have a less dense molecular configuration due to the presence of double bonds, which reduces intermolecular forces and results in lower bulk density. Thus, the observed decrease in density is not solely due to methanol dilution, but is also a direct consequence of the shift in FAME distribution toward lighter and more thermally deformable structures. This condition becomes important in the context of deposit formation, as lower density implies a decrease in droplet momentum upon impingement on the hot surface. Droplets with lower density tend to have smaller inertial forces, thus reducing the droplet's tendency to stick and form a precursor liquid film on the hot wall.

In fuel injection systems, density is a key parameter that affects atomization characteristics,

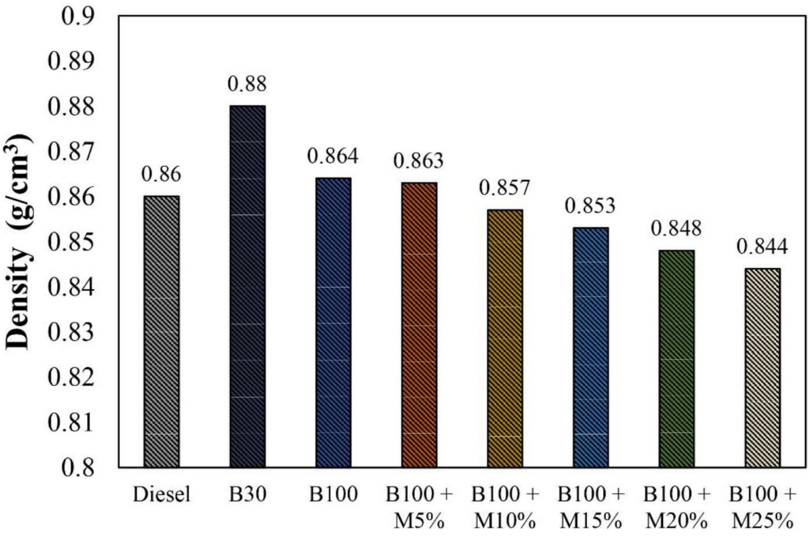


Figure 3. Density of blend fuel

spray penetration, and droplet size distribution. A decrease in biodiesel–methanol density leads to a reduction in droplet kinetic energy at the same injection pressure, making the droplets more prone to fragmentation and faster evaporation. In the B100M10 blend, the recorded density is approximately 0.857 g/cm³, a value very close to the density of conventional diesel. This indicates that adding approximately 10% methanol can adjust the physical characteristics of biodiesel to make it more compatible with existing diesel injection systems, without requiring significant modifications to the injection device. This finding has strong and relevant practical implications for the application of diesel engines fueled by biodiesel blends.

From a deposit formation perspective, lower density contributes to a weakening of the droplet's adhesive force against the hot surface. The combination of low density and high volatility shortens the droplet's residence time in the liquid phase, thus inhibiting the formation of a stable liquid layer that is a precursor to deposits. Thus, the decrease in density due to the addition of methanol acts as a passive but effective mechanism in mitigating deposits, especially when combined with an increase in surface temperature as shown in the HSDT results. This approach confirms that controlling the physical properties of the fuel is an important strategy in deposit control, not just controlling the combustion reaction.

Figure 4 depicts that pure biodiesel (B100) has a significantly higher viscosity compared to conventional diesel and biodiesel B30, which is 11.90 cSt. This value reflects the typical characteristics of palm oil biodiesel, which is rich in long-chain FAME compounds, especially methyl palmitate and methyl oleate, which have high molecular weights and strong intermolecular forces. With the addition of methanol, the viscosity of biodiesel undergoes a significant and monotonic decrease, from 11.90 cSt at B100 to 8.09 cSt at B100M25. This decrease is equivalent to a viscosity reduction of over 30%, indicating that methanol effectively acts as a fuel rheology modifier. The decrease in the viscosity of biodiesel-methanol is not only due to the much lower intrinsic viscosity of methanol, but also to changes in the molecular structure of the fuel mixture. GC-MS results showed an increase in the unsaturated FAME fraction, particularly methyl oleate and methyl linoleate, as the methanol content increased. This unsaturated compound has a less symmetrical molecular configuration due to the presence of double bonds, which reduces the molecule's ability to pack closely together.

Additionally, methanol acts as a small, polar molecule that can insert itself between the long FAME chains, weakening intermolecular forces (van der Waals forces) and reducing flow resistance. This interaction causes the biodiesel–methanol system to transition from a viscous flow regime toward a flow regime that more closely resembles a light Newtonian fluid. Viscosity is a key parameter that controls droplet size, spray angle, and atomization quality in diesel injection systems. High viscosity, such as in B100, leads to the formation of large droplets, which have longer evaporation times and a high tendency to

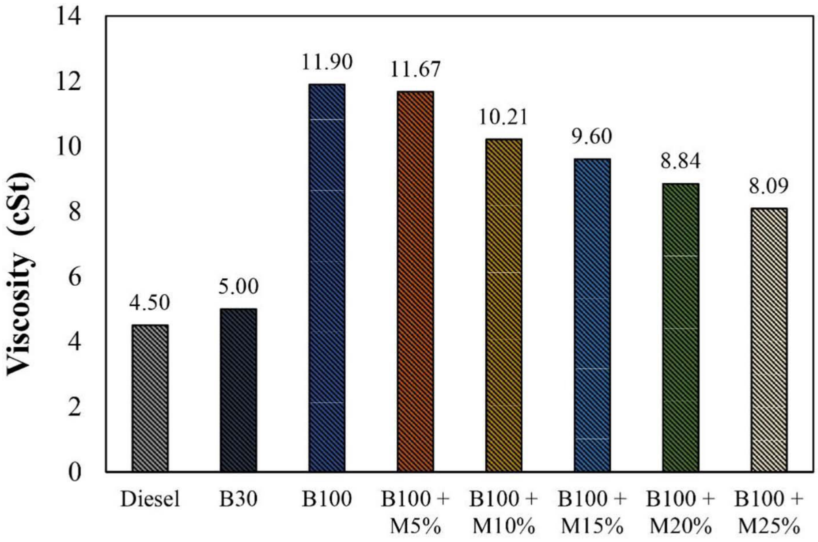


Figure 4. Viscosity of blend fuel

stick to hot surfaces. The decrease in viscosity due to the addition of methanol directly improves atomization quality, resulting in smaller droplets with a larger specific surface area. This condition accelerates the evaporation process and reduces the likelihood of a liquid film precursor forming on the hot wall. Therefore, viscosity reduction becomes a key factor bridging the changes in the fuel's physical properties with the deposit formation mechanisms observed in the HSDT testing.

The decrease in viscosity became more significant after adding methanol above 10%. In this range, the viscosity dropped from 10.21 cSt (B100M10) to 9.60 cSt (B100M15) and continued to decrease to 8.09 cSt (B100M25). This phenomenon indicates the presence of a rheological transition zone, where the influence of methanol on the mixture's microstructure becomes more dominant than the inherent properties of biodiesel.

Nevertheless, the viscosity values for the entire biodiesel-methanol mixture still remain above that of conventional diesel. This indicates that the addition of methanol improves atomization without causing the risk of over-atomization, which can lead to the formation of rich zones and increased particulate emissions. Thus, there is an optimal viscosity range that supports rapid evaporation while maintaining combustion stability. Low viscosity contributes to a reduction in the thickness of the liquid layer and a shortening of the liquid phase residence time. Droplets with low viscosity are more easily spread and evaporate before undergoing oxidative reactions or thermal polymerization that result in carbon residue.

Figure 5 shows that pure biodiesel (B100) has a calorific value of 9.356 cal/g, which is lower than conventional diesel (13,487 cal/g) and B30 biodiesel (9.709 cal/g). Adding methanol to biodiesel consistently results in a decreasing trend in calorific value, with the lowest value recorded for B100M20 (8.473 cal/g) and a slight increase for B100M25 (8.543 cal/g). This decrease in calorific value is a direct consequence of the low calorific value of methanol, which is theoretically far below that of biodiesel. However, the implications of this decrease are not solely negative, particularly in the context of deposit formation on hot surfaces.

Biodiesel and methanol are oxygenated fuels. Increasing the methanol fraction effectively increases the oxygen-to-carbon ratio (O/C ratio) in the fuel mixture, which thermodynamically lowers the combustion energy per unit mass. Additionally, the shift in FAME composition toward unsaturated compounds also contributes to a decrease in calorific value because the total bond energy stored in the molecular structure becomes lower compared to saturated compounds. Thus, the observed decrease in calorific value reflects the chemical and structural transformation of the fuel, not merely the diluting effect of methanol. This strengthens the argument that the thermal properties of biodiesel–methanol must be understood as a result of multi-component interactions.

Calorific value plays a crucial role in determining the maximum temperature of droplets during contact with a hot surface. Fuels with high calorific values tend to produce higher

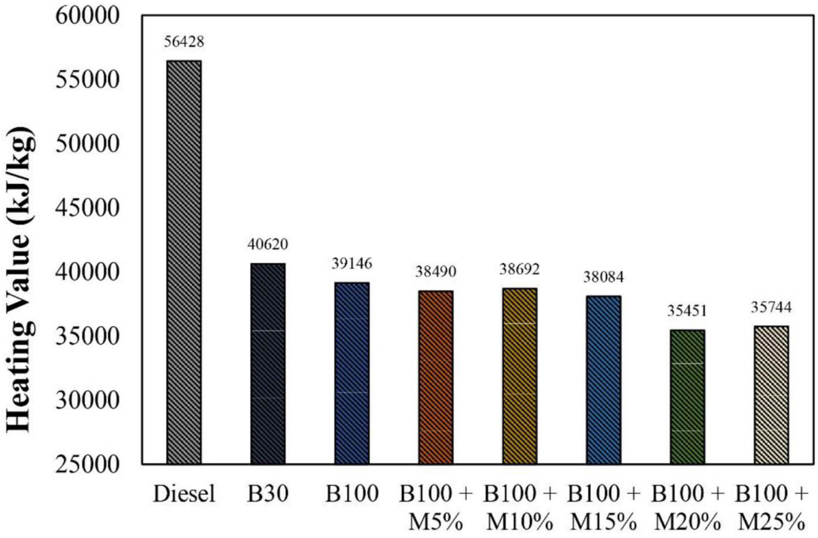


Figure 5. Heating values of Biodiesel with methanol

local temperatures, thereby increasing the rates of thermal decomposition, oxidative reactions, and polymerization of heavy molecules, ultimately leading to the formation of carbonaceous residues. Conversely, the lower calorific value of biodiesel-methanol leads to a decrease in the intensity of thermal reactions in the liquid phase, thereby inhibiting the formation of cracking and coking-based deposits. In other words, the lower calorific value acts as a passive mechanism for deposit control, especially when combined with increased volatility and reduced viscosity.

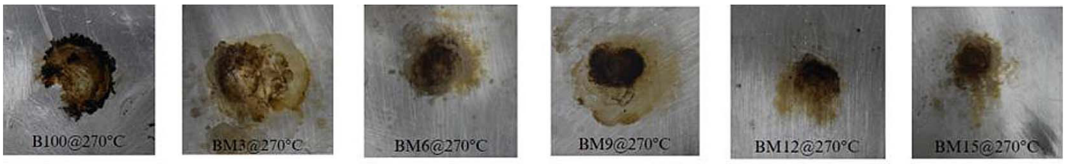
At a methanol concentration of 5–10%, the decrease in relative calorific value is moderately moderate, while the physical properties have significantly improved. This indicates a compromise zone (trade-off) between reducing the fuel's specific energy and improving evaporation quality and mitigating deposits. At higher methanol concentrations above 15%, the decrease in calorific value becomes more significant, potentially reducing engine power and increasing fuel consumption. However, from a deposit formation perspective, these conditions are actually becoming more favorable. These findings confirm that the optimization of biodiesel–methanol formulations must consider the balance between energy performance and the cleanliness of the injection system.

The decrease in calorific value works synergistically with the decrease in density and viscosity to suppress deposit formation. Lower density and viscosity accelerate droplet evaporation, while a lower calorific value reduces the tendency for advanced thermal reactions during the liquid phase. This combination results in a thermophysical environment that is not conducive to the formation of a liquid film precursor and carbon residue. This integrative approach is one of the main contributions of the research, as it shows that deposit formation can be controlled by engineering the thermophysical properties of the fuel, rather than solely thru antioxidant additives or modifications to the injection system.

HSDT deposits

Figure 6 shows the photograph of deposit formation in the hot plate surface with temperature of 130 °C for different methanol content in biodiesel. The amount of deposit produced by mixing methanol and palm oil biodiesel is represented by the black region on the hot plate in the photograph. The results of the study indicate that when methanol is added to biodiesel, the amount of deposit tends to decrease. This indicates that the production of palm oil biodiesel deposits can be inhibited by adding an additive of methanol. The graphic below provides greater detail on results of deposit for different temperature and methanol content by using the HSDT method.

The results of the Hot Surface Deposit Test (HSDT) in Figure 7 indicates that the formation of palm oil biodiesel deposits is highly influenced by the simultaneous interaction between the methanol content in the fuel and the surface temperature. The deposit area decreased significantly with increasing methanol fraction across the entire temperature range tested between 230 and 290



(1) (2) (3) (4) (5) (6)

Figure 6. Visualization of deposit in the hot plate surface

°C, indicating that methanol plays an active role in controlling the fundamental mechanisms of deposit formation, rather than simply acting as a fuel diluent. Under methanol-free conditions, the maximum deposit forms at the lowest surface temperature of 230 °C, reflecting the dominance of the liquid film formation surface wetting regime. Conversely, adding methanol up to 15% can drastically reduce the deposit area to below 5 cm^2, even at relatively low temperatures, indicating a fundamental shift in droplet–surface dynamics.

Independent surface temperature increases also contribute to deposit reduction, but the mechanisms involved are physically different. At low temperatures, the evaporation rate of biodiesel droplets is not fast enough to prevent the formation of a stable liquid layer on the hot surface. This liquid layer acts as a liquid film precursor, which subsequently undergoes oxidation and thermal polymerization, resulting in carbonaceous residue that accumulates as a deposit. As the surface temperature increases, the droplet heating conditions approach the maximum evaporation rate point (MEP), resulting in a very short liquid phase residence time and a drastic reduction in the likelihood of liquid film formation. This explains the decreasing trend in deposits as surface temperature increases, even without the addition of additives.

The role of methanol becomes crucial when combined with an increase in surface temperature. Methanol enhances the temperature effect thru several synergistic thermophysical mechanisms. First, methanol increases the volatility of the fuel mixture due to its lower boiling point and heat of vaporization compared to FAME, thus promoting initial droplet evaporation before biodiesel reaches its thermal decomposition temperature. Second, the reduction in viscosity and density caused by the addition of methanol improves atomization characteristics and lowers the momentum of droplet impingement against the hot surface, directly reducing the tendency for surface wetting. Third, the shift in molecular composition toward the dominance of unsaturated FAME reduces the thermal stability of the liquid phase and accelerates the droplet transition from liquid to vapor phase. The combination of these three mechanisms effectively shifts the deposition regime from a liquid-film-dominated regime toward an evaporation dominated regime.

In addition to macroscopic thermophysical effects, the evaporation of biodiesel–methanol droplets is also governed by internal mass transfer. Due to its higher volatility, methanol preferentially evaporates from the droplet surface; however, its continuous supply is limited by diffusion from the droplet interior. This results in a transient concentration gradient, where the outer layer becomes methanol-depleted while the core remains relatively rich. Consequently, the evaporation process shifts toward a diffusion-limited regime, where internal transport resistance controls the effective release rate of methanol. This gradual release sustains enhanced interfacial volatility, shortens liquid residence time, and delays the exposure of less volatile FAME components, thereby suppressing liquid film formation and subsequent deposit generation.

In internal diffusion, the significant difference in boiling points between methanol and FAME can induce internal bubbling within the droplet during heating. As methanol vaporizes at a much lower temperature, localized vapor pockets may form inside the droplet, leading to bubble growth and occasional micro-disruption of the liquid structure. This bubbling phenomenon can enhance internal mixing and accelerate mass transfer, effectively overcoming diffusion limitations. Furthermore, the mechanical action associated with bubble growth and collapse may contribute to the disruption of the liquid film and the partial detachment of weakly adhered deposits from the surface. This effect provides an additional pathway for deposit reduction, complementing the evaporation-driven mechanism. Therefore, the combined influence of methanol release controlled by diffusion and micro-mixing induced by bubbles plays an important role in

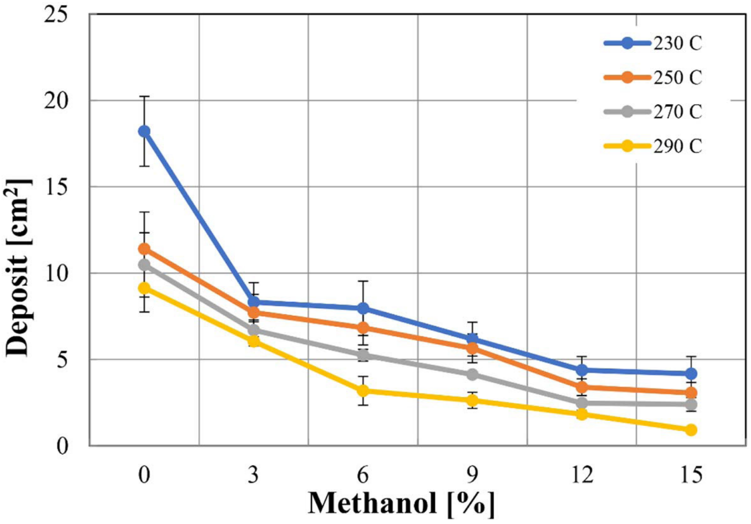


Figure 7. Formation of deposit for different methanol content and heating temperature

governing the overall deposit mitigation behavior of biodiesel–methanol droplets.

The synergistic effect between methanol and surface temperature is evident from the nonlinear response of the deposit area to variations in both parameters. At low temperatures, the effect of methanol on deposit reduction is still relatively gradual. However, at medium to high temperatures between 270–290 °C, even small additions of methanol are able to significantly reduce the deposit area. This phenomenon indicates that methanol acts as an evaporation catalyst, an additive whose effectiveness increases as the system's thermal conditions approach the maximum evaporation regime. This finding has important implications because it shows that deposit mitigation does not necessarily have to be achieved thru increased extreme temperatures, but can be engineered more efficiently thru fuel formulation.

Integrated analysis of HSDT results, physical characteristics, and fuel thermal properties revealed that deposit formation is the result of the convergence of three main factors: the dominance of unsaturated FAME at the molecular level, decreased density and viscosity at the meso level, and high volatility and lower calorific value at the thermal level. These three factors simultaneously shorten the residence time of the liquid droplet phase and suppress the reaction pathway for carbon residue formation. Thus, HSDT not only serves as a phenomenological testing tool but also as direct experimental validation of the evaporation kinetics-based deposit control mechanism.

Unlike most previous studies that focused on the oxidative stability of fuel or the macroscopic performance of the engine, this research demonstrates that the formation of biodiesel deposits can be controlled thru engineering the kinetics of droplet evaporation. The HSDT technique allows for the isolation of evaporation and surface wetting mechanisms without the bias of the combustion process, thus providing a deeper fundamental understanding. Thus, this study offers a new paradigm in biodiesel deposit mitigation, namely shifting the deposit formation pathway from thermal reaction dominance toward rapid evaporation thru the selection and optimization of appropriate alcohol additives.

Despite providing valuable insight into droplet evaporation and deposit formation mechanisms, the HSDT has inherent limitations compared to real engine conditions. In diesel engines, droplets experience high pressure, turbulent gas flow, and strong convective heat and mass transfer, whereas the present HSDT operates under atmospheric pressure in a quiescent environment, neglecting these effects. Additionally, nucleation and bubble dynamics in real systems are influenced by injector geometry and surface characteristics, while this study employs a simplified flat surface. Consequently, the observed evaporation behavior and deposit formation may not fully represent actual engine conditions. Nevertheless, HSDT effectively isolates evaporation-controlled mechanisms, and the results should be interpreted as mechanistic insights rather than direct quantitative predictions for engine applications.

CONCLUSIONS

This study systematically evaluated the effect of methanol addition on deposit formation behavior of palm oil biodiesel using a HSDT by integrating molecular composition, thermophysical properties, and evaporation-driven mechanisms. Based on the experimental results, the following conclusions can be drawn:

1. The addition of methanol induces a clear shift in FAME composition from saturated to unsaturated methyl esters, as evidenced by the reduction of methyl palmitate from approximately 51% to about 38% and the corresponding increase in methyl oleate to nearly 49% at higher methanol fractions. This molecular-level modification directly reduces the intrinsic tendency of biodiesel to form thermally stable carbonaceous deposits.
2. Biodiesel density and kinematic viscosity decrease significantly with increasing methanol content. Compared to neat biodiesel, density is reduced by approximately 2–3%, while viscosity decreases by more than 30% at the highest methanol fraction. These changes substantially improve atomization quality and accelerate droplet evaporation, thereby shortening the liquid-phase residence time on hot surfaces.
3. The calorific value of the biodiesel methanol blends decreases progressively with methanol addition, with a reduction of approximately 9–10% relative to neat biodiesel. This reduction suppresses thermal cracking, oxidation, and polymerization pathways that contribute to carbon residue formation during droplet–surface interaction.
4. HSDT results confirm that deposit area decreases drastically with increasing methanol content and surface temperature. At 230 °C, the deposit area decreases from about 18 cm^2 for neat biodiesel to below 5 cm^2 with 15% methanol addition, while at 290 °C the deposit area is reduced to approximately 1 cm^2. These results demonstrate a transition in the deposit formation regime from liquid-film-dominated to evaporation-dominated behavior.
5. The combined results indicate that methanol addition in a moderate range, approximately 10–15% provides an effective formulation strategy for low deposit biodiesel fuels, achieving significant deposit suppression without requiring substantial modifications to existing diesel engine system.

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