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Stability Assessment of Ethanol Added Algae-Biodiesel Blend for Naturally Aspirated CI Engines

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Abstract

This article investigates the preparation and stability of advanced biodiesel blends, specifically BD15E15 (70 % diesel, 15 % algae biodiesel, 15 % ethanol), aiming to optimise their properties for Compression Ignition (CI) engine applications. The research examines the synergistic effects of mechanical stirring and ultra-sonication on blend stability, focusing on the influence of emulsifier type (SPAN 80 and TWEEN 80), emulsifier concentration (0.5 % and 1 % v/v), stirring time (60, 120, and 180 minutes), and ultra-sonication duration (15 and 30 minutes). Twelve different blends were formulated and subjected to a seven-day stability assessment, primarily through visual observation of phase separation. The experimental results revealed that TWEEN 80, particularly at a concentration of 0.5 % v/v, significantly outperformed SPAN 80 in maintaining blend homogeneity. The most stable blend, achieved with TWEEN 80, was prepared using 120 minutes of mechanical stirring at 2000 RPM (Sample S8). Subsequent ultrasonication of this optimised blend further enhanced its stability. Notably, a 15-minute ultrasonication treatment yielded a more uniform mixture by improving the dispersion of biodiesel, ethanol, and diesel components, attributed to the cavitation effect. However, extending the ultrasonication duration to 30 minutes resulted in excessive heat generation, leading to increased ethanol evaporation and subsequent phase separation, thereby compromising blend stability. This study underscores the critical role of precise control over emulsifier selection, stirring parameters, and ultrasonication time in achieving stable biodiesel-ethanol-diesel blends.

Major Findings: *TWEEN 80 at 0.5 % v/v provided superior blend stability, with the optimal formulation (Sample S8) achieved using 120 minutes of mechanical stirring at 2000 RPM. Ultrasonication for 15 minutes further improved dispersion, but 30 minutes caused excessive heat, leading to ethanol evaporation and phase separation.*

Keywords: *Algae Biodiesel, Blend, Emulsifier, Phase Separation, Stability*

1.0 Introduction

Biodiesel, recognised as a renewable and sustainable substitute for conventional diesel, has gained considerable attention due to its potential to mitigate greenhouse gas emissions and reduce dependency on fossil fuels[1–7]. Synthesised through the transesterification of vegetable oils, animal fats, or waste cooking oils, biodiesel can be blended with diesel in varying proportions, commonly denoted as BXX, where XX represents the percentage of biodiesel in the mixture[8]. Biodiesel exhibits certain limitations, including higher viscosity, oxidative instability, and cold flow issues, demanding the development of optimised biodiesel-diesel-ethanol blends to improve fuel properties and combustion efficiency[9]. These biodiesel-diesel blends have been extensively investigated for their influence on engine performance, combustion characteristics, and emissions[10,11]. The formulation of

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biodiesel blends entails the precise mixing of biodiesel with diesel fuel, which subsequently alters the physicochemical properties of the resultant fuel, including viscosity, density, cetane number, and calorific value[12–14]. These modifications directly impact combustion efficiency, engine performance, and emissions. The incorporation of oxygenated compounds, such as ethanol, has been demonstrated to enhance combustion efficiency and lower particulate matter emissions[15,16]. However, concerns related to fuel stability, increased NOx emissions, and the optimisation of blend compositions remain key research challenges[17,18].

The combustion characteristics of biodiesel blends are primarily dictated by parameters such as injection timing, fuel composition, and the presence of oxygenated additives[10,11,19]. Empirical studies indicate that biodiesel blends generally exhibit higher heat release rates and shorter ignition delays than conventional diesel, contributing to enhanced thermal efficiency and a reduction in Carbon Monoxide (CO) and unburned Hydrocarbon (HC) emissions[12,16]. Nevertheless, the elevated nitrogen oxide (NOx) emissions associated with biodiesel combustion necessitate further exploration of mitigation strategies, including emulsified fuel formulations and advanced injection techniques[20,21].

Recent advancements in biodiesel blend optimisation have investigated the integration of nanoparticles and emulsification techniques to improve fuel stability and combustion performance. The incorporation of metal oxide nanoparticles, such as titanium dioxide (TiO_2), has been shown to enhance the thermal conductivity and catalytic properties of biodiesel blends, thereby improving combustion stability and reducing emissions[22–24]. Similarly, water-in-biodiesel emulsions stabilised through ultrasonic homogenization have demonstrated potential in mitigating NOx emissions and enhancing fuel economy[25]. Despite the environmental and performance-related advantages associated with biodiesel blends, challenges about fuel stability, NOx emissions, and blend optimisation persist. Addressing these limitations necessitates continued research into novel fuel formulations, additive incorporation, and combustion enhancement techniques[26,27]. This study aims to contribute to the existing body of knowledge by examining the preparation and stability of advanced biodiesel blends and their implications for combustion characteristics, engine performance, and emissions. A particular focus is placed on the role of innovative additives and emulsification techniques in optimising fuel properties and mitigating adverse effects.

2.0 Literature Review

In response to the need for eco-friendly energy solutions, enhancing the stability of biodiesel fuel blends has emerged as an important area of research. Biodiesel adoption comes with benefits such as a decreased greenhouse gas emission rate and increased lubricity, but biodiesel's higher viscosity and higher tendency to oxidise make it challenging to produce stable blends with diesel and other components. Researchers have used various techniques like emulsifiers and surfactants as binding elements, mechanical stirring and ultra-sonication as process elements, etc., to better stabilise the blended mixture. This paper attempts to study and address the problem of blend stability sustainability by focusing more on the nature of the additives, the blending techniques, and their impact. One of the earliest studies in this area was conducted by Lin *et al.*, who investigated the combustion characteristics of diesel fuel containing oxygenated additives. Their work laid the foundation for understanding how blending oxygenated compounds with diesel can improve combustion efficiency and reduce emissions. They emphasised the importance of precise blending ratios to achieve optimal performance, as excessive oxygenates could lead to phase separation or reduced energy density[28]. A significant advancement in fuel blend preparation came with the study by Xiong *et al.*, who examined the microstructure and combustion-explosion properties of micro-emulsified diesel with different surfactants. Their research demonstrated that micro-emulsification techniques could produce stable fuel blends with improved atomization and combustion properties. They tested various cosurfactants, such as oleic acid, and found that the choice of cosurfactant significantly influenced the stability and droplet size distribution of the emulsion. Smaller droplet sizes were associated with better combustion efficiency and lower emissions[29]. Yusop *et al.*, further explored the preparation of blended palm biodiesel-diesel fuel. They studied the physicochemical properties of these blends and their effects on engine performance and emissions. Their

findings indicated that careful blending of biodiesel with diesel could enhance fuel properties, such as viscosity and cetane number, while maintaining stability. They also noted that higher biodiesel concentrations (above 20%) could lead to increased viscosity and potential stability issues, such as sedimentation over time[30]. Redel-Macías *et al*., investigated ternary blends of diesel fuel oxygenated with ethanol and castor oil. They emphasised the importance of precise blending ratios to achieve stable mixtures. Their study revealed that ternary blends could improve combustion efficiency and reduce emissions, but the stability of these blends depended on the ethanol content and blending technique. They found that ethanol concentrations above 10% could lead to phase separation, especially at lower temperatures. To address this, they recommended the use of stabilisers or co-solvents to maintain blend homogeneity[31]. Kumar *et al*., conducted a detailed study on the solubility and physicochemical properties of biodiesel-ethanol-diesel blends. They found that the stability of these blends was highly dependent on the ethanol concentration and the blending method. Their research provided valuable insights into optimising blend formulations to prevent phase separation and ensure consistent fuel performance. They tested various blending techniques, including mechanical stirring and ultrasonic homogenization, and found that ultrasonic homogenization produced more stable blends with smaller droplet sizes. They also highlighted the importance of temperature control during blending, as higher temperatures could accelerate phase separation[32]. Mondal and Mandal compared the stability of water-emulsified diesel prepared by mechanical homogenization and ultrasonic dispersion methods. They found that ultrasonic dispersion produced more stable emulsions, with smaller droplet sizes and better long-term stability. Their study highlighted the importance of the preparation method in achieving stable fuel mixtures. They also noted that the addition of surfactants, such as Span 80, could further enhance stability by reducing interfacial tension between water and diesel[33]. Abdul Karim *et al*., explored the characteristics of water-in-biodiesel emulsions produced using an ultrasonic homogeniser. They emphasised the role of ultrasonic energy in creating stable emulsions with uniform droplet distribution. Their findings demonstrated that ultrasonic homogenization could significantly improve the stability of water-in-biodiesel emulsions, making them suitable for use in diesel engines. They also investigated the effect of water content on emulsion stability and found that water concentrations between 5% and 10% provided the best balance between stability and combustion performance. Higher water content led to increased viscosity and reduced stability over time[25]. Zare *et al*., investigated the impact of copper oxide nanoparticles on the stability and performance of biodiesel blends. They found that nanoparticle additives could enhance the stability of biodiesel blends by preventing agglomeration and sedimentation. Their research suggested that nanoparticle additives could be a viable solution for improving the stability of alternative fuel blends. They tested various nanoparticle concentrations and found that 50 ppm of copper oxide nanoparticles provided the best stability and combustion performance. They also noted that nanoparticles could act as catalysts, improving combustion efficiency and reducing emissions[34].

Suhel *et al*., studied the stability of waste plastic oil blends with ZnO nanoparticles. They found that the addition of nanoparticles improved the stability of the blends by reducing oxidation and sedimentation. Their study highlighted the potential of nanoparticle additives to enhance the stability of alternative fuels. They tested various nanoparticle concentrations and found that 100 ppm of ZnO nanoparticles provided the best stability and combustion performance. They also noted that nanoparticles could improve the thermal stability of the blends, reducing the risk of degradation at high temperatures[35]. Bello *et al.,* investigated the oxidative stability of biodiesel using fruit peel waste extracts. They compared predictive modelling via RSM and ANN techniques to optimise the stability of biodiesel blends. Their findings demonstrated that waste-derived additives could significantly improve the oxidative stability of biodiesel, offering a sustainable and cost-effective solution. They tested various fruit peel extracts, such as orange and banana peels, and found that orange peel extract provided the best stability due to its high antioxidant content. They also noted that the addition of 1% orange peel extract could increase the induction period of biodiesel by up to 50%, significantly improving its oxidative stability[36]. Recent research has focused on advanced techniques to enhance the stability of fuel mixtures. Patil *et al*., used a hybrid Taguchi-TOPSIS technique to optimise multi-

additive fuel blends for stability and performance. Their study demonstrated that advanced optimisation methods could achieve superior stability and performance in fuel blends. They tested various additives, including antioxidants, surfactants, and nanoparticles, and found that a combination of 0.5% antioxidant, 1% surfactant, and 50 ppm nanoparticles provided the best stability and combustion performance. They also noted that the hybrid optimisation technique could significantly reduce the time and cost of blend formulation[37]. Deka *et al.*, explored the stability of novel methanol/diesel blends. They used predictive modeling to optimise blend formulations and enhance stability. Their research highlighted the potential of methanol blends as stable and sustainable fuel alternatives. They tested various methanol concentrations and found that blends with up to 15% methanol provided the best stability and performance. They also noted that the addition of cosolvents, such as isopropanol, could further enhance stability by preventing phase separation[38].

Chandran *et al.*, investigated the stability of water-in-biodiesel-diesel emulsion fuel stabilised with *Polyglycerol polyricinoleate* emulsifier. They found that the emulsifier could significantly improve the stability of the emulsion, preventing phase separation and sedimentation. Their study provided valuable insights into the use of emulsifiers for enhancing fuel stability. They tested various emulsifier concentrations and found that 2% *Polyglycerol polyricinoleate* provided the best stability and combustion performance. They also noted that the emulsifier could reduce the interfacial tension between water and biodiesel, improving the uniformity of the emulsion[39]. Vellaiyan studied the stability of alcohol-blended water emulsified cottonseed oil biodiesel. Their research demonstrated that careful formulation and blending techniques could achieve stable emulsions with improved performance and emissions characteristics. They tested various alcohol concentrations and found that blends with up to 10% alcohol provided the best stability and performance. They also noted that the addition of surfactants, such as Tween 80, could further enhance stability by reducing interfacial tension[4].

While the focus of this review is on blend preparation and stability, it is important to acknowledge the broader implications of stable fuel blends on engine performance and emissions. Zheng *et al.*, investigated the performance and emission characteristics of diesel engines fueled with ethanol-biodiesel-diesel blends. They found that stable blends with up to 10 % ethanol reduced NOx and PM emissions but increased fuel consumption due to ethanol›s lower energy content. This highlights the trade-offs between blend stability, engine performance, and emissions[15]. Noor *et al.*, reviewed the use of biodiesel, emulsified biodiesel, and bioethanol as fuels in diesel engines, emphasising the importance of blend stability in achieving consistent performance and emissions reduction. They noted that unstable blends could lead to inconsistent combustion, increased emissions, and engine damage over time[17]. Kumari *et al.*, evaluated the performance and emission characteristics of diesel engines fueled by biodiesel and hydrogenated biodiesel with varying injection timing. They found that stable blends with optimised injection timing could significantly reduce NOx and PM emissions while maintaining engine performance. This underscores the importance of combining blend stability with engine optimisation techniques[20].

3.0 Materials and Methods

3.1 Materials

Diesel fuel available commercially at the nearby marketplace was selected for this testing. The reason for selecting commercially available diesel fuel is to maintain the uniformity of physico-chemical properties throughout the whole research work. Ethanol with 99 % purity was used as an additive at 15 % of v/v for the preparation of the sample of blends. Algae oil obtained commercially was used to produce biodiesel in the quantity of 15 % v/v. throughout this test blend was designated by BD15E15 (standard diesel 70 % v/v + 15 % v/v Algae + 15 % v/v ethanol). A 15 % v/v quantity of algae oil and ethanol was selected, considering the maximum quantity of blending for final experimentation on a single-cylinder four-stroke CI engine for optimisation. Properties for Algae biodiesel and blend were measured as per the ASTM standard for testing and are given in Table 1.

The solubility of ethanol in biodiesel is a key challenge as the polarity of both materials is different. Ethanol is polar, while Biodiesel is non-polar. Two emulsifiers,

Table 1. Properties of biodiesel blend[6]

Properties	Method	Diesel	BD15	BD15E15
Total acid number (mg KOH/g)	ASTM D664	0.1	0.2	0.25
Density (kg/m^3)	ASTM D287	836	856	848
LCV (Lower Calorific Value) (MJ/kg)	ASTM D4809	43500	42316	41800
Flash point (°C)	ASTM D9358T	56	62	58
Fire point (°C)	ASTM D9358T	62	74	70
Dynamic viscosity (mm^2/s)	ASTM D445	2.57	3.5	2.87
Cetane number	ASTM D603	47	52	54

SPAN 80 ($C_{24}H_{44}O_6$) and Tween 80 were identified to achieve a stable, homogeneous mixture[40]. SPAN 80 is a *Sorbitan monooleate* emulsifier whose HLB(Hydrophilic-Lipophilic Balance) number is 4.7, while TWEEN 80 is a *Polyoxyethylene Sorbitan Monooleate* whose HLB number is 15. The HLB number, which ranges between 0 to 20, indicates the balance between the hydrophilic (water-loving) (HLB number 0 -10) and lipophilic (oil-loving) (HLB number 10-20) properties of an emulsifier. The physico-chemical properties obtained from the chemical manufacturer are listed in Table 2 below.

Table 2. Physio-chemical properties of emulsifier[40]

Properties	SPAN 80	Tween 80
Physical state at 20 °C	Liquid	Liquid
Flash point (°C)	>149	>113
Density (g/cm3)	1	1.07
Acid value	3.36	0.28
Saponification value	150.47	53.26

Remi's hot plate magnetic stirrer was used as a mechanical device to provide the kinetic energy to the mixture to create a homogeneous mixture. The Remi 2mlh model, based on PMDC (Permanent Magnet DC) technology, was used for this experimentation, which has a 5-litre maximum stirring capacity and 2000 RPM maximum stirring speed as shown in Figure 1.

A digital ultrasonic bath was used to check the effect of ultrasonication on the stability of the mixture, which produced the ultrasonic waves at a fixed frequency of 40 kHz.



Figure 1. The hot plate magnetic stirrer[8].



Figure 2. The digital ultrasonic bath[8].

3.2 Method

The whole experiment was conducted on BD15E15 (standard diesel 70 % v/v + 15 % v/v Algae + 15 % v/v ethanol at normal room temperature and 1 bar atmospheric pressure. The fuel blend was selected considering the design of the experiment selected for optimisation of the CI engine performance parameter[40]. To prepare this blend, the emulsifier quantity in % v/v, stirrer speed in RPM, stirrer time in minutes, and ultrasonication time in minutes were selected to check their effect on the stability of the blend. The whole experiment was conducted in two phases. At first, the effect of the magnetic stirrer was evaluated, and in the second phase, the combined effect of the stirrer and ultrasonication was checked with the best stable mixture achieved with the magnetic stirrer.

3.2.1 Preparation of the Sample for Stability

A total of 12 samples coded like S1, S2, S3….S12 were prepared to check the stability of the mixture using a magnetic stirrer and considering the various parameters as discussed earlier. Checking the effect of both emulsifier-SPAN 80 and TWEEN 80 in the amounts of 0.5 ml and 1 ml was considered for the total sample volume of 100 ml. Maximum 2000 RPM was considered for the magnetic stirrer, and 30 min., 60 min, and 90 min durations were selected for stirring the fuel blend. During this, the surface temperature was measured by a

Table 3. Details of samples[40]

Emulsifier(E)	Samples	Proportion (% v/v)	Speed (RPM)	time (minutes)
SPAN 80	S1	0.5	2000	60
	S2	0.5	2000	120
	S3	0.5	2000	180
	S4	1	2000	60
	S5	1	2000	120
	S6	1	2000	180
TWEEN 80	S7	0.5	2000	60
	S8	0.5	2000	120
	S9	0.5	2000	180
	S10	1	2000	60
	S11	1	2000	120
	S12	1	2000	180

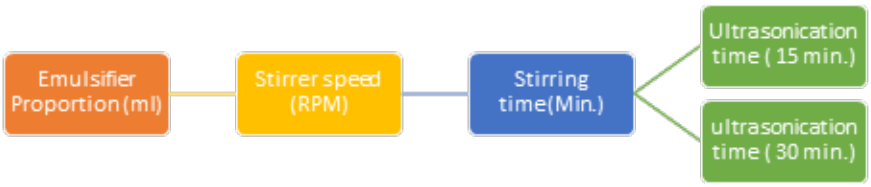


Figure 3. Combined effect of mechanical stirring and ultrasonication[41].

digital thermometer to regulate it. The experiments were conducted by varying the parameters like the proportion of emulsifier and stirring time, respectively, as mentioned in Table 3.

The best stable fuel blend with the above parameters will then be utilised to check the effect of ultrasonication as mentioned below. Ultrasonication time duration was selected as 15 minutes and 30 minutes to avoid the evaporation of the ethanol at high temperature[40]. As the ultrasonication time increases, it causes the temperature of the water used in the bath, and hence the temperature rise of the fuel blend.

In both cases, the photographic observation method for visual physical inspection was adapted for phase separation only. The first observation for each blend was taken after 2 minutes of every sample preparation. Then, observations were taken at every 1-hour interval for the first day of the respective sample preparation. For the next six days, observations were collected every 24 hours for every sample, considering the total seven days of the observation cycle.

4.0 Results and Analysis

4.1 Fuel Blends: Stability Analysis

Visual examination for phase separation over a seven-day observation period allowed one to evaluate the stability of the fuel blends. First phase assessed emulsifier type, emulsifier concentration, stirring speed, and stirring time; second phase examined the combined effect of stirring and ultrasonic waves.

4.2 Emulsifiers and Stirring Times Effects

Twelve samples in all (S1–S12) were made with varying SPAN 80 and TWEEN 80 concentrations as emulsifiers. The ready mixes were magnetically stirred at 2000 RPM for different lengths (60, 120, and 180 minutes). Results show that the samples using SPAN 80 Blends (S1–S6 showed modest stability with phase separation seen at decreased stirring times. While it did not fully stop phase separation, increasing the emulsifier content from 0.5 % to 1 % improved homogeneity. Stirring time affected dispersion; samples with longer stirring times showed improved dispersion but were still prone to ultimate phase separation. TWEEN 80 Blends (S7–S12) showed the least phase separation during the first phase of testing, S8 (0.5 % v/v emulsifier, 2000 RPM, 120 min) demonstrating greater stability and least phase separation after seven days of observation. Although additional stirring times did not always result in further improvement, samples containing 1% TWEEN 80 also showed good stability. Low viscosity of TWEEN 80 as compared to SPAN 80 could be one of the reasons for achieving better stability in samples. This suggests that ideal stability is reached at a particular threshold of stirring time and emulsifier concentration.

4.3 The Effect of Combined Effect of Mechanical Stirring and Ultrasonication

The influence of ultrasonic waves was investigated after S8 was chosen as the most stable mix from the magnetic stirrer phase. Two separate ultrasonic durations-15 min and 30 min-were used on the selected blend. 15 Minute Ultrasonic improved the fuel mix's stability without appreciable temperature increase that would cause ethanol evaporation. Over seven days, the mix kept homogeneity for a longer period with little phase separation noted. Better stability resulted from the effective improvement in the dispersion of biodiesel, ethanol, and diesel components made by the cavitation effect from ultrasonic waves. Although at first producing adequate dispersion, prolonged ultrasonic treatment caused too much heat generation, which compromised the mix stability. Possibly increased ethanol evaporation by the higher temperature resulted in earlier phase separation than during the

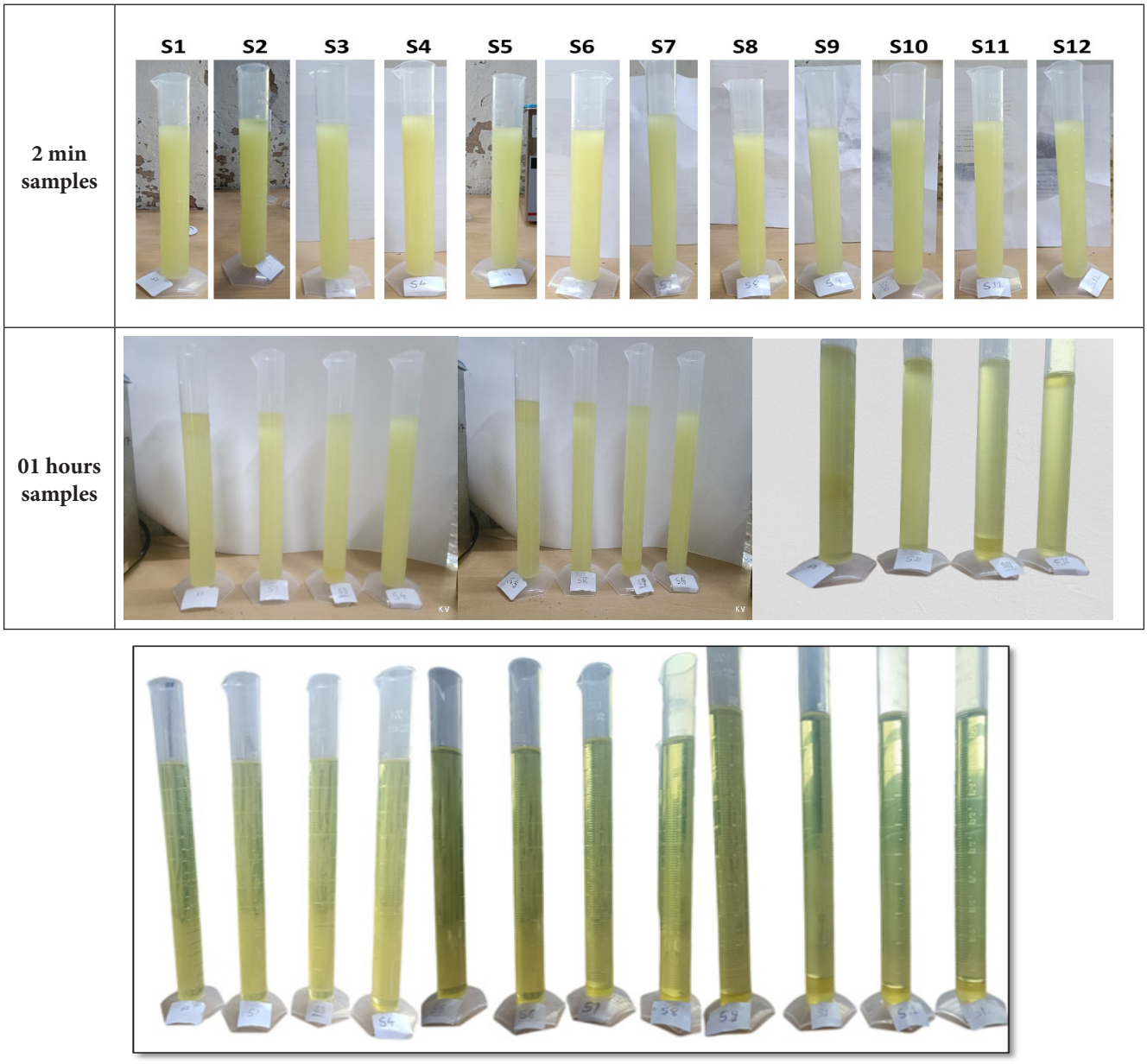


Figure 4. Effect of emulsifier and magnetic stirrer after 07 days.

15-minute treatment. This implies that by raising fuel volatility, extended ultrasonic treatment beyond a certain limit could turn detrimental.

The photographic observation approach allowed one to assess the combined effect of mechanical stirring and ultrasonic waves. Over seven days, the stability of all samples was tracked, with special focus on phase separation. First two minutes: Every sample showed initial dispersion, but there were minor homogeneity fluctuations found. Higher emulsifier concentrations of the samples revealed improved initial mixing. While blends exposed to 30-hour ultrasonics showed evidence of ethanol evaporation-induced separation, S8 (magnetic stirrer only) and S8 with 15-minute ultrasonics demonstrated the best stability for the first three days. Faster destabilisation most certainly resulted from the thermal impacts of continuous ultrasonic waves.

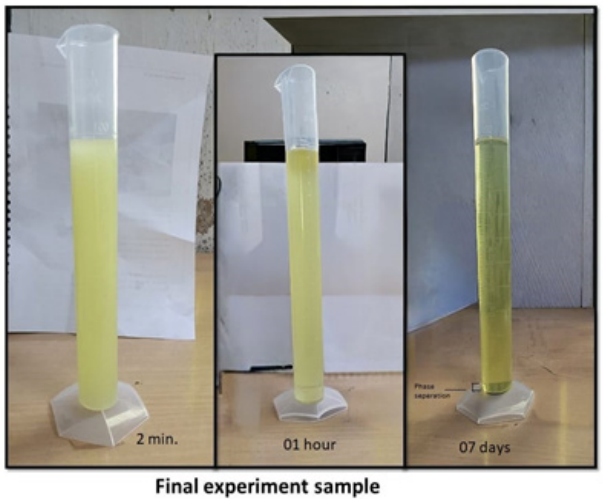


Figure 5. Final sample with 15 minutes of ultrasonication.

5.0 Conclusion

Among the given tested conditions, TWEEN 80 at 0.5 % v/v with 120 minutes of stirring at 2000 RPM (Sample S8) produced the most stable blend. Phase stability was substantially influenced by emulsifier type and concentration; TWEEN 80 exceeded SPAN 80 in both respects. Further improvement in stability came from ultrasonic waves, but too much ultrasonic action (30 minutes) caused ethanol evaporation, therefore compromising blend homogeneity. This emphasises the need to choose the ideal ultrasonic frequency to maximise dispersion and reduce heat impacts. The best condition found to improve the stability of BD15E15 mixes was a 15-minute ultrasonic treatment. Ultrasonic cavitation greatly enhanced molecule interaction inside the blend, therefore producing a more uniform mixture with increased stability. According to the study, mechanical stirring combined with controlled ultrasonic agitation can greatly improve fuel blend stability-a condition vital for useful applications in CI engines. These results imply that a stable algal biodiesel-ethanol blend for CI engine use depends on exact control over emulsifier concentration, stirring settings, and ultrasonic time. Future research should look at other ways to reduce ethanol evaporation during processing and the thermal impacts of ultrasonic waves on long-term stability.

Future research should explore advanced methods for low evaporation of ethanol and assess the long-term thermal stability. Researchers may evaluate the effect of ultrasonic frequency, too.

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