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Effect of Different Preparation Methods on the Stability of Low-Carbon Alcohol Blended Fuels

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Abstract: The n-butanol/low-carbon alcohol/diesel microemulsion system is a good alternative fuel to diesel. In this study, the microemulsions were formulated in four ways: ultrasonication, vortex oscillation, shaker mixing and spontaneous formation. The results reveal that the ultrasonication method is significantly influenced by temperature. Specifically, at 45 °C, the quantity of cosolvent added during the ultrasonic process can be reduced by a maximum of 25% compared to that at 25 °C. However, while the amount of cosolvent required is the lowest at 45 °C, the stability of the emulsion is the poorest. In all cases of this study, the stability of the microemulsion increases when the volume ratio of the lower carbon alcohol exceeds 60%. The lowest amount of co-solvent and high stability were achieved using the shaker mixing method at both 25 °C and 35 °C. Although the quantity of cosolvent required at 45 °C is second only to the lowest, its stability surpasses that of the ultrasonication method. Therefore, it is more effective to choose the shaker mixing method that provides uniform and ordered forces for the preparation of microemulsion liquids.

Keywords: low-carbon alcohol; diesel; microemulsions; fuel preparation

1. Introduction

As the population increases and society develops, people need more and more energy to meet their needs. Fossil fuels are the main source of energy, yet they are non-renewable, cannot always meet human needs and are being consumed in large quantities. According to the International Energy Agency (IEA), world energy demand will increase by 50% in the year 2030 [1]. It is therefore necessary to find an alternative to this depleting fossil resource. Diesel is one of the main sources of energy used for rapid industrialization. Diesel engines are used in the agricultural, transport and power plant sectors. Emissions from diesel engines, such as carbon monoxide, unburned hydrocarbons and particulate matter, have a very bad impact on human health and the environment [2], as well as emitting large amounts of greenhouse gases. Developed countries have already achieved their greenhouse gas emission reduction targets, and the rate of reduction will decrease after 2020 [3], a projection that also shows how challenging China’s ‘double carbon’ target will be.

In past decades, many alternative fuels have been proposed, such as methanol, biodiesel, biogas, natural gas, hydrogen, butanol, etc. [4,5]. Among the many alternative fuels, methanol has drawn increasing attention in the research of alternative fuel applications for internal combustion engines due to its abundant resources, appropriate price, easy production and good physical and chemical properties [6]. In addition, methanol has good combustion performance, high thermal efficiency, low specific energy consumption and low particulate matter and nitrogen oxide emissions [7]. The natural energy structure of China consists of more coal and less oil, and methanol as a coal-based fuel is widely
available and inexpensive. Methanol production in 2022 has been close to 10 million t, of which more than 1 million t are used for internal combustion engines [8]. China has the largest methanol production and production capacity [9], and methanol is one of the very promising alternative fuels in China.

Typically, there are two ways to achieve co-combustion of diesel and alcohol in CI engines: by directly injecting a mixture of diesel and alcohol into the cylinder [10–12] or by injecting diesel and alcohol separately through a dual fuel injection system [13,14]. The injection of a mixture of diesel and alcohol is a viable method as there are no modifications to the engine’s fuel system and combustion efficiency can be improved by injecting a diesel/methanol or diesel/ethanol mixture [15]. However, the difference in polarity between methanol and diesel results in methanol being immiscible in diesel and ethanol having low solubility in diesel, so the addition of a surfactant or co-solvent is usually required to prepare stable blends of alcohols and diesel.

Liu et al. [16] investigated the effect of different alcohol additives on the solubility of ethanol in diesel fuel and found that alcohols with higher carbon numbers in the straight chain structure had better co-surfactants and that hydroxyl groups performed better than ketone groups in the preparation of ethanol/diesel blends. Gong’s study examined the impact of higher alcohols with varying carbon numbers and branched chain structures on the stability of methanol/diesel blends. The results revealed that n-butanol proved to be the most effective co-surfactant for the preparation of stable methanol/diesel blends, enabling their long-term storage without the occurrence of phase separation [17]. Cao et al. [18] found that the carbon chain length of n-propanol, n-butanol and n-pentyl alcohol were suitable among the three alcohol co-solvents, and its molecular structure could well meet the solubility characteristics in methanolic diesel. Therefore, the choice of n-butanol as a co-solvent is suitable. Microemulsions are more stable and preparing fuels into microemulsions has a long shelf life [19].

The formation of microemulsions is spontaneous and typically necessitates no external work. However, when employed in industrial settings, the emulsification of oil and water phases often takes considerable time. Therefore, an external force is commonly employed to facilitate the homogenization of the mixture. The application of external force to the microemulsion involves converting electrical energy into various other forms of energy. Whether or not there exists a distinction between these forms of energy and the subsequent variations in the microemulsion they induce, and if such a difference does exist, its significance remains to be determined. Calculating the precise amount of energy injected into the emulsion is not feasible; instead, its analysis must be based on the process and its outcomes, which can only be validated through a series of experimental demonstrations.

Huang et al. [19] employed three methods for preparing diesel microemulsions: magnetic stirring, magnetic stirring combined with ultrasonication, and magnetic stirring with microwave treatment. Furthermore, they thoroughly investigated the impact of various degrees of ultrasonication on the stability of microemulsions. Currently, the study of co-solvents and co-surfactants necessary for methanolic diesel fuel preparation has witnessed certain advancements. Nevertheless, there remains a paucity of systematic research and theoretical analysis pertaining to the stability disparities of microemulsions arising from diverse preparation techniques. Huang et al. [20] concluded that there is a difference in the effect of different treatment levels of ultrasonication on the stability of microemulsions. Zhang et al. [21] compared the contribution of each influencing factor to stability in the process of configuring microemulsions for methanol content, which had the greatest effect, followed by preparation temperature, stirring time and amounts of additives, and stirring speed had the least effect.

There has been some progress in the study of co-solvents and co-surfactants required for the preparation of methanol diesel. Waluyo et al. [22] used ethanol as a methanol/gasoline co-solvent, the interaction forces between methanol/ethanol molecules (hydrogen bonding) make methanol and gasoline miscible and resolve phase separation due to differences in polarity. Stronger hydrogen bonds than water are created between methanol
and ethanol molecules thereby increasing intermolecular forces and reducing interfacial tension. Methanol and diesel have large differences in polarity leading to immiscibility. The polar and hydrogen bonding forces within methanol molecules exceed those found in diesel. Additionally, n-butanol possesses moderate polar solubility parameters and hydrogen bonding solubility parameters, enabling it to serve as a mediator to a certain extent in bridging the gap between methanol and diesel fuel molecules [23]. Taking into account the disparities in the effect and stability of various mixing methods when adding co-solvents, we can further investigate the underlying principles. If we are able to discern the laws governing the disparities in microemulsions caused by different preparation techniques, these insights can be effectively utilized in industrial applications. This will allow us to choose the most efficient and fuel-saving way, and also achieve the best fuel utilization. In terms of the differences in microemulsion stability brought about by preparation methods, many studies have usually been carried out on ultrasonication [24–26], and systematic research and theoretical analysis of other methods are still lacking.

This study is based on the influence and analysis of the preparation methods on low-carbon alcohol/diesel, mainly on the co-solvent addition and stability. The aim is to select the preparation conditions with the least amount of co-solvent addition and the longest microemulsion stabilization time and to find the laws of macro-phenomena and micro-realities in the process. The experimental ideas and methods used can provide methodological ideas for studies in which energy input is involved in the formulation of low-carbon alcohol fuels.

2. Materials and Methods

2.1. Experimental Methods

The blended fuel used in this study contained the following components: commercially available -20# diesel fuel, n-butanol (analytically pure, from Tianjin Komeo Chemical Reagent Co., Ltd., Tianjin, China), anhydrous methanol (AR-grade, from Tianjin Jiangtian Chemical Technology Co., Ltd., Tianjin, China), and oil red O (95% purity, from Shanghai Marel Biochemical Technology Co., Ltd., Shanghai, China).

-20# diesel fuel has a density of 0.84–0.86 g/mL at 20 °C, a viscosity of 2.5–8 mPa·s, and a closed flash point of 50 °C. Methanol is more polar and diesel fuel is a mixture of non-polar complex hydrocarbons (carbon number between 10 and 22) dominated by cetyl hydrocarbons, diesel fuel and methanol are not normally soluble. In this study, experimental data were obtained by titration, initially configuring a 5 mL system of methanol diesel fuel as in Table 1 and using a 1000 μL pipette to add n-butanol to the layered solution, with 0.1 mL of n-butanol added each time until the layering disappeared after the last 0.1 mL was added and the solution became clear and transparent. In this study, three temperatures were set for control experiments, and a thermostatic water bath with 0.1 °C accuracy was used to preheat the test samples for 5 min, after which the titration experiments were carried out at each of the three temperatures.

After preheating the methanol/diesel solution, four methods were used to mix the solution in this study, including spontaneous formation, vortex oscillation, shaker mixing, and ultrasonication. The spontaneous formation method was conducted in a digital thermostatic water bath specifically for titration experiments. Additionally, the vortex oscillation method involved the use of a VORTEX-GENIE2 (Scientific Industries SI™, Bohemia, NY, USA) adjustable speed vortex mixer operating at a speed of 3200 rpm. Test tubes were placed on this mixer to undergo oscillation. The shaker functioned as a thermostatic incubation shaker, operating at a speed of 300 rpm. Meanwhile, the ultrasonication method used a thermostatic digital ultrasonic cleaner with a frequency of 50 KHz. The volume data obtained for methanol, diesel, and n-butanol was subsequently represented in a ternary diagram. The microemulsion with a methanol/diesel volume ratio of 3:7, prepared through four distinct preparation methods, was chosen for particle size measurement. The Anton Paar Nanoparticle Size & Zeta potential Analyzer instrument was employed for the
measurement, and a particle size graph was subsequently plotted. The measurement principle is Dynamic Light Scattering (DLS), measuring range from 0.3 nm to 10 µm (particle diameter). The accuracy is better than +/-2% on NIST traceable standards, and the repeatability is better than +/-2% on NIST traceable standards. Diesel will be stained red by oil red O. The volume ratio of methanol/diesel 3.7 was still selected, and the stained methanol/diesel emulsion was observed by biomicroscope when the microemulsion was not formed by insufficient addition of n-butanol (0.5, 1, 1.5 mL).

### Table 1. Methanol/diesel raw volume.

<table>
<thead>
<tr>
<th>Methanol volume ratio/vol%</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol volume/mL</td>
<td>0.5</td>
<td>1.0</td>
<td>1.5</td>
<td>2.0</td>
<td>2.5</td>
<td>3.0</td>
<td>3.5</td>
<td>4.0</td>
<td>4.5</td>
</tr>
<tr>
<td>Diesel volume/mL</td>
<td>4.5</td>
<td>4.0</td>
<td>3.5</td>
<td>3.0</td>
<td>2.5</td>
<td>2.0</td>
<td>1.5</td>
<td>1.0</td>
<td>0.5</td>
</tr>
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</table>

#### 2.2. Emulsification Curve Plotting

Microemulsions that have been left for a period of time are found to cluster with droplets becoming turbid and eventually delaminated. In this study, the stability of microemulsions was characterized using the Aging Method, where microemulsions were placed at a constant configured temperature to record the stability time of each group of microemulsions at three temperatures. The stability of the microemulsions was expressed in terms of emulsification efficiency, which was calculated as in Equation (1).

\[
\eta = \frac{t_i}{t_m}
\]  

(1)

where \( \eta \) is the emulsification efficiency (100%), \( t_i \) is the stability time (h) of each sample in each group of microemulsions, \( t_m \) is the stability time (h) of the most stable sample in each group of microemulsions. The magnitude of the emulsification efficiency ranges between 0 and 1, with the closer to 1 the more stable the sample. It should be emphasized that the aim of this study was to investigate the differences in n-butanol co-solvent addition and microemulsion stability due to four different co-solvent methods and temperatures.

### 3. Results and Discussions

#### 3.1. Effect of Different Preparation Methods on Microemulsions

3.1.1. Effect of Different Preparation Methods on the Amount of Co-Solvent Addition

If both surfactant and co-surfactant are added to the oil-water system, the surfactant and co-surfactant (alcohols) are adsorbed at the interface at the same time. This causes the oil-water interfacial tension to decrease dramatically, even to ultra-low interfacial tension \((10^{-2} \text{ mN/m}^{-1})\), forming microemulsions. Some surfactants, such as the ionic surfactant AOT with a double hydrocarbon chain and nonionic surfactants, can generate microemulsions without the aid of a surfactant. This phenomenon is related to the surfactant’s ability to lower the interfacial tension. In addition to ultra-low interfacial tension, there are other factors that influence the spontaneous formation of microemulsions. For example, at low interfacial tension, the interfacial bending instability arising from thermal fluctuations at the interface and the change in the entropy of dispersion of droplets in solution also contributes to the generation of microemulsions.

The four mixing methods used in this paper are as described previously. Under the same methanol addition ratio, the ternary plot of the volume percentage of microemulsion formed by methanol diesel n-butanol is shown in Figure 1, which is the ternary plot at 25 °C, 35 °C and 45 °C, respectively. The upper part of the curve is the zone of mutual solubility, and the lower part of the curve is the zone of two-phase coexistence. Keep adding n-butanol co-solvent to the liquid so that the microemulsion is formed just right, which constitutes the point on the curve. The lower the amount of co-solvent that needs to be added, the better the co-solvency of the preparation method. As shown in Figure 1, the area of the spontaneous intercalation zone was the smallest at 25 °C, 35 °C and 45 °C, i.e.,
this method had the worst solubilizing effect. In the process of microemulsion formation, n-butanol can promote the combination of methanol diesel through the action of dipole or hydrogen bonding. There is a large oil–water interfacial tension between the two phases of diesel and methanol, and a large amount of energy input can increase the chance of contact between the three molecules. The other three modes can provide energy to help the two phases of microemulsion fuse, while spontaneous formation can only rely on molecular diffusion. Therefore, the spontaneous formation method has a poor solubilizing effect for microemulsions.

**Figure 1.** Ternary plot of volume percentage of methanol/diesel/n-butanol microemulsion: (a) 25 °C; (b) 35 °C; (c) 45 °C.

The highest energy density is provided by the ultrasonication method, which relies on the medium molecules to transfer mechanical waves to low-carbon alcohol fuels, producing a series of mechanical, cavitation and thermal effects. In the liquid, under the action of ultrasound vibration, tiny bubble nuclei exist. When the sound pressure reaches a certain threshold, these bubbles expand rapidly. Subsequently, they suddenly close, generating shock waves during the closure. This expansion, closure, and oscillation, along with other kinetic processes, are collectively termed ultrasonic cavitation. Part of the ultrasonic wave’s energy is absorbed by the medium and fuel. We can control this absorption only at a constant temperature. However, the effect of this energy on intensifying molecular movement within the liquid cannot be ignored. Cavitation also increases with
temperature, coupled with increased temperature, faster molecular motion and increased efficiency of intermolecular collisions. The effect of temperature on the ultrasonication method is significant in the promotion of multiple effects. With the increase in temperature, the solubilization effect of the ultrasonication method was significantly improved, and the addition of n-butanol could be reduced by 4–25% for every 10 °C increase. At 45 °C, the mutual solubilization zone of the ultrasonication method was the largest, and the solubilization effect was the best. At 25 °C, the addition of n-butanol in the ultrasonication method exceeded that of the spontaneous formation method in some proportions, i.e., the advantage of the ultrasonic mode in solubilizing effect at low temperatures was not obvious.

Both vortex oscillation and shaker mixing involve stirring through mechanical external forces. Vortex oscillation features an intense upward spiral movement of the liquid, while shaker mixing exhibits a more uniform and orderly motion, simulating a human shaking a test tube. To balance the potential energy of microemulsion formation, which is the interfacial energy driving emulsion delamination, work must be applied to the system. This work accelerates the formation of microemulsions by reducing the interfacial energy barrier [27]. The shaker mixing method is most effective at 25 and 35 °C and is second only to the ultrasonication method at 45 °C. Temperature variations have less effect on the shaker mixing and vortex oscillation methods. The solubilizing effect of the shaker mixing method only shows a small increase in temperature from 35 °C to 45 °C, reducing the addition of n-butanol by up to 3%.

Methanol and n-butanol, as short-chain alkanes, have hydroxyl groups at one end of their molecules. The partial charge of the hydroxyl group can trigger intermolecular interactions—the formation of hydrogen bonds [28], which cause these molecules to be attracted to each other and tightly aligned. Methanol/n-butanol molecular interactions tend to form molecular clusters so that they behave like single substances. These molecular clusters have a large specific surface area, which increases the total surface tension and helps to enhance the interaction between methanol/n-butanol molecular clusters and nonpolar diesel fuel [22,29]. Increased molecular motion at higher temperatures makes it easier to overcome the interfacial tension between droplets and the demand for n-butanol decreases. At the same time, warming causes hydrogen bonds to break very easily, the methanol/n-butanol molecular clusters disappear, and the methanol/diesel interactions weaken, requiring more n-butanol to be added. At elevated temperatures, the superimposed effects of these two actions will combine to affect the formation of microemulsions [30]. Therefore, except for ultrasonic miscibility, the solubilizing effect brought about by temperature increase to the other three modes is not significant.

3.1.2. Effect of Different Preparation Methods on Particle Size

Four kinds of microemulsions with a methanol/diesel volume ratio of 3:7 in Figure 1b were taken, and the particle size of microemulsions was measured every ten minutes, plotting the change curve of the microemulsions’ static particle size in Figure 2. The particle size of microemulsions formulated by spontaneous formation and shaker mixing is basically unchanged with the extension of time, and the stability is strong. Once the external force was withdrawn, the particle size of the microemulsion decreased rapidly, which indicated that the internal state of the microemulsion gradually tended to stabilize from the initial chaos. The average particle size of the ultrasonically treated microemulsions was 56 nm within 10 min after formulation, and then showed a clear trend of particle size reduction, with the average particle size decreasing by 59% to 23 nm from 10 min to 20 min. The average particle size of the microemulsions changed less and stabilized after 20 min. Similarly, the microemulsion treated with vortex oscillation showed the same trend of particle size change, with a 41% reduction in average particle size from 34 nm to 20 nm from 10 min to 20 min. Therefore, it can be found that the average particle size of microemulsions after the completion of formulation in the ultrasonication method is larger than that of vortex oscillation, which is more chaotic and relatively unstable. The difference in
the change in the mean particle size of microemulsions emphasizes that the two treatments, ultrasonication and vortex oscillation, are very different from shaker mixing and spontaneous processes in terms of the mechanism of action on microemulsions. Compared to the shaker mixing and spontaneous formation processes, ultrasonication and vortex oscillation acted more aggressively on the microemulsions, leaving the microemulsions in a chaotic and unstable state. The average particle size of the microemulsions formulated by the four methods remained basically stable after 50 min.

Figure 2. Microemulsion static particle size change curve.

To gain a deeper understanding of the microemulsion formation process and particle size variations across four formulations, emulsions with varying n-butanol concentrations were observed under a biomicroscope. Specifically, methanol and diesel volumes of 1.5 mL and 3.5 mL, respectively, were used for these observations, as depicted in Figure 3. The n-butanol additions of (a) (d) (g) (j) in Figure 3 are 0.5 mL, (b) (e) (h) (k) have n-butanol additions of 1 mL, (c) (f) (i) (l) the amount of n-butanol added is 1.5 mL. Microemulsions can be divided into single-phase microemulsions and multi-phase microemulsions. There are three main types of single-phase microemulsions: W/O, bicontinuous and O/W, and W/O microemulsions consist of three phases: oil-continuous, water-core and interfacial film. The water core comprises a certain amount of co-surfactant, while the oil continuous phase also contains co-surfactant along with a minor quantity of water. The interfacial membrane is composed primarily of surfactant and co-surfactant, and it is noteworthy that the surfactant in this system is exclusively located on the interfacial membrane. O/W microemulsions are comprised of a water continuous phase, an oil core, and an interfacial membrane. Notably, the polar groups of both surfactant and co-surfactant are oriented towards the water continuous phase on the interfacial membrane. In the bicontinuous structure, oil and water become continuous phases at the same time. In the system, any portion of the oil that forms oil droplets encircled by the water continuous phase also contributes to the formation of an oil continuous phase. This oil continuous phase is composed of other parts of the oil droplets, which in turn enclose the water situated between the oil droplets. Concurrently, the aqueous droplets within the system coalesce to create a water-continuous phase. This phase encircles the oil phase situated between the droplets, thereby establishing an intricate oil–water bicontinuous structure.

In this situation, the emulsions formed are all W/O type. Figure 3a–c illustrates the spontaneous emulsion formation process. In this case, methanol and diesel exhibit a distinct phase interface when using a dosage of 1 mL of n-butanol. Without external assistance, methanol dissolves into the diesel fuel. Subsequently, methanol molecules at the
interface tend to aggregate due to interfacial tension, resulting in the formation of larger alcohol molecules. As the quantity of n-butanol increases, the oil-water distribution becomes slightly more uniform. However, numerous n-butanol droplets remain unenclosed by diesel, explaining the need for additional n-butanol to facilitate spontaneous solubilization. Figure 3d–f demonstrates the emulsion formation using the shaker mixing approach. The resulting emulsion closely resembles that formed through spontaneous methods. The external force generated by the shaker mixing effectively disperses numerous small droplets of methanol or diesel around the oil-water interfacial film. Consequently, the integration of oil and water is more effective in (f) compared to (c), resulting in a more uniform emulsion.

Figure 3. Micrographs of microemulsions with different n-butanol additions: spontaneous, (a): add 0.5 mL n-butanol, (b): add 1.0 mL n-butanol, (c): add 1.5 mL n-butanol; shaker mixing method, (d): add 0.5 mL n-butanol, (e): add 1.0 mL n-butanol, (f): add 1.5 mL n-butanol; ultrasonication, (g): add 0.5 mL n-butanol, (h): add 1.0 mL n-butanol, (i): add 1.5 mL n-butanol; vortex oscillation, (j): add 0.5 mL n-butanol, (k): add 1.0 mL n-butanol, (l): add 1.5 mL n-butanol.
Figures 3g–l present emulsions formulated through ultrasonication and vortex oscillation, respectively. When 0.5 mL of n-butanol is added, a key distinction between spontaneous formation and shaker mixing is the application of external forces with significantly higher energies. These forces enable numerous methanol droplets to overcome interfacial tension and penetrate into the diesel fuel, ultimately becoming encapsulated. Figure 3h shows that methanol under ultrasonication is dispersed into droplets of uneven sizes as it undergoes collision with diesel, and this dispersion becomes more homogeneous the more n-butanol is added. Compared with the other three methods, it is evident that the energy of ultrasonication can penetrate deeply into the liquid and be effectively transmitted through intermolecular transfer. As a result, the microemulsion produced by ultrasonication is less likely to sustain a uniform state once the external energy is removed, indicating its reduced stability.

3.2. Influence of Low-Carbon Alcohol Types on Solubilising Effects

The volume percentage ternary diagrams of microemulsion formed by ethanol/diesel/n-butanol at 25 and 35 °C are shown in Figure 4. The experimental results indicate that a minimal amount of n-butanol is sufficient to intercalate ethanol and diesel. This is primarily attributed to the smaller polarity difference between ethanol and diesel compared to methanol and diesel. Ethanol/diesel can be completely miscible at 45 °C, and the temperature elevation has a significant improvement on the dissolving ability of ethanol/diesel. A similar trend is observed in the methanol/diesel preparation, where the shaker mixing exhibits the most effective dissolution assistance at low temperatures. Furthermore, an increase in temperature significantly enhances the dissolution assistance effect of the ultrasonication method.

![Ternary plot of volume percentage of ethanol/diesel/n-butanol microemulsion](image)

**Figure 4.** Ternary plot of volume percentage of ethanol/diesel/n-butanol microemulsion: (a) 25 °C; (b) 35 °C.

3.3. Stability of Microemulsions

The stability of the microemulsions produced was investigated by measuring the delamination time of each sample at three temperatures (25, 35 and 45 °C). The ratio of the delamination time of each sample in the 3 groups to the longest time in the group was expressed as the emulsification efficiency, which reflects the stability of the microemulsions, the nearest to 100% the more stable [31].
3.3.1. Emulsification Curve of Methanol Diesel Microemulsion

The emulsification curves of methanol/diesel/n-butanol at three temperatures are presented in Figure 5. These curves reveal that microemulsions with a smaller volume of methanol/diesel and intermediate ratios exhibit poorer stability. However, as the ratio exceeds 7:3, the stability of the microemulsions increases significantly. Jiao et al. [32] formulated methanol-diesel microemulsions using a fixed emulsifier HLB value of 5.1. As the volume fraction of methanol increased from 5% to 20%, the methanol–diesel emulsion became less stable. Contrary to the experimental conclusion of this study at the same methanol percentage, similar conclusions were reached by Zhang et al. [21]. The reason may be due to the strong emulsion-breaking effect of methanol, and the surfactant cannot effectively reduce the interfacial tension and form a stable interfacial film. When n-butanol was used as a co-solvent, the situation did not occur. Taking the methanol/diesel volume ratio of 1:9 as an example, a large number and volume of diesel molecules are wrapped outside the molecular cluster composed of methanol/n-butanol. External disturbances or gravity can cause parts of the methanol/n-butanol molecular cluster to detach from their associated diesel molecules. This detachment results in rapid aggregation under gravity due to the high specific gravity of the diesel molecules, leading to poor stability. Intermediate proportions of microemulsions contain almost equal numbers of all three molecules. When the stabilizers formed by these molecules are disrupted, they are more likely to aggregate with similar molecules. This aggregation is due to an increase in interfacial tension that cannot be overcome, rather than being further encapsulated to form a stable microemulsion. Microemulsions with higher methanol addition ratios can wrap the exfoliated diesel molecules well and prolong the stabilization time of the entire microemulsion. The volume ratio of methanol/diesel is one of the key factors affecting the stability of microemulsions. By optimizing this ratio, we can significantly improve the stability of the microemulsion, thus providing a guarantee for its performance and service life in practical applications.

![Emulsification efficiency vs. Methanol-diesel Ratio](image1)

![Emulsification efficiency vs. Methanol-diesel Ratio](image2)
At 25 °C and 35 °C, the shaker mixing method required the least amount of n-butanol to be added to the microemulsions. However, when the temperature was increased to 45 °C, the microemulsions prepared by the ultrasonication method were significantly less stable, although the n-butanol addition was also the least. The particle size of the microemulsion formulated by the ultrasonication method in Figure 2 decreased significantly, from 56 nm to 24 nm, within just 10 min. This rapid reduction can be attributed to the temporary storage of energy within the microemulsion, which aided in reducing the amount of n-butanol required. However, it did not enhance the stability of the microemulsion. Vortex oscillation is characterized by its rapid and homogeneous mixing, which, similarly to ultrasonication, prompts rapid and disordered movement within the microemulsion. However, Figure 3I demonstrates that, towards the endpoint of the titration, the microemulsion’s state aligns more closely with that of spontaneous formation and shaker mixing. The vortex oscillation provides energy in a way that gives the microemulsion a chance to disperse uniformly, but it does not achieve a good emulsification effect because the action energy is not as strong as that of ultrasonication. Therefore, it is still necessary to maintain sufficient n-butanol addition during the preparation process to ensure the formation of microemulsions. In summary, we can conclude that there is a positive correlation between the dosage of n-butanol and the stability of microemulsions, which ultimately depends on the results of his combined effect with the preparation method. In the pursuit of a preparation method with low co-solvent dosage and good stability, the shaker mixing method seems to be the most suitable choice.

3.3.2. Emulsification Curve of Ethanol-Diesel Microemulsion

The emulsification curves of ethanol/diesel at 25 °C and 35 °C are shown in Figure 6. The stability of ethanol/diesel is slightly inferior to that of methanol/diesel. This difference is primarily attributed to the smaller amount of n-butanol added to ethanol/diesel, and its stability is mainly maintained by the interaction force between ethanol and diesel. However, this interaction force is weaker compared to the interaction force between the molecular clusters of methanol/n-butanol and diesel molecules. Since the ethanol addition at 35 °C is more than 50% less than at 25 °C, the stability is correspondingly poorer. For methanol and ethanol, the stability of microemulsions is related to the amount of n-butanol added. Employing a particular preparation technique to minimize the quantity of n-butanol incorporated during the microemulsion formulation process can result in inferior stability of the microemulsions. Using a single preparation method, it is challenging to achieve a balance between minimizing n-butanol addition and maintaining good stability. Perhaps a combination of two or more methods can be explored to formulate
microemulsions. Controlling the order and timing of these methods could address this issue, providing a potential avenue for further investigation in future research.

![Graph showing emulsification efficiency for different methods and ethanol-diesel ratios.](image)

**Figure 6.** Ethanol/diesel emulsification curve: (a) 25 °C; (b) 35 °C.

4. Conclusions

In this study, the processes and effects of energy input in microemulsions were thoroughly examined through experimental analysis, encompassing both macroscopic and microscopic viewpoints. Specifically, methanol/diesel/n-butanol and ethanol/diesel/n-butanol microemulsions were formulated using four distinct preparation methods at varying temperatures. Based on these experiments, the following conclusions were derived:

1. Temperature has an effect on the composition of microemulsions. In particular, high temperatures significantly reduce the amount of co-solvent added by the ultrasonication method by up to 25%. This is mainly due to the high-energy mode that ultrasound acts in. Except for the ultrasonication method, the addition of n-butanol was less affected by temperature in the other three preparation methods. This is mainly attributed to the combined effect of increased molecular motion and weakened hydrogen bonding during the warming process, which makes the effect of temperature on the n-butanol dosage insignificant. At 25 and 35 °C, the shaker mixing has the best co-solvent capacity.

2. The ultrasonication method at 45 °C has the best solubilizing capacity but the prepared microemulsion is less stable. The reasons for the differences in solubilizing ability and stability between the four microemulsion preparation methods were clearly presented by microscopic observation.

3. The stability of the microemulsion is typically enhanced when a greater proportion of low-carbon alcohol is incorporated. There exists a positive correlation between the quantity of co-solvent added and the stability of the microemulsion, and insufficient amounts of co-solvent can result in unstable microemulsions.

In this study, the utilization of a shaker for formulating microemulsions is advocated, considering both the economic cost and the preservation of microemulsions. The experimental results prove that using the above analytical methods, i.e., combining the characteristics of the energy input and the microscopic phenomena and macroscopic differences, it is possible to draw exact conclusions and reliable analyses.

**Author Contributions:** Conceptualization, C.J.; Data curation, J.D.; Writing—original draft, J.D.; Methodology, C.D.; Validation, J.H.; Formal analysis, Z.G.; Visualization, X.L.; Supervision, T.X.;
Project administration, G.Z.; Funding acquisition, H.L. All authors have read and agreed to the published version of the manuscript.

**Funding:** The authors would like to acknowledge the financial support to the research provided by the National Natural Science Foundation of China through the Project of 52176125. Also, the project was supported by Open Fund of Shanghai Key Laboratory of Plant Functional Genomics and Resources (PFGR202302).

**Data Availability Statement:** The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding authors.

**Conflicts of Interest:** The authors declare no conflicts of interest.

**References**


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