Strategies for Improved Stability of Methanol-in-Diesel Emulsions

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This study is motivated by the need to present a robust methodology for preparing stable methanol-in-diesel emulsions for use in compression ignition engines with the specific objective of maximizing the methanol content. Specifically, it involved exploring the feasibility of methanol-in-diesel emulsions with conventional surfactants such as Tween-80 and Span-80 and nonconventional surfactants such as 1-dodecanol, pentanol, and butanol. The hydrophilic–lipophilic balance (HLB) values of the surfactant varied from 7 to 15 to investigate the role of the surfactant HLB on the stability of the macroemulsion. It is observed that the macroemulsion with an HLB value of 10 provides the best stability results. Using surfactant HLB value of 10, three macroemulsions with 10 wt%, 15 wt%, and 20 wt% of methanol were prepared using ultrasonication. However, only the macroemulsion with 10 wt% of methanol was observed to be stable for at least 20 days after preparation. Next, the microemulsions of diesel–methanol were produced by using nonconventional surfactants such as 1-dodecanol, pentanol, and butanol. Among these, 1-dodecanol was found out as the most suitable surfactant owing to its ability to form microemulsions with any mixing ratio of diesel–methanol and its high cetane number (63.6). This study has clearly brought out the strategies for preparing both macro and microemulsions. Overall, the results presented in the current work are expected to aid efforts in adapting compression ignition engines for diesel–methanol fuel blends. [DOI: 10.1115/1.4054019]

Keywords: macroemulsion, microemulsion, HLB value, stability, diesel, methanol, alternative energy sources, fuel combustion, renewable energy

1 Introduction

Diesel is one of the most common fuels for the internal combustion engines, whose demand is increasing continuously with rapid automobile usage. However, from the points of requiring sustainable alternatives for diesel and improving air quality, alcohols are emerging as favorable alternatives. Alcohols offer numerous advantages such as easy availability, different production sources, and so on. [1,2]. Low viscosity, high oxygen content, high latent heat of vaporization, and better cold start ability of alcohols facilitated better combustion and emission characteristics when mixed with diesel [3–5]. Methanol and ethanol are the most commonly used alcohols as a fuel in many countries.

The simplest alcohol, methanol, can be produced from different sources including syngas, natural gas, methane, and biomass [6]. In addition, it has the highest system efficiency among all the liquid fuels produced from biomass [7]. However, immiscibility of methanol with diesel makes it challenging to use it as a part replacement or blend. The methanol molecule is a polar molecule owing to an unequal charge distribution. Conversely, the diesel molecule is nonpolar (evenly distributed negative and positive charges) [8]. The difference in the polarity of these liquids along with a very short molecule chain length of methanol and difference in surface tension prevent them from mixing together [9]. A surfactant can be used, which reduces the surface tension difference and helps to make an emulsion.

Emulsions are classified into two categories based on phase as follows: three-phase emulsion and two-phase emulsion. Two-phase emulsions can be further subcategorized into two types as follows: water-in-oil (W/O) type emulsion and oil-in-water (O/W) type emulsion [10,11]. Mostly, water-in-diesel (W/O) type emulsions are used for fuel purpose. Also, based on dispersed droplet size, emulsions are categorized into three types as follows: nanoemulsion, macroemulsion, and microemulsion [12]. Macroemulsions has a dispersed droplet size range of 1–20 μm, whereas microemulsions and nanoemulsions have a size range of 100 nm. Although microemulsions exhibit the same dispersed droplet size range (less than 100 nm) as nanoemulsions, they form spontaneously, whereas nanoemulsions are obtained by special preparation methods such as high-speed homogenization and ultrasonication [12–15]. Microemulsions are both kinematically and thermodynamically stable [16]. However, macroemulsions can separate into two phases given sufficient time as they are unstable thermodynamically. This separation can happen by different procedures such as coalescence, flocculation, sedimentation, Ostwald ripening, phase inversion, and creaming as shown in Fig. 1.

Coalescence is the most common mechanism for the separation of an emulsion wherein dispersed droplets come together because of van der Waals attraction force and eventually create a separation layer by combining together. This separation process can be delayed by choosing a suitable surfactant amount, preparation method [18], and a suitable surfactant HLB value [19]. The surfactant molecules diffuse to the dispersed droplets boundary and form a layer between the droplet and the continuous phase. This layer prevents dispersed droplets from coalescence. Choosing a suitable surfactant for methanol-in-diesel macroemulsion is very challenging as the effect of the surfactant HLB value on the stability is yet not well understood. A surfactant HLB value of 5 is suitable for water-in-diesel macroemulsion [20], and a surfactant HLB value of 12.9 is suitable for oil-in-ethanol macroemulsion [21]. To the best of our knowledge, no study has been reported about the suitable surfactant HLB value for a stable methanol-in-diesel emulsion. Several surfactants have been recommended for preparing stable alcohol-in-oil emulsion in the literature, such as butanol, n-hexanol, n-octanol, and 1-dodecanol [22,23]. However, no
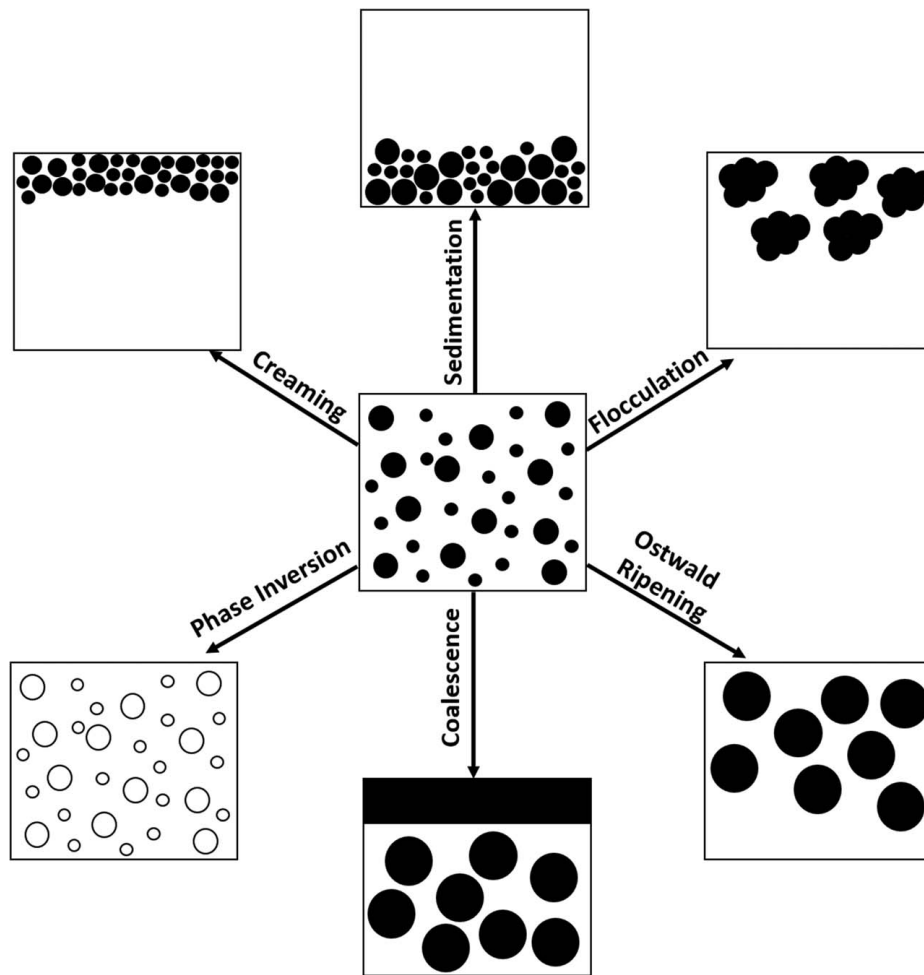
Fig. 1 Different mechanisms of emulsion destabilization: creaming, Ostwald ripening, flocculation, coalescence, creaming, and phase inversion [17]

specific study on the exploration of suitable surfactants for methanol-in-diesel emulsion is available. A few engine studies using methanol-in-diesel emulsions show reduced nitrogen oxide (NO_x) emission and enhanced thermal efficiency [24–26]. Contrary, some studies show reduced thermal efficiency and enhanced NO_x emission with methanol-in-diesel emulsions [27,28]. Thus, it is crucial to fundamentally understand the effect of a surfactant on the stability of an emulsion. A detailed study on the stability assessment of methanol-in-diesel emulsions using different surfactants is required to provide an insight into the effect of surfactant and its content. Also, there are very few studies on exploring microemulsions of methanol-in-diesel [29–31]. Moreover, there is a need to explore surfactants, which can offer a cetane number boost to the emulsion, because of the lower cetane number of methanol [32]. Thus, numerous gaps are present in the literature. To the best of our knowledge, the present study is the first to address the aforementioned gaps in the literature relating to methanol-in-diesel emulsions. The current study reports efforts to explore various surfactants to maximize the methanol content in methanol-in-diesel emulsions and assessing the emulsion stability.

2 Methodology

In this section, the methodology for preparing methanol-in-diesel macroemulsion and microemulsion along with the selection procedure of surfactants is presented. The first sub-section consists of the preparation and the surfactants used for preparing macroemulsions. Section 2.1 consists of the preparation method and details of the

surfactants used for preparing microemulsions. Section 2.3 discusses the stability assessment protocols for both macroemulsions and microemulsions.

2.1 Methodology of Methanol-in-Diesel Macroemulsion Preparation. The selection of a suitable surfactant was an essential part of this study. Methanol-in-diesel macroemulsions were prepared using surfactants such as Tween-80 and Span-80. Both the surfactants are nonionic in nature [33,34]. The amounts of nonpolar and polar groups of a nonionic surfactant molecule can be quantified using the hydrophilic lipophilic balance (HLB) value. It should be noted that the HLB value is used only for the surfactant and not for the emulsion. The "hydrophilic" surfactant has more affinity for polar liquids, and "lipophilic" surfactant has affinity for nonpolar liquids. The surfactant affinity can be quantified by

Table 1 Details of surfactants for macroemulsion preparation

Surfactant name	Chemical name	Formula	Boiling point (°C)	HLB value
Span-80	Sorbitan monooleate	$C_{24}H_{44}O_6$	579 °C	4.3
Tween-80	Polyoxyethylene (20) sorbitan monooleate	$C_{64}H_{124}O_{26}$	695 °C	15

Table 2 Properties of butanol, pentanol, 1-dodecanol, diesel, and methanol

Properties	Butanol [42]	Pentanol [43]	1-Dodecanol [44]	Diesel [45]	Methanol [45]	Measurement method
Density (kg/m^3) at 25 °C	811	814.8	830.9	840	796	EN ISO 3675
Kinematic viscosity at 40 °C (cSt)	2.27	2.89	21.7 (at 20 °C)	3	0.58	EN ISO 3104
Boiling point (°C)	118	138	259	180–360	65	ASTM D86
Cetane number	25	20	63.6	40–55	3–5	ASTM D613
Heat of vaporization (KJ/kg)	581	308.05	493.7	230–600	1200	ASTM E2071-21
Auto-ignition temperature (°C)	385	300	275	315	392	ASTM E659
Oxygen content (wt%)	21.6	18.15	8.6	0	50	–
Molecular weight (g/mol)	74	88.15	186	170–198	32	–

the HLB value, which can be described as follows [35]:

$$\text{HLB} = \frac{20 * M_h}{M_h + M_l} \qquad (1)$$

where the subscripts "*l*" stands for lipophilic and "*h*" stands for hydrophilic. The symbols M_h and M_l stand for the hydrophilic molecular mass and lipophilic molecular mass, respectively. A mixture of Tween-80 and Span-80 was chosen as the surfactant. Table 1 shows the details of the surfactants. The overall HLB value of the mixture of two surfactants is calculated using the following equation [11]:

$$\text{HLB}_{comb} = (\text{HLB}_S * W_S) + (\text{HLB}_T * W_T) \qquad (2)$$

where the mass ratio of Tween-80 is represented by W_T and the mass ratio of Span-80 is represented by W_S.

Emulsions can be prepared by numerous equipment such as homogenizer, ultrasonicator, colloid mill, mechanical stirrer, impinging stream-rotating packed bed, and so on [36–38]. Sonication and high-speed stirring are widely used to prepare macroemulsions [39]. Initially, an attempt was made to prepare macroemulsion using a high-speed stirrer at 12,000 rpm. Methanol is a highly volatile liquid, and it evaporates under normal ambient conditions if kept in an open container. The evaporation rate increased during the emulsion preparation, which led to a decrease in the methanol amount within the emulsion. Thus, preparing macroemulsion using the high-speed stirrer was not pursued. The ultrasonication method was finally used for several of its advantages over the high-speed stirrer. Ultrasonication can be conducted by enclosing diesel, methanol, and surfactant in a closed container, thereby preventing evaporation of methanol. A high-frequency sound wave is used in the ultrasonication technique to cause breakup of a large droplet of the dispersed phase into smaller droplets [40]. In this study, it was discovered that preparing a methanol-in-diesel macroemulsion with more than 10 wt% methanol content using Tween-80 & Span-80 as the surfactant is not feasible. This led to the exploration of using microemulsions to increase the methanol content in the emulsion.

2.2 Methodology of Methanol-in-Diesel Microemulsion Preparation.
First, the surfactants that were used to prepare the microemulsions are presented. Next, the preparation method to produce microemulsions is presented. A surfactant molecule interacts with both the continuous phase and the dispersed phase of a microemulsion by serving as a bridge between them [41]. Three different surfactants 1-dodecanol, pentanol, and butanol were used to prepare microemulsions. The properties of the surfactants are listed in Table 2. It can be seen from Table 2 that 1-dodecanol has the highest cetane number among three surfactants, which makes it suitable for use in diesel engines.

The preparation of microemulsion was conducted at an ambient temperature of 25 °C. Initially, the surfactant is poured into a closed beaker containing a known mixture of diesel and methanol with constant stirring until the whole mixture becomes transparent.

Next, the total weight of the beaker with all the liquids is measured. As diesel and methanol amounts are known a priori, the weight of the surfactant can be estimated. The quantities of diesel and methanol were varied to obtain the full range of solubility of the methanol, diesel, and surfactant.

2.3 Stability Assessment of Emulsion.
Ensuring the stability of emulsion during IC engine operation is very important. However, there are no clear protocols for assessing the stability of emulsions in the literature [46]. In this study, stability assessment of emulsion was done by both visual observation and measurement of size distribution of dispersed droplets. A change in size of dispersed droplets with time indicates the coalescence among dispersed droplets in an emulsion. Sometimes, this can occur when the emulsion is subjected to physical stress and shear. The increased droplet sizes can then again stay constant with time after the physical process is complete, indicating that the emulsion is still stable, in spite of the increase in dispersed drop size. However, if there is a continuous coalescence among dispersed droplets, then this leads to the separation of methanol within emulsion and formation of a separation layer. The formation of a small visible separation layer is a clear indication of the destabilization of the emulsion. As long as there is no separation layer present, the emulsion is considered as stable, despite a larger dispersed droplet size distribution. The measurement of dispersed droplet size distribution in macroemulsion was carried out using an optical microscope because the average dispersed droplet size is greater than 1 μm. The measurement of dispersed droplet size distribution in microemulsions was done by using dynamic light scattering (DLS) technique (Zetasizer nanoseries-ZEN 3690), as the average dispersed droplet size is less than 200 nm. The DLS technique is not suitable for dispersed droplet size measurement for macroemulsion as it is incapable of measuring droplet size of more than 3 μm. An optical microscope was used to measure the dispersed droplet size distribution in macroemulsions. Along with the dispersed phase drop size distribution, visual observation was also used to identify any separation layer in an emulsion sample. The presence of a small visible separation layer was a clear indication of the lack of stability of the emulsion.

3 Results and Discussion

The results on methanol-in-diesel macroemulsions are discussed in Secs. 3.1–3.4. The subsequent sections present results on methanol-in-diesel microemulsions.

3.1 Effect of Surfactant Hydrophilic–Lipophilic Balance Value on a Methanol-in-Diesel Macroemulsion.
The purpose of this study is to find an optimum surfactant HLB value, which can be used to prepare stable methanol-in-diesel macroemulsions. Thus, nine different surfactant HLB values were selected for this study. The stability analysis of the macroemulsions was done only by visual observation. The ultrasonication technique was used to prepare macroemulsions at an ambient temperature of

Table 3 Composition of methanol-in-diesel macroemulsions with different surfactant HLB values

HLB_{comb}	Diesel (wt%)	Span-80 (wt%)	Tween-80 (wt%)	Methanol (wt%)
7	88	1.496	0.504	10
8	88	1.308	0.692	10
9	88	1.122	0.878	10
10	88	0.934	1.066	10
11	88	0.748	1.252	10
12	88	0.56	1.438	10
13	88	0.374	1.626	10
14	88	0.186	1.814	10
15	88	0	2	10

25 °C. The surfactant was a mixture of Tween-80 and Span-80. Different surfactant HLB values were obtained by varying the Span-80 and Tween-80 amount according to Eq. (2).

Table 3 presents the composition of all the nine macroemulsions. For each macroemulsion, the total content of Span-80 and Tween-80 was fixed at 2 wt%. The diesel and methanol content was fixed at 88 wt% and 10 wt%, respectively, for all the macroemulsions. All the macroemulsions were prepared with 25 min of ultrasonication time.

Figure 2 shows the images of seven containers that consist of the macroemulsions prepared with different surfactant HLB values. This image was taken 6 h after preparation of the macroemulsions. The left-most tube in the image represents a macroemulsion prepared with a surfactant holding a HLB value of 9, and the right-most tube is filled with a macroemulsion prepared with a surfactant holding a HLB value of 15. It is clear that there are separation layers present at the bottom of some tubes. The macroemulsion with surfactant having a HLB value of 15 exhibits the highest separation layer thickness at the bottom of the tube. The separation layers mainly consist of diesel because diesel has a higher density than methanol. The separation layer thickness decreases with the decrease in surfactant HLB value, and there is no separation layer present for the macroemulsion with surfactant HLB value of 10. The macroemulsion with the surfactant HLB value of 7 exhibits a separation layer at the top of the tube, which probably consists of methanol because of its lower density than that of diesel. The separation layer thickness of methanol decreases with the increase in the surfactant HLB value. It is observed that the macroemulsion with surfactant HLB value of 10 exhibits no separation layer either at the top or at the bottom of the tube.
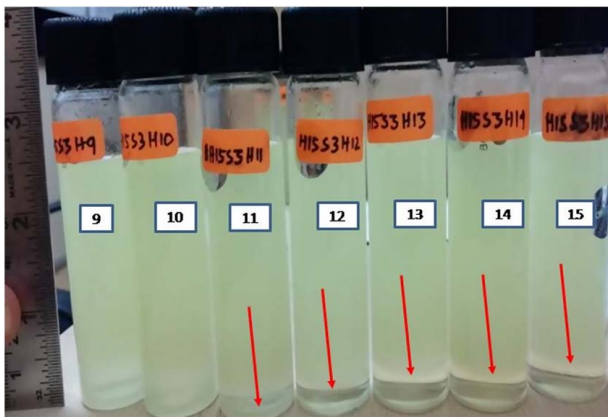

Fig. 2 Macroemulsions with different surfactant HLB values (from 9 to 15) 6 hours after preparation at an ambient temperature of 25 °C. The arrows indicate separation layers, and the numbers represent surfactant HLB values. The macroemulsions were prepared with 10 wt% of methanol and 2 wt% of surfactant.

Then, the possible reasons of this behavior are explained next. Span-80, with an HLB value of 4.3, is a lipophilic surfactant, whereas Tween-80, with an HLB value of 15, is a hydrophilic surfactant. The affinity of a surfactant toward methanol increases with an increase in the surfactant HLB value because of the high hydrophilicity of the surfactant. As a result, a large part of the surfactant molecules is located inside the dispersed methanol droplets, while a small part of the surfactant molecules is located in the continuous diesel medium. Thus, the surfactant molecules are ineffective to form a stable emulsion; as a result, some amount of diesel is separated within the macroemulsion.

Similarly, at a HLB value of less than 10, the surfactant has a higher affinity toward diesel. As a result, a large part of the surfactant molecules is located inside the continuous diesel medium, while a small part of the surfactant molecules is located inside the dispersed methanol droplets. Thus, the surfactant layers formed outside the dispersed droplets might not be strong enough to prevent methanol droplets from coalescing together. As a result, methanol separates and creates separation layer within the macroemulsion. For a HLB value of 10, the surfactant molecules may create a stable layer outside the dispersed droplets, which prevent droplets from coalescing together and form a stable macroemulsion. Thus, the surfactant HLB value of 10 is found to be the optimum value for creating highly stable diesel–methanol macroemulsions.

3.2 Effect of the Ultrasonication Time on Dispersed Droplet Size Distribution in Macroemulsion.

This section describes the study to evaluate the optimum time required for ultrasonication in the preparation of macroemulsions. Ultrasonication time in this study refers to the time for which methanol, diesel, and surfactant were ultrasonicated together during preparation of the macroemulsion. This time period has a significant effect on the stability of the macroemulsion as well as the size distribution of the dispersed droplets. It was found out from the literature that the dispersed droplet size decreases, whereas the stability of a macroemulsion increases with an increase in the ultrasonication time [14].

Four different ultrasonication times of 15 min, 20 min, 25 min, and 30 min were chosen. The surfactant was a mixture of Span-80 and Tween-80 with a combined HLB value of 10. Figures 3(a)–3(d) represent the size distribution of dispersed droplets in the macroemulsions prepared with 15, 20, 25, and 30 min of ultrasonication time, respectively. As shown in Fig. 3(a), around 27% of the total droplets lie in the range of 5–7 μm even though the dispersed droplet diameters are in the range of 3–47 μm. The size distribution narrowed down with an increase in the ultrasonication time to 20 min as shown in Fig. 3(b). Approximately 55% of total dispersed methanol droplets are in the size range of 3–5 μm. The maximum dispersed droplet size was observed to be around 19 μm, and the average value is around 6 μm.

The dispersed droplet size decreases further with an increase in the ultrasonication time to 25 min as shown in Fig. 3(c). Approximately 62% of total dispersed droplets of the macroemulsion are in the range of 3–5 μm, and the average value is around 7 μm. No droplet below 3 μm is observed for the macroemulsions prepared with ultrasonication time of 15 min and 20 min. However, there are many dispersed droplets in the range of 1–3 μm for the macroemulsion prepared with 25 min of ultrasonication time although the average values of the dispersed droplet size for the 20 and 25 min cases are almost similar.

Surprisingly, the dispersed droplet size marginally increases with an increase in the ultrasonication time to 30 min as shown in Fig. 3(d). Approximately 25% of total dispersed droplets of the macroemulsion are in the range of 7–9 μm, and the average value is around 10 μm. There are no dispersed droplets below 5 μm.

It can be concluded that dispersed droplet size decreases with an increase in the ultrasonication time. A higher ultrasonication time corresponds to higher energy input, which enhance the chances of breakup of the larger droplets into smaller droplets. Also, the higher duration of ultrasonication enhances the diffusion of the
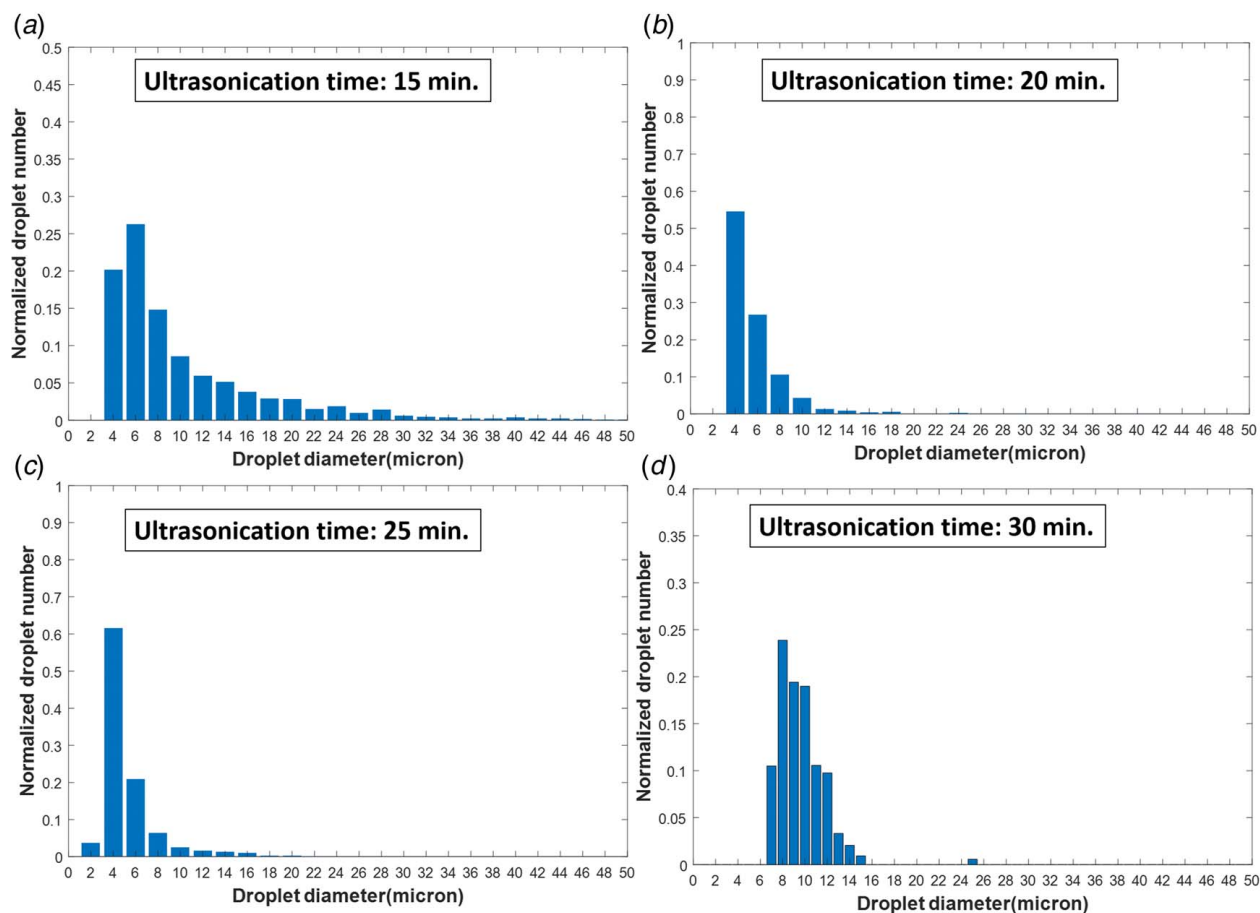
Fig. 3 (a)–(d) Dispersed droplet size distribution of the macroemulsions prepared with 15, 20, 25, and 30 min of ultrasonication time, respectively. The macroemulsions were prepared with 10 wt% methanol and 2 wt% surfactant (HLB value of 10).

surfactant molecules into the dispersed methanol–diesel interface. This in turn creates a stable layer of surfactant, which can prevent the coalescence of the dispersed methanol droplets and produce stable emulsions. It appears that a very high ultrasonication time leads to increase in the interactions and re-coalescence among the dispersed droplets [47,48]. This is attributed to the higher dispersed droplet size as observed for the ultrasonication time of 30 min. Thus, the ultrasonication time of 25 min is found out to be the most suitable for macroemulsion preparation due to the lower average dispersed droplet diameter and size range.

3.3 Effect of Methanol Content in Macroemulsion Stability. The purpose of this study is to maximize the methanol content in methanol-in-diesel macroemulsions. To achieve this, macroemulsions were prepared using different amounts of methanol step by step. First, a macroemulsion with 10 wt% of methanol was prepared, and the stability was assessed by both visual observation and measuring dispersed droplet size distribution under the optical microscope. Next, macroemulsions with 15 wt% and 20 wt% methanol were prepared. As a surfactant, a mixture of Tween-80 and Span-80 was used maintaining the overall surfactant HLB value of 10 for all the macroemulsions.

Figure 4 represents the images of the macroemulsion at different times after preparation. The macroemulsion with 10 wt% methanol was prepared with ultrasonication time of 25 min. The surfactant was a mixture of Span-80 and Tween-80 with combined surfactant HLB value of 10. The total surfactant amount was 2 wt%. After preparing the macroemulsion, it was kept in a test tube and visually observed for 40 days as shown in Fig. 4. Microscopic images of the macroemulsion were taken just after the preparation, and 200 h after preparation to study the change in the dispersed
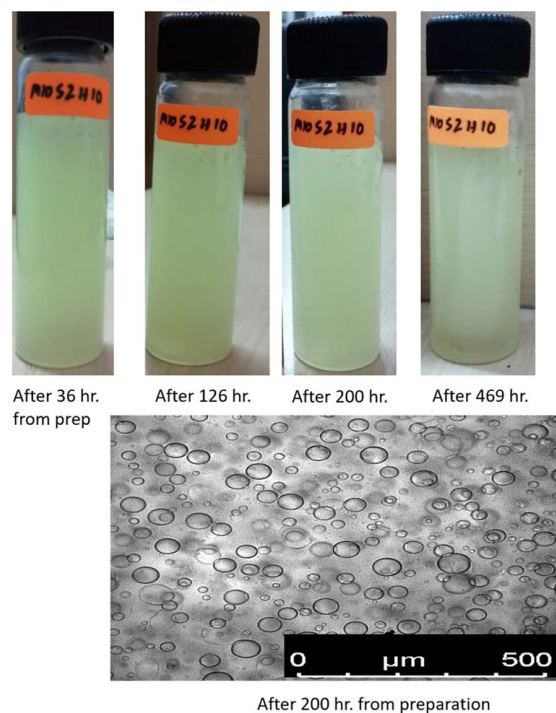

After 36 hr. from prep   After 126 hr.   After 200 hr.   After 469 hr.

After 200 hr. from preparation

Fig. 4 Macroemulsion with 10 wt% of methanol and 2 wt% of the surfactant was prepared using ultrasonication time of 25 min at an ambient temperature of 25 °C. The surfactant was a mixture of Span-80 and Tween-80 with combined HLB value of 10.

droplet size distribution. It is observed that the macroemulsion is stable up to 469 h after preparation, with a progressive phase separation afterward. The average dispersed droplet size after preparation was around 7 μm, whereas it changed to around 28 μm 200 h after preparation. This indicates that the rate of coalescence was not high enough to create larger dispersed droplets. There was no separation layer observed even up to 469 h after preparation.

Next, a macroemulsion with 15 wt% methanol was prepared by using ultrasonication time of 25 min, and a mixture of Tween-80 and Span-80 as surfactant by keeping the combined surfactant HLB value at 10. Different amounts of surfactant, starting from 2 wt%, were used to avoid the separation layer formation and to prepare a stable macroemulsion.

Figure 5 shows the images of the macroemulsions prepared using different amounts of surfactant varying from 3 to 6 wt%. Arrows in the images indicate the separation layers formed in the macroemulsions. As shown in Fig. 5(b), it is observed that the separation layer thickness at the bottom of the test tubes increases with the increase in the surfactant amount from 4 to 6 wt%. The macroemulsion with 4 wt% surfactant also exhibits a small separation layer at the bottom of the container. But as the surfactant amount changes from 4 to 3 wt%, the position of the separation layer changes from the bottom to the top of the container. Separation layers are also observed at the top of the container for macroemulsions with 3.4 and 3.7 wt% of surfactant as shown in Fig. 5(a). As methanol has a lower density than that of the diesel and the surfactant, the separation layers that are present at the top of the test tubes mainly consist of methanol. The separation layers may be caused by the insufficient amount of surfactant because of which the surfactant molecules failed to create a layer around the dispersed methanol droplets. This leads to rapid coalescence among dispersed methanol droplets and further creates a separating layer at the top of the container. The separation layer at the bottom of the container consists of diesel and surfactant, which was observed for the macroemulsion with surfactant amount equal to or more than 4 wt%. Overall, it was not possible to create a stable macroemulsion with 15 wt% of methanol.

Next, a macroemulsion with 20 wt% methanol was prepared by using ultrasonication time of 25 min, and a mixture of Tween-80 and Span-80 was prepared as surfactant by keeping the combined surfactant HLB value at 10.

Surfactants amounts varied from 4 wt% to 6 wt% in steps of 1 wt% to prepare a macroemulsion with 20 wt% of methanol and diesel. All the macroemulsions were prepared at the ambient temperature of 25 °C. As shown in Fig. 6, the arrows in the images indicate the separated layers present in the macroemulsions. It is observed that all the
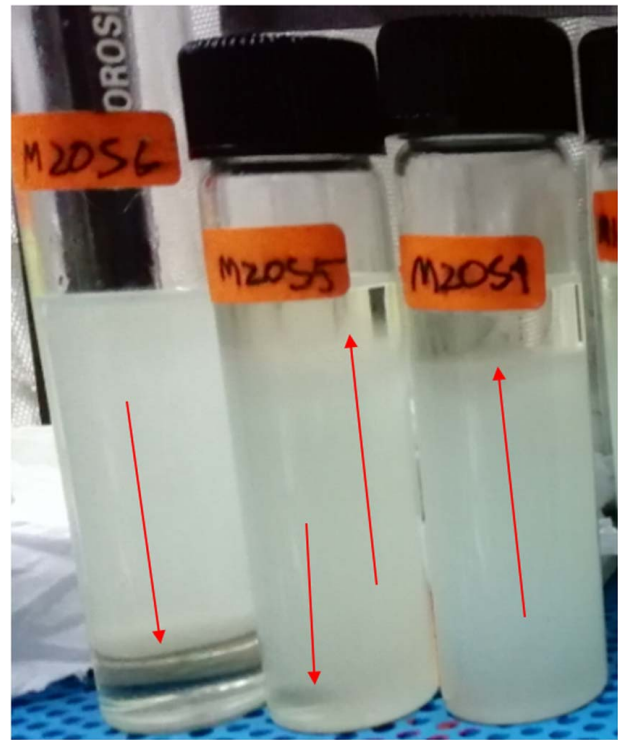
Fig. 6 Macroemulsions (20 wt% methanol) with different amounts of surfactant, prepared using ultrasonication time of 25 min. A mixture of Tween-80 and Span-80 was used by keeping the combined surfactant HLB value constant at 10. The arrows indicate the separation layer.

three macroemulsions exhibit a separation layer present either at the bottom or at the top of the test tubes. Coalescence due to numerous dispersed droplets interactions could be the reason behind this separation as explained later. As the methanol amount in the mixture is relatively high, the number of dispersed droplets is also high. Hydrodynamic interaction between the dispersed droplets increases because of high dispersed droplet density. As a result, chances of a collision between two droplets increase, which may result in further coalescence. The separation layers were observed immediately after preparation. Overall, it was not possible to create a stable macroemulsion with 20 wt% of methanol.

Thus, a stable macroemulsion with 10 wt% methanol and 2 wt% surfactant (Span-80 and Tween-80 mixture) was successfully produced using the ultrasonication technique. It is very important to assess the stability of the macroemulsion under typical engine fuel injection conditions. For this purpose, the effect of high-pressure diesel injection system on dispersed droplet size distribution was investigated, which is discussed in Sec. 3.4.

3.4 Injection Pressure Effect on Dispersed Droplets Size of Macroemulsion.
In a combustion engine, the liquid fuel goes through a high-pressure injection system before being sprayed into the engine cylinder. There is no study till date in the literature that has evaluated the methanol-in-diesel macroemulsions stability, subjected to such high pressure and shear.

In this study, a high-pressure injection system is set up as schematically shown in Fig. 7. This experimental setup (Fig. 7) used in the present study has been described in detail elsewhere [49]. The experimental setup consists of a fuel supply system, an injector controller, and a pressure controller. The fuel supply system comprises several components, such as a high-pressure fuel pump, a fuel filter, a fuel tank, an injector, and a common rail connected in series. The pressure controller with a rated injection pressure of
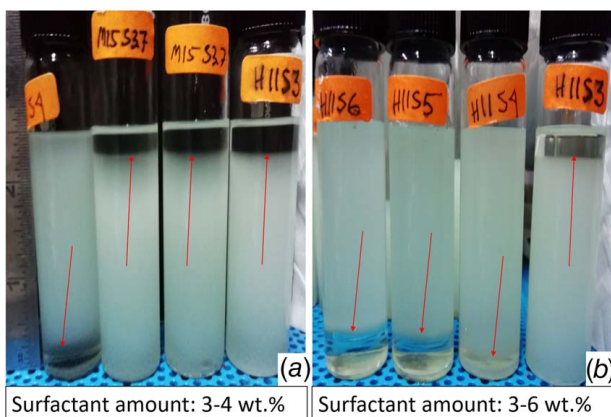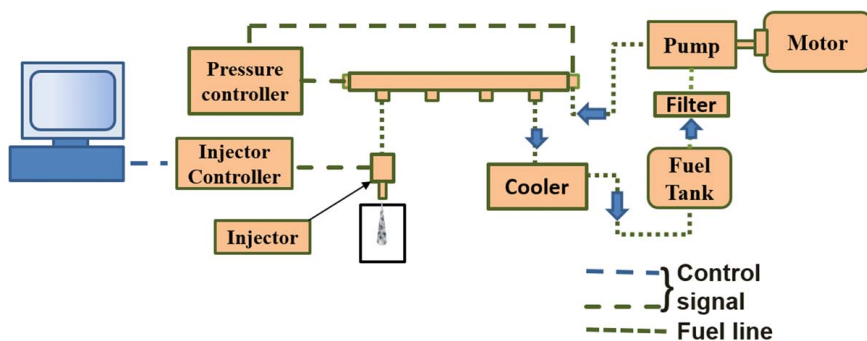

Fig. 5 Macroemulsions with 15 wt% of methanol using different amounts of surfactants. All macroemulsions were prepared using an ultrasonication time of 25 min. The surfactant was a mixture of Span-80 and Tween-80 with combined surfactant HLB value of 10. The arrows point to the separation layer.

Fig. 7 Schematic diagram of the experimental setup to collect the injected macroemulsion from a high-pressure diesel injector

1600-bar is used to maintain the common rail pressure at a fixed value. The fuel injector is a single-hole solenoid diesel injector with an orifice diameter of 190 μm. The injector is operated by a controller, which can control the injection duration. The duration of each injection was maintained at 1 ms during this study. The macroemulsion with 10 wt% methanol and 2 wt% surfactant is then injected at a pressure of 500-bar. The injected macroemulsion was collected and examined with an optical microscope. Moreover, the macroemulsions were also visually observed for their stability.

The normalized number of droplets is represented by the ordinate of the plots. The droplet size is represented by the abscissa in micrometers. The histograms clearly indicate that the macroemulsion has retained a similar dispersed droplet size distribution even after being subjected to high shear in the injector and high pressure in the tank. To quantitatively compare the two histograms

in Figs. 8(a) and 8(b), the area A3.5–4.5 of each histogram corresponding to a percentage of droplets in the range of diameter between 3.5-μm and 4.5-μm is calculated and compared. For example, in Fig. 8(a), this translates to 20% of total droplets in the size range of 3.5–4.5-μm. In Fig. 8(b), 10% of total droplets are in the size range of 3.5–4.5 μm. It is observed that for both the samples, a large number of the dispersed droplets are having size between 2 and 12 μm. The average values of dispersed droplets in the macroemulsion before and after injection are 8.5 and 8.8 μm, respectively. A similar droplet size distribution and average dispersed droplet diameter imply that there is less rate of coalescence of dispersed droplets as the emulsion goes through shear and high pressure. It is important to notice that the macroemulsion remains stable even after being injected through the high-pressure injection system. This can be confirmed through visual
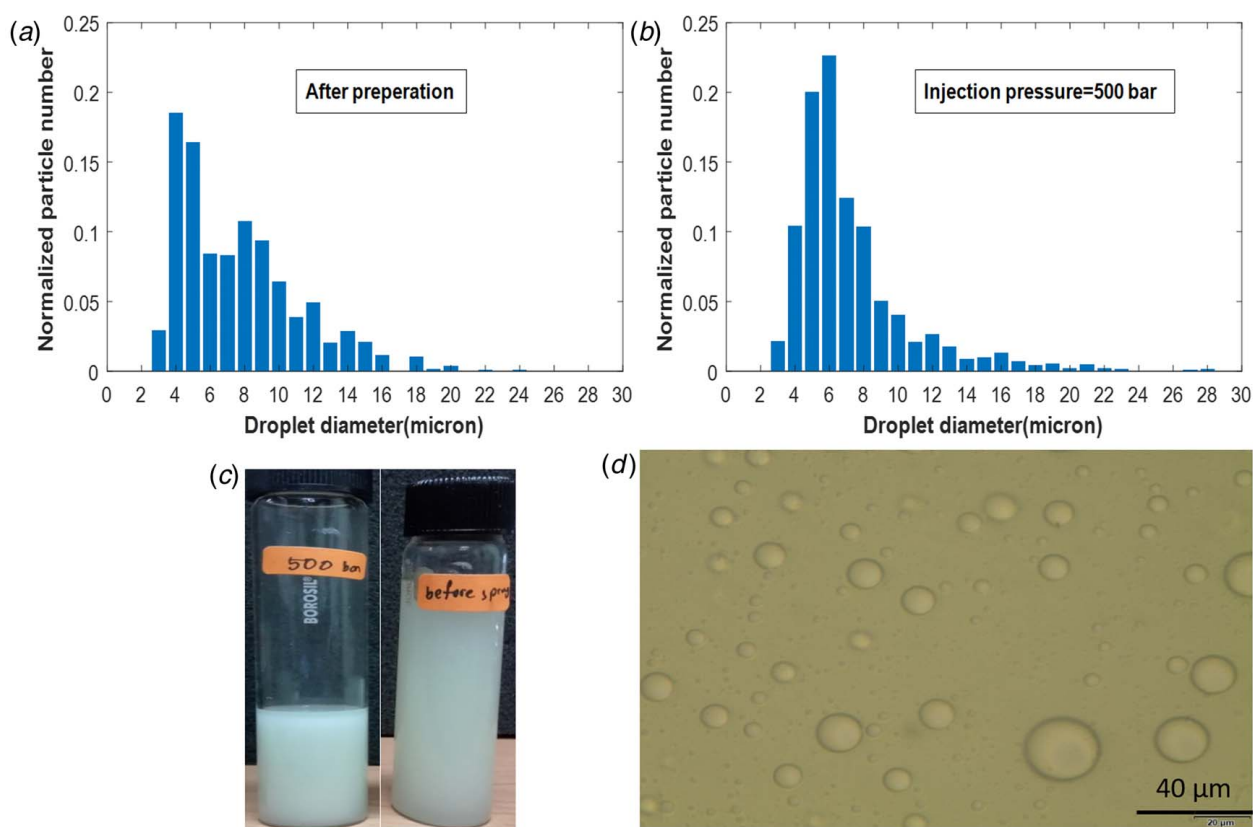

Fig. 8 (a) and (b) Size distribution of dispersed methanol droplets in the macroemulsion just before and after being injected at 500 bar pressure, respectively. (c) Images of the macroemulsions just after and before being injected. (d) A microscopic image of the emulsion just after being injected. The macroemulsion was prepared with 10 wt% methanol and 2 wt% surfactant (HLB value of 10).
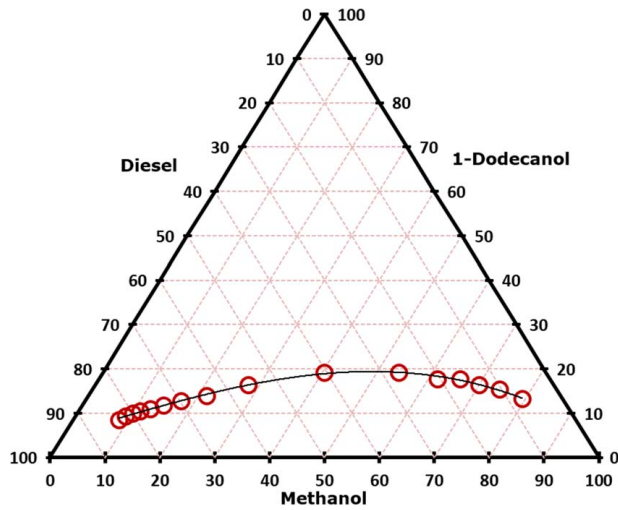
Fig. 9 Ternary phase diagram for methanol, diesel, and 1-dodecanol microemulsion at an ambient temperature of 25 °C

observation also. No separation layer is present in the macroemulsion as shown in Fig. 8(c). During the injection process, the dispersed droplets go through the high-pressure system (common rail, diesel injector), which increases the probability of coalescence. However, it appears that the layers of surfactant around the dispersed droplets are strong enough to prevent them from coalescence.

3.5 Methanol-in-Diesel Microemulsions. The main purpose of this study is to maximize the methanol content in diesel–methanol mixtures by producing microemulsions, while ensuring that the cetane number of the final emulsion is not lowered significantly, especially below that of diesel. In this section, first, the results of microemulsions with different methanol–diesel ratio using 1-dodecanol as the surfactant are presented, and the stability assessment of the microemulsion is discussed.

The surfactant 1-dodecanol is miscible with both diesel and methanol as it contains a long carbon chain and a hydroxyl group. Figure 9 represents a ternary phase diagram of methanol, diesel, and 1-dodecanol.

The ternary phase diagram is a graphical representation of the three liquids that coexist at various ratios. Each red point represents a microemulsion with a certain amount of diesel, methanol, and

1-dodecanol given in weight percentage basis, which can be calculated from the diagram itself as explained next. A line from a red point parallel to the 1-dodecanol line intersects the diesel line at a point. The value at that point represents the diesel percentage in the microemulsion corresponding to the red point. Similarly, two lines from the red point parallel to the diesel line and the methanol line intersect the methanol line and the 1-dodecanol line, respectively, at two separate points. The values at those points represent the methanol and the 1-dodecanol percentages, respectively, in the microemulsion. The line connecting all the red points represents the minimum amount of 1-dodecanol required to prepare the microemulsions at different ratios of diesel and methanol. The red points were obtained by experimentally mixing various proportions of diesel, methanol, and 1-dodecanol together. It is observed from the diagram that the 1-dodecanol content reduces in the microemulsions with a reduction in the methanol content. A similar trend is observable for the microemulsions with a higher amount of methanol content. The peak point in the curve represents a microemulsion of 20 wt% methanol, 20 wt% 1-dodecanol, and 40 wt% diesel. At a point where the methanol content is as low as 8 wt% and the diesel content is 84 wt%, only 8 wt% of 1-dodecanol is required to obtain the microemulsion. The most important finding from this diagram is that the maximum amount of 1-dodecanol required is 20 wt% for any mixing ratio of diesel and methanol. It is very important to assess the stability of the microemulsion of methanol, diesel, and 1-dodecanol.

Stability assessment of the microemulsion using 1-dodecanol as the surfactant is discussed next. The stability assessment was done by both visual observation and measuring the size distribution of dispersed droplets in the microemulsion. Figure 10(a) shows the size distribution of dispersed droplets in the microemulsion with 25 wt% methanol and 16 wt% 1-dodecanol, which was obtained using the DLS measurement (dynamic light scattering). The measurement was taken after 37 days from the preparation of the microemulsion. The mean value of dispersed droplet diameter is 11.01 nm ± 2.67 nm, whereas the same is approximately 10 nm after preparation of the microemulsion. It is observed that the mean value of the dispersed droplet size is unchanged. As shown in Fig. 10(b), it is also observed visually that the color of the microemulsions does not change even 37 days after preparation of the sample. The results indicate that the microemulsion prepared with 1-dodecanol is highly stable.

3.6 Effect of the Surfactant Chain Length on Microemulsion. In this section, the effect of the surfactant chain length on diesel–methanol microemulsion formation is studied.
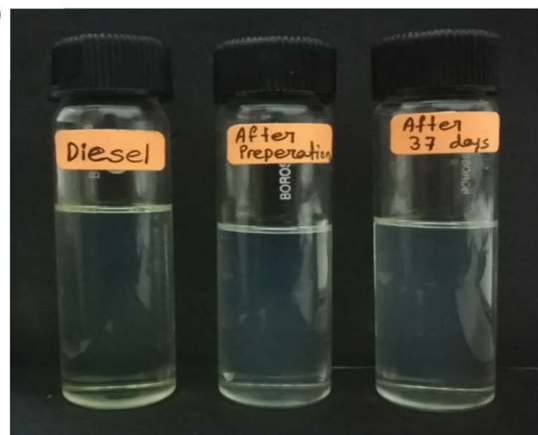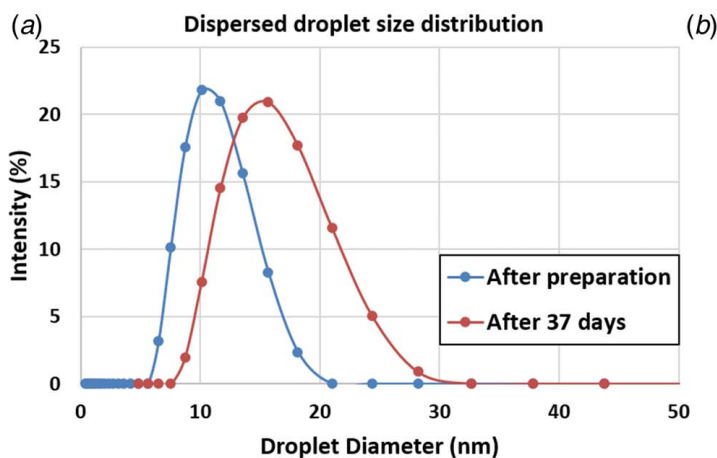

Fig. 10   (a) Dispersed droplet size distribution of microemulsion with 25 wt% methanol measured after preparation, and the same microemulsion after 37 days from preparation. (b) Image of three test tubes with diesel, the microemulsion after preparation, and the same microemulsion after 37 days from preparation.
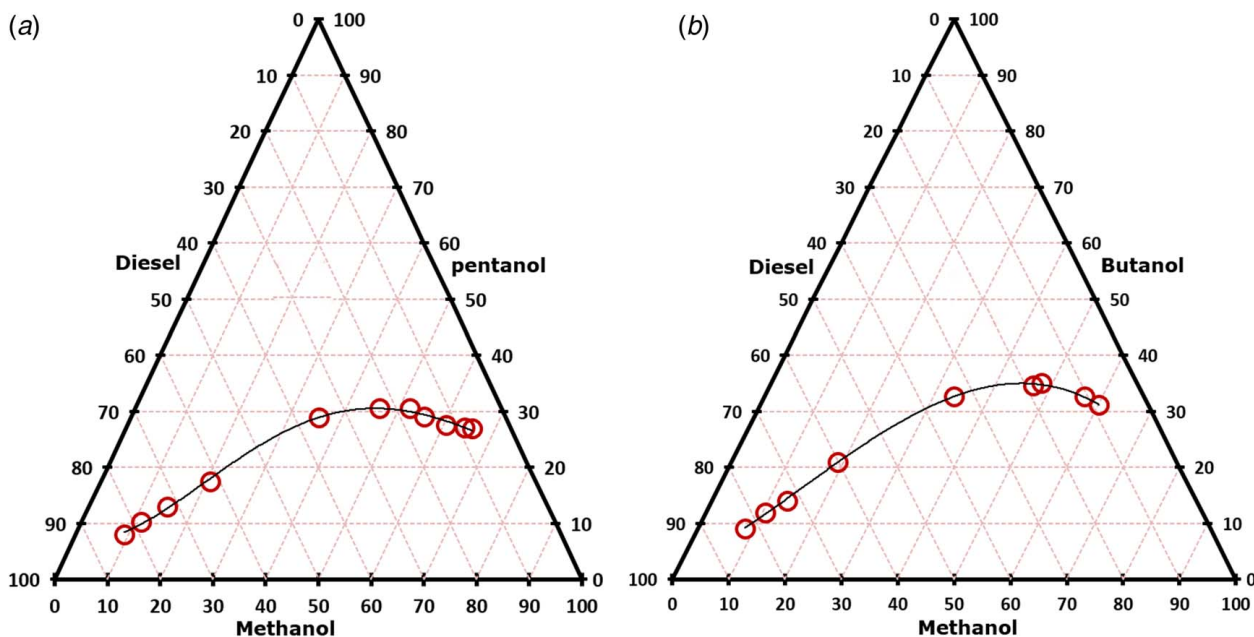
Fig. 11 *(a)* and *(b)* Ternary phase diagram of methanol–diesel–pentanol and methanol–diesel–butanol, respectively

The three surfactants being investigated have different numbers of carbon atoms in their molecular structure. The results with 1-dodecanol are already presented in Sec. 3.5. The effect of the other two surfactants, namely, pentanol and butanol, are studied, and the results are presented in this section. Two ternary phase diagrams with pentanol and butanol as surfactants are shown in Fig. 11.

As shown as in Fig. 11(*a*), with the fraction of methanol as low as 9 wt%, a microemulsion can be produced using 8 wt% pentanol as the surfactant. The required amount of pentanol increases with an increase in the methanol amount. An important finding from this diagram is that the maximum amount of pentanol that is required

is 31 wt% for any mixing ratio of diesel and methanol. The peak of the curve represents a microemulsion of 46 wt% methanol, 31 wt% pentanol, and 23 wt% diesel. The ternary phase diagram for butanol as a surfactant shows a similar trend as that of pentanol. The maximum amount of butanol that is required is 36 wt% for any mixing ratio of diesel and methanol, whereas the same is 31 wt% for pentanol and 20 wt% for 1-dodecanol.

The variation in emulsification capacity of surfactants with different carbon chain lengths is explained next. The emulsification capacity of a surfactant is defined as the ratio of methanol fraction to the fraction of surfactant in a microemulsion. A high value implies high emulsification capacity of the surfactant. It is observed
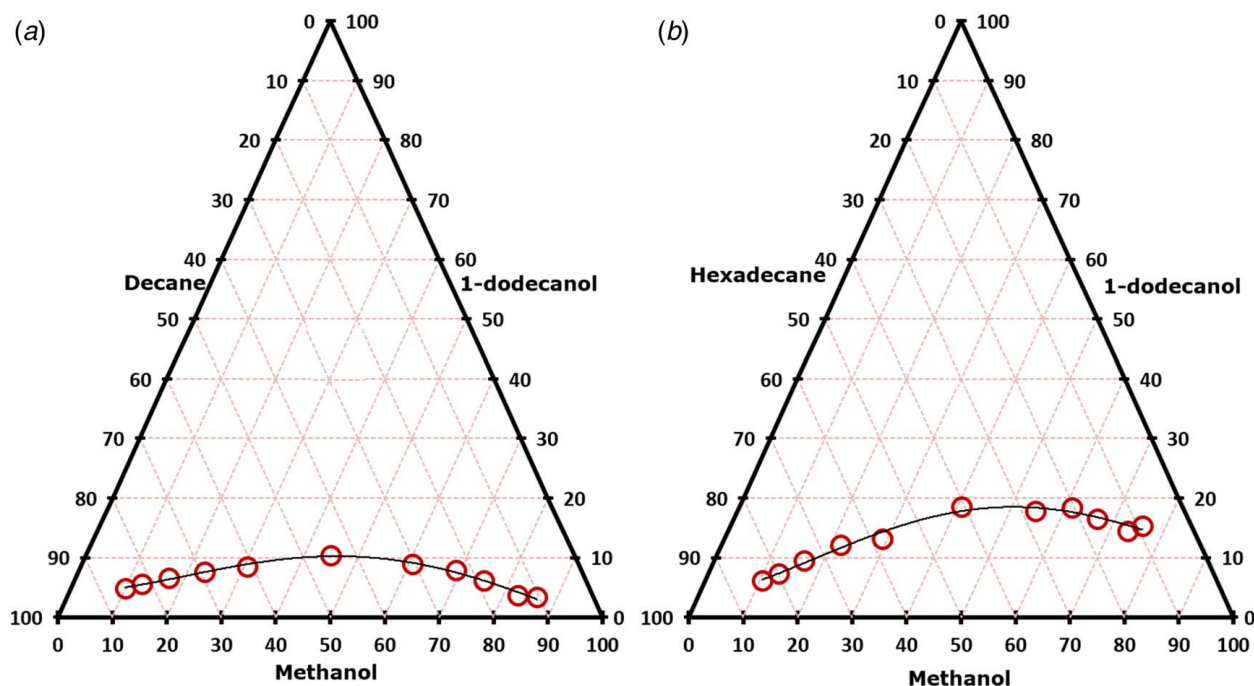

Fig. 12 *(a)* Ternary phase diagram of 1-decane, methanol, and 1-dodecanol. *(b)* Ternary phase diagram of hexadecane, methanol, and 1-dodecanol. 1-dodecanol acts as the surfactant.

that the carbon chain length of the surfactant molecule has a considerable effect on its emulsification capacity. The 1-dodecanol molecule has the longest carbon chain length, while butanol has the shortest carbon chain length among the three chosen surfactants. It is reported that the emulsification capacity of a surfactant in a microemulsion depends on the molecular chain length of the continuous phase, the dispersed phase, and the surfactant [50]. A surfactant molecule with longer carbon chain can facilitate a more stable microemulsion, which might be attributed to the enhanced interface activity of the surfactant molecule [51]. Among the three surfactants, 1-dodecanol has the highest chain length with 12-carbon, and butanol has the lowest carbon chain length with 4-carbon. Thus, 1-dodecanol has more emulsification capacity than butanol and pentanol because of its longest molecular chain length among the chosen surfactants.

3.7 Effect of Oil Carbon Chain Length on Microemulsion.
In this section, the results of a study concerning the effect of oil carbon chain length on microemulsion formation are presented. Here, oil refers to the continuous phase of an emulsion, such as diesel in methanol-in-diesel emulsion. Two different fuels other than diesel, hexadecane ($C_{16}H_{34}$) and 1-decane ($C_{10}H_{22}$) were selected for this purpose. Hexadecane and 1-decane molecules contain 16 carbons and 10 carbons, respectively. Both fuels are knows as surrogate fuels for diesel [52]. 1-Dodecanol was used as the surfactant to prepare microemulsions. Two ternary phase diagrams with the two oils are shown in Fig. 12. Figure 12(a) represents the ternary phase diagram of hexadecane, methanol, and 1-dodecanol with hexadecane as the continuous phase. This figure also represents the ternary phase diagram of 1-decane, methanol, and 1-dodecanol with 1-decane as the continuous phase.

It can be seen from the two ternary phase diagrams that the microemulsion of 1-decane and methanol requires the less amount of 1-dodecanol as compared to the microemulsion of hexadecane and methanol. As shown in Fig. 12(a), the peak point of the curve represents a microemulsion of 1-decane, methanol, and 1-dodecanol with fractions of 45 wt%, 45 wt%, and 10 wt%, respectively. Similarly, at the peak point of the curve shown in Fig. 12(b), the fractions of hexadecane, methanol, and 1-dodecanol are 41 wt%, 41 wt%. 18 wt%, respectively. It can be concluded that the surfactant requirement to prepare microemulsion of hexadecane-methanol is higher than that of 1-decane-methanol. This is attributed to the molecular structure and molecular polarity of the continuous phase molecule. Methanol is immiscible with nonpolar liquids such as diesel, hexadecane, and 1-decane because of its polar nature. The carbon chain portion of a 1-dodecanol molecule can create a bond with a nonpolar oil molecule (hexadecane or 1-decane), and simultaneously, the hydroxyl portion can facilitate hydrogen bonding with a methanol molecule. Thus, the 1-dodecanol molecule can act as a bridge between the oil and methanol molecules. The emulsification capacity of a surfactant decreases with an increase in the chain length of the oil molecule [50]. Thus, the surfactant requirement for oil with shorter chain molecule is lesser than that of oil with a longer chain molecule.

4 Conclusions
The present study focuses on obtaining stable methanol-in-diesel emulsions while maximizing the methanol content. This is done by using both macroemulsions and microemulsions using novel surfactants. Tween-80 and Span-80 have been used as surfactants to prepare macroemulsions using the ultrasonication technique. The optimum ultrasonication time and the optimum surfactant HLB value for obtaining stable macroemulsions have been evaluated. Also, the effect of the high-pressure fuel injection system on the macroemulsion stability has been assessed. Microemulsions have been prepared using surfactants such as 1-dodecanol, pentanol, and butanol. The effect of surfactant and oil chain length on

microemulsion has been reported. The results show a comprehensive picture of the parameters affecting the emulsion stability, and the important findings from the current study are presented as follows:

- A methanol-in-diesel macroemulsion with 10 wt% methanol and 2 wt% surfactant was stable up to 469 h after preparation. The surfactant was a mixture of Tween-80 and Span-80 with an overall surfactant HLB value of 10.
- It is not feasible to produce a macroemulsion with more than 10 wt% of methanol. However, more than 10 wt% of methanol can be mixed with diesel by utilizing microemulsions.
- The surfactant, 1-dodecanol, permits any ration of methanol and diesel to be emulsified. In addition, due to high cetane number, 1-dodecanol is ideal to compensate the cetane number loss to the emulsion fuel. Butanol and pentanol can also be used as surfactants to prepare microemulsion.
- The optimum surfactant HLB value for preparing a methanol-in-diesel macroemulsion is 10.
- The ultrasonication is observed to a suitable method for preparing methanol-in-diesel macroemulsion, and the optimum ultrasonication time is found out to be around 25 min.
- Novel stability assessment protocols have been developed for use of these emulsion fuels in IC engines. Measurements of the size distribution of dispersed droplets in the methanol-in-diesel macroemulsions before and after fuel injection are compared to assess the stability of these emulsion fuels for use in engines. It is found out that the stability of the macroemulsions is not affected significantly by the injection pressure.

Nomenclature

M_h = hydrophilic molecular mass
M_l = lipophilic molecular mass
HLB_{comb} = combined HLB value of two surfactants

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