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Water-in-Diesel Emulsion, WiDE: Characterization with An Environmentally Friendly Surfactant

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Abstract

Diesel engines are efficient and cost-effective, but their emissions contribute to environmental pollution and health concerns. Policies worldwide target reductions in CO, CO2, PM, and NO emissions from diesel exhaust. This study explores the potential of water-in-diesel emulsion (WiDE) as a sustainable fuel by incorporating an environmentally friendly surfactant derived from renewable raw material (RRM) namely UMPSA surfactant. In addition, physico-chemical characterization was done to evaluate the performance WiDE formulated with Triton X-100, Span 80 in compared to UMPSA surfactant. In this study. 2% UMPSA surfactant, 5% Span-80, and 5% Triton X-100 were used to emulsify 30% water into 70% diesel, creating WiDE with water as the continuous phase and diesel as the dispersed phase. The research findings highlight the potential of WiDE as sustainable fuel by employing RRM's based surfactant while maintaining performance parity. This research breakthrough holds immense promise for advancing the development and adoption of WiDE as a viable and environmentally conscious alternative in the field of fuel technology.

Keyword: water-in-diesel emulsion, UMPSA surfactant, Span 80, Triton X-100, environmentally friendly.

1. Introduction

Outdoor air pollution, responsible for approximately 4.2 million global deaths annually, is a significant concern, with diesel exhaust being a major contributor (WHO, 2021). Diesel engines, prized for efficiency and cost- effectiveness, have led to a growing environmental challenge due to emissions like carbon monoxide, hydrocarbons, particulate matter, and nitrogen oxides (Reşitoğlu, Altinişik, & Keskin, 2015). Diesel exhaust's potential health effects are worrisome, particularly due to mutagens, carcinogens, and toxic pollutants it contains, posing risks such as airway inflammation, allergies, asthma, and chronic bronchitis, notably in children (Kagawa, 2002; IARC, 2012). Water-in-Diesel Emulsion (WiDE) is a type of fuel that blend water into diesel, stabilized by surfactants or emulsifiers. WiDE improves combustion efficiency, lowers CO_2 and NO_x emissions, and enhances engine performance (Abdurahman et al., 2016). Water presence influences combustion efficiency by enhancing particle oxidation (Vellaiyan & Amirthagadeswaran, 2016). Increasing water content in the fuel reduces CO_2 emissions, while the cooling effect of water vapor leads to lower NO_x emissions (Abdul Karim et al., 2014). This research aims to characterize WiDE formulated with UMPSA surfactant, Span 80, and Triton X-100 in terms of stability, physico-chemical properties, andcost.

Physico-chemical properties, such as viscosity and density, hold crucial roles in fuel system operation (Rand, 2010), with the presence of water increasing density and influencing storage and transport dynamics (Abdul Karim et al., 2014). Ensuring that the physico-chemical properties of emulsion fuel remain within acceptable limits becomes essential to minimize the need for extensive system modifications (Vellaiyan & Amirthagadeswaran, 2016). Emulsion stability is critical for engine operation, preventing damage to the combustion system. The surfactant's role in preventing water droplet separation from diesel is crucial for stability (Abdul Karim, Khan, Aziz, & Tan, 2014). Emulsion stability hinges on surfactant selection, impacting droplet stabilization (Nour, Abdurahman, & Yunus, 2007). However, it is important to consider the broader implications of synthetic surfactants for the environment and human health. An example is Triton X-100, a synthetic surfactant noted for its resistance to biodegradation, which can lead to its accumulation and impact soil, organisms, and crops (Shin, Jho, & Park, 2021).

As fossil fuel supplies decline, diesel prices continue to rise, affecting various sectors (U.S. Energy Information Administration, 2022; Diesel Technology Forum, 2022). In response to this trend, WiDE technology emerges as an economically viable solution, as it enhances combustion efficiency and overall performance (Vellaiyan & Amirthagadeswaran, 2016). However, despite its benefits, the economic feasibility of WiDE faces challenges due to the excessive costs associated with surfactants (Abuebite et al., 2020). To tackle this cost barrier and further promote sustainability, researchers are actively exploring the use of renewable raw materials to develop environmentally friendly and cost-effective surfactants (Benvegnu, Plusquellec, & Lemiègre, 2008).

2. Materials and Methods

2.1 Raw Materials

The materials that will be used include commercial diesel, tap water, Span 80 (R&M Chemicals), Triton X- 100 (Sigma Life Science), and UMPSA surfactant (synthesized in-house).

2.2 Methods

The emulsion will be composed of 30% water to 70% diesel and 2% UMPSA surfactant, and for the emulsion made from commercialized surfactant, it will be composed of 30% water to 70% diesel and 5% surfactant. To prepare the emulsion, diesel and surfactant will be poured into a 5L plastic beaker. The solution will be blended using a mechanical homogenizer at a mixing rate of 2000 rpm for 15 minutes at room temperature (Saad, Abdurahman, & Yunus, 2021).

As the homogenizer runs, water will be added little by little until the desired emulsion ratio is achieved. This will ensure that the emulsion is prepared consistently and uniformly, and the mechanical homogenizer will provide efficient and effective mixing. Moreover, the addition of water little by little will enable the preparation of a stableemulsion with minimal phase separation.

2.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis of WiDE is conducted by utilizing Attenuated Total Reflection (ATR) method. FTIR offers a quick and convenient way to study the emulsion's components, such as water, diesel, and additives, without extensive preparation (Lin et al., 2016). FTIR is valuable for quantifying water content, and understanding interactions between water and diesel components, aiding in optimizing emulsion formulations for better performance and environmental impact.

2.4 Gas chromatography–mass spectrometry (GC–MS)

The GC-MS methodology for WiDE, employing a GC-2010 system, is characterized by specific parameters ishighlighted in Table 2.1 and oven temperature program in Table 2.2.

Table 2.1: Parameters for GC-MS Analysis

Parameters	**Magnitude**
Column Oven Temperature	50°C Injection Temperature 250°C
Injection Mode	Split
Total Flow	21.6 mL/min
Column Flow	1.69 mL/min
Linear Velocity	47.2 cm/sec

Purge Flow	3.0 mL/min
Split Ratio	10.0

Table 2.2: Oven Temperature Program

	RateTemperature(°C)	Hold Time(min)
-	50.0	1.00
	10300.00	10.00

2.5 Viscometry and Density Meter

The viscosity of WiDE was determined using viscometry through two distinct methods. In the first method, the temperature was incrementally increased from 28°C to 100°C, while in the second method, the shear rate was systematically increased from 170 to 425 s^{-1}.For the temperature method, the emulsion was subjected to a controlled temperature ramp with continuous shear measurements, allowing the viscosity change to be observed over the temperature range. For the shear rate method, the emulsion was subjected to a progressive increase in shear rates while maintaining a constant temperature, facilitating the evaluation of viscosity variation at different shear stresses. Additionally, the density of WiDE was determined using an in-house method based on the KEM density meter.

2.6 Cost Estimation of Raw Materials

To estimate the costs associated with the raw materials used in the formulation of WiDE, a rough calculation can be employed through the following steps. Firstly, determine the cost of diesel fuel by multiplying the volume of diesel fuel utilized by its unit price per liter. Secondly, compute the cost of water by multiplying the volume of water incorporated by its respective unit price per liter. Lastly, ascertain the cost of surfactant by multiplying the volume of surfactant utilized by its unit price per liter. Summing up these individual costs provides the overall emulsion cost, represented as in equation 1.

Total Emulsion Cost = Cost of Diesel Fuel + Cost of Water + Cost of Surfactant ....(1)

Notably, the cost of water, when scaled down to laboratory quantities, is typically negligible and may not significantly impact the overall budget. It is imperative to note that this cost estimation should be regarded as a rough approximation, serving as a foundational reference for budgetary considerations within the research framework.

3. Results And Discussion

3.1 Chemical Characterization

3.1.1 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR results shown in figures 3.1 and 3.2 demonstrate a pronounced similarity between the WiDE produced with an in-house synthesized surfactant (UMPSA surfactant) and the reference product from a well-established brand, Span 80 as the benchmark. This similarity arises from the shared structural characteristics of oleic acid-based components in both surfactants. In contrast, the FTIR analysis of the synthetic surfactant Triton X-100 from figure 3.3 reveals significant disparities in its molecular composition relative to the oleic acid-based surfactants.

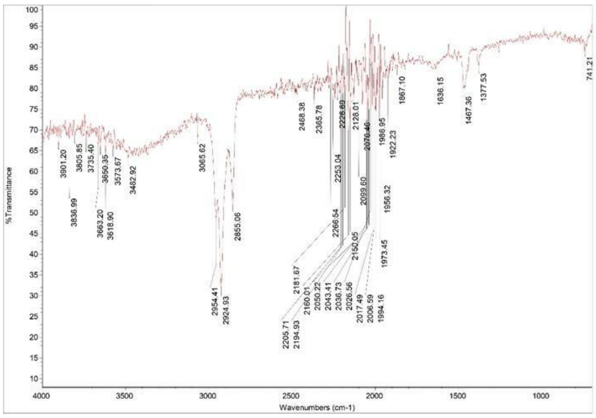


Figure 3.1: FTIR Result of WiDE Formulated with UMPSASurfactant

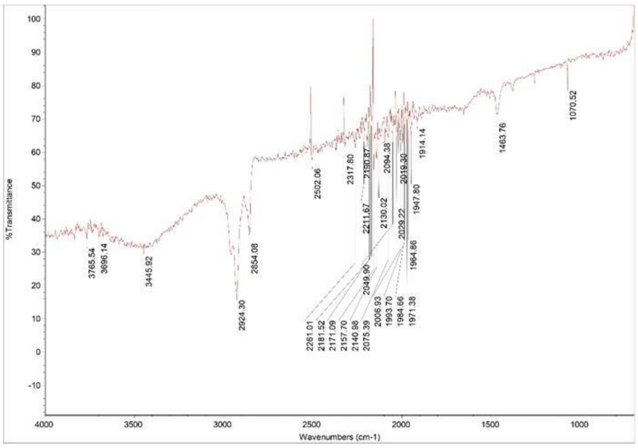


Figure 3.2: FTIR Result of WiDE Formulated with Span 80

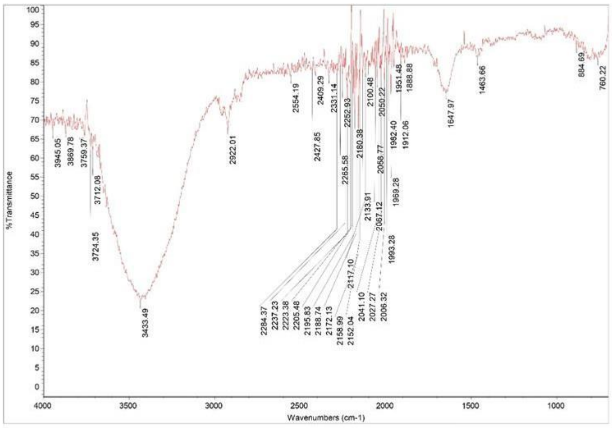


Figure 3.3: FTIR Result of WiDE Formulated with Triton X-100

3.1.2 Gas chromatography–mass spectrometry (GC–MS)

The GC-MS analysis of WiDE with UMPSA surfactant revealed a complex mixture of hydrocarbons and other compounds. Notable peaks included Tridecane, 4,8-dimethyl-, which was present in substantial quantities. Similar to the UMPSA surfactant emulsion, GC-MS analysis of

WiDE with Span 80 Tridecane, 4,8-dimethyl-, was present in significant quantities. The GC-MS analysis of WiDE with Triton X-100 surfactant exhibited a diverse mixture of compounds, with Tridecane, 4,8-dimethyl-, being a prominent component. Decane, 2,3,5,8-tetramethyl-, was also present at notable levels.

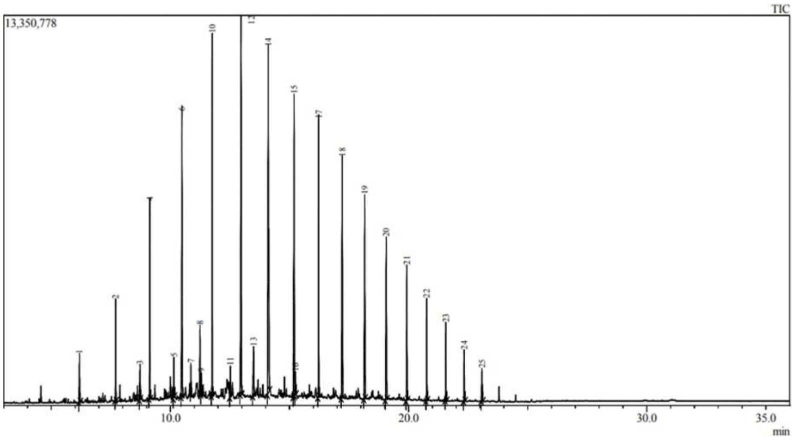


Figure 3.4: GC-MS Peak of WiDE Formulated with UMPSA Surfactant

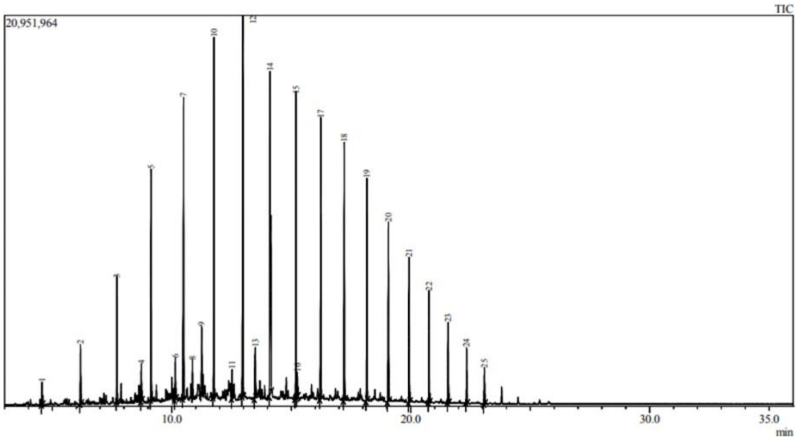


Figure 3.5: GC-MS Peak of WiDE Formulated with Span 80

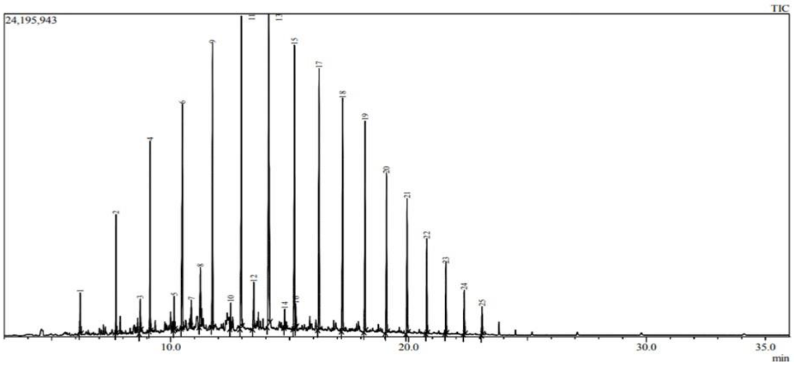


Figure 3.6: GC-MS Peak of WiDE Formulated with Triton X-100 Table 3.1: Chemical Composition of WiDE with 3 Different Surfactants

Peak	UMPSA Surfactant		Span 80		Triton X-100	
	Height, %	Chemical Compound	Height, %	Chemical Compound	Height, %	Chemical Compound
1	1.35	Nonane, 2-methyl	0.60	Nonane, 2-methyl	1.24	Nonane, 2-methyl-
2	2.83	decane, 4,8-dimethyl	1.55	Nonane, 2-methyl	3.64	decane, 4,8-dimethyl
3	0.96	Octane, 2,3,7-trimethyl	3.33	decane, 4,8-dimethyl	1.00	Decane, 2-methyl
4	5.54	decane, 4,8-dimethyl	0.98	Octane, 2,3,7-trimethyl	5.83	decane, 4,8-dimethyl
5	1.12	1-Iodo-2-methylundecane	6.16	decane, 4,8-dimethyl	1.03	ecane, 2,3,5,8-tetramethyl
6	7.98	decane, 4,8-dimethyl	1.10	1-Iodo-2-methylundecane	6.92	decane, 4,8-dimethyl
7	0.86	2,3-Dipropyl-cyclopropanecarboxylicacid, eth	7.94	decane, 4,8-dimethyl	0.75	2,6,10-trimethylundecanoicAcid, 2,2,2-trifluo
8	1.88	Decane, 3,7-dimethyl	0.95	2,3-Dipropyl-cyclopropanecarboxylic acid, ethy	1.80	adecane, 4,11-dimethyl
9	0.61	Tetradecane, 2-methyl	1.83	Decane, 3,7-dimethyl	8.77	decane, 4,8-dimethyl
10	9.97	decane, 4,8-dimethyl	9.64	decane, 4,8-dimethyl	0.79	Tridecane, 3-ethyl
11	0.87	Octadecane	0.79	Tridecane, 3-ethyl	9.56	Tridecane, 4,8-

						dimethyl
12	10.52	decane, 4,8-dimethyl	10.03	decane, 4,8-dimethyl	1.41	Pentadecane, 2,6,10-trimethyl
13	1.37	adecane, 2,6,10-trimethyl	1.35	adecane, 2,6,10-trimethyl	9.39	Octadecane
14	9.57	Octadecane	8.66	Octadecane	0.59	Tricosane, 2-methyl
15	8.4	Octadecane	8.18	Octadecane	8.69	Octadecane
16	0.65	decane, 2,6,10,14-tetramethyl	0.66	decane, 2,6,10,14-tetramethyl	0.74	exadecane, 2,6,10,14-tetramethyl
17	7.77	Octadecane	7.48	Octadecane	8.03	Octadecane
18	6.65	Octadecane	6.77	Octadecane	7.11	Octadecane
19	5.58	Nonadecane, 2-methyl	5.89	Nonadecane, 2-methyl	6.42	adecane, 2-methyl
20	4.5	Nonadecane, 2-methyl	4.72	Nonadecane, 2-methyl	4.91	adecane, 2-methyl
21	3.74	Eicosane, 2-methyl	3.86	Nonadecane, 2-methyl	4.13	adecane, 2-methyl
22	2.81	Eicosane, 2-methyl-	2.96	Nonadecane, 2-methyl	2.89	Eicosane, 2-methyl
23	2.15	Nonadecane, 2-methyl	2.14	Nonadecane, 2-methyl	2.17	adecane, 2-methyl
24	1.4	Nonadecane, 2-methyl	1.48	Eicosane, 2-methyl	1.34	Eicosane, 2-methyl
25	0.91	Eicosane, 2-methyl	0.96	Nonadecane, 2-methyl	0.86	Eicosane, 2-methyl

3.2 Physical Characterization

3.2.1 Viscosity

Viscosity behavior of WiDE formulations incorporating UMPSA surfactant, Span 80, and Triton X-100, considering temperature and shear rate variations as depicted in Figures 3.7 to 3.12. Increasing temperature leads to a consistent viscosity decrease across all formulations due to reduced intermolecular forces. Examining shear rate effects, WiDE with UMPSA surfactant initially sees viscosity rise as shear rate increases from 170 s^{-1} to 350 s^{-1}, followed by a decrease, likely linked to micelle alignment and disruption. WiDE with Span 80 displays intricate behavior: viscosity increases from 170 s^{-1} to 255 s^{-1}, then decreases to 340 s^{-1}, and increases once more beyond 340 s^{-1}, reflecting complex interactions between surfactant stabilization and structural changes. Conversely, WiDE with Triton X-100 consistently exhibits decreasing viscosity with rising shear rates, attributed to the surfactant's reduction of intermolecular interactions. Understanding these viscosity trends is vital for optimizing the utility of WiDE formulations across diverse applications.

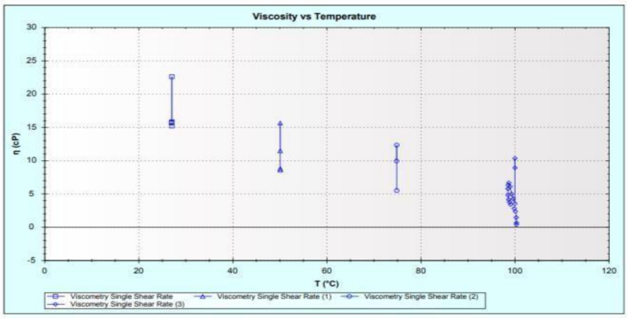


Figure 3.7: Viscosity Behavior of WiDE Formulated with UMPSA Across Temperature Variations

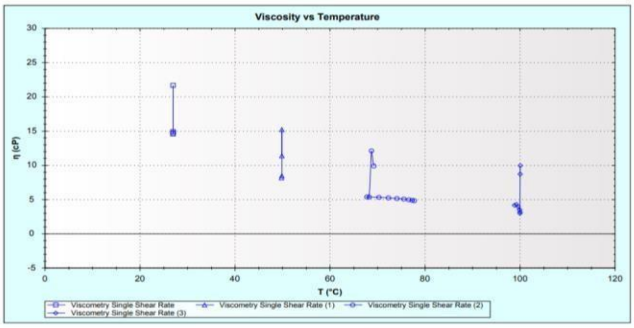


Figure 3.8: Viscosity Behavior of WiDE Formulated with Span 80 Across Temperature Variations

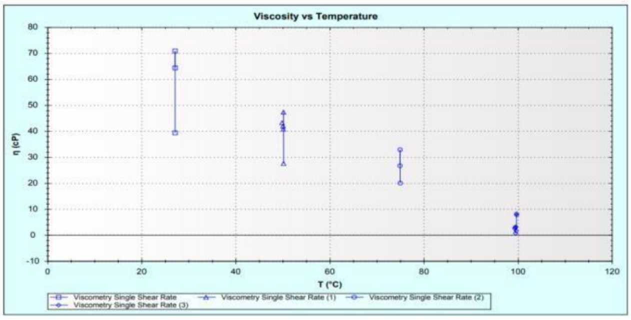


Figure 3.9: Viscosity Behavior of WiDE Formulated with Triton X-100 Across Temperature Variations

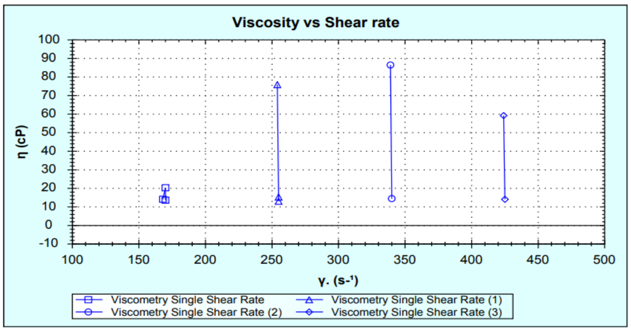


Figure 3.10: Viscosity Behavior of WiDE Formulated with UMPSA Surfactant Across Shear Rate Variations

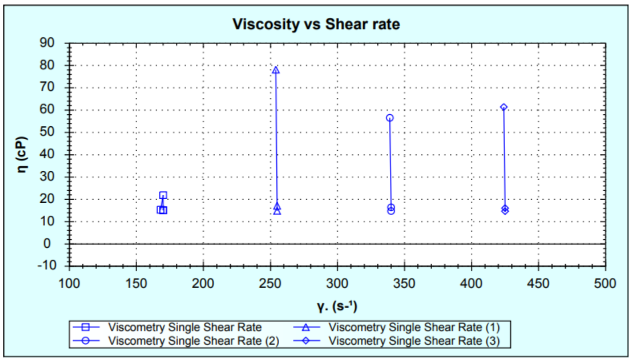


Figure 3.11: Viscosity Behavior of WiDE Formulated with Span 80 Across Shear Rate Variations

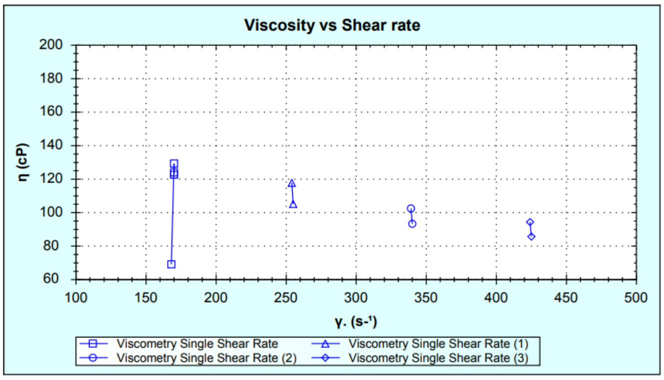
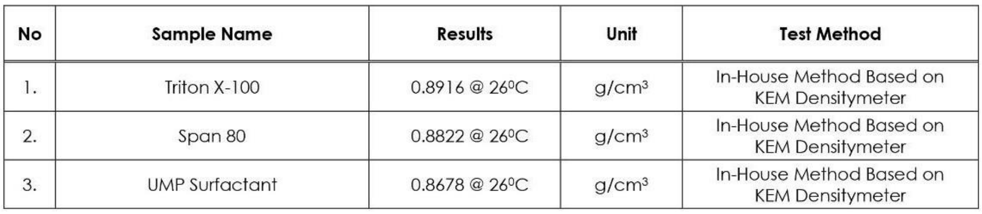


Figure 3.12: Viscosity Behavior of WiDE Formulated with Triton X-100 Across Shear Rate Variations

3.2.2 Density

UMPSA-based WiDE displays the lowest density at 0.8678 g/cm^3, while Span 80-based WiDE has a slightly higher density of 0.8822 g/cm^3, and Triton X-100-based WiDE exhibits the highest density at 0.8916 g/cm^3.



No	Sample Name	Results	Unit	Test Method
1.	Triton X-100	0.8916 @ 26⁰C	g/cm³	In-House Method Based on KEM Densitymeter
2.	Span 80	0.8822 @ 26⁰C	g/cm³	In-House Method Based on KEM Densitymeter
3.	UMP Surfactant	0.8678 @ 26⁰C	g/cm³	In-House Method Based on KEM Densitymeter

Figure 3.13: Density of WiDE with 3 Different Surfactant at 26°C

3.3 Cost Breakdowns of Raw Materials

The cost breakdown in table 3.2 reveals significant variations in the overall cost per liter among the WiDE formulations. Notably, WiDE formulated with UMPSA surfactant stands out as the most cost-effective option at RM 2.405 per liter. In contrast, WiDE formulations with Span 80 and Triton X-100 are relatively more expensive, with costs of RM 6.505 and RM 5.485 per liter, respectively.

Table 3.2: Raw Materials Cost Analysis

WiDE with UMPSA Surfactant: Diesel cost: RM 2.15 per liter Surfactant cost: RM 45 per liter Quantity of surfactant used: 0.02 liters per liter of WiDECost of diesel fuel: 0.7 x RM 2.15 = RM 1.505 per liter Cost of UMPSA surfactant: 0.02 x RM 45 = RM 0.9 per liter Total cost per liter of WiDE: RM 1.505 (diesel) + RM 0.9 (UMPSA surfactant) = RM 2.405 per liter
WiDE with Span 80: Diesel cost: RM 2.15 per liter Surfactant cost: RM 100 per liter Quantity of Span 80 used: 0.05 liters per liter of WiDE Cost of diesel fuel: 0.7 x RM 2.15 = RM 1.505 per liter Cost of Span 80: 0.05 x RM 100 = RM 5 per liter Total cost per liter of WiDE: RM 1.505 (diesel) + RM 5 (Span 80) = RM 6.505 per liter
WiDE with Triton X-100: Diesel cost: RM 2.15 per liter Surfactant cost: RM 79.60 per liter Quantity of Triton X-100 used: 0.05 liters per liter of WiDECost of diesel fuel: 0.7 x RM 2.15 = RM 1.505 per liter Cost of Triton X-100: 0.05 x RM 79.60 = RM 3.98 per liter Total cost per liter of WiDE: RM 1.505 (diesel) + RM 3.98 (Triton X-100) = RM 5.485 per liter

4. Conclusions

In conclusion, the findings from this study indicate a remarkable similarity between UMPSA surfactant and Span 80 in the production of WiDE, as evidenced by FTIR analysis. Additionally, GC-MS analysis identified Tridecane, 4,8- dimethyl-, as a dominant compound in all WiDE variants. Viscosity behavior across the different surfactants displayed an identical pattern, with viscosity decreasing as temperature increased; specifically, WiDE with UMPSA surfactant mirrored the viscosity pattern of Span 80, while Triton X-100 had the highest initial viscosity but the most significant reduction with increasing temperature. Furthermore, WiDE with UMPSA surfactant exhibited the lowest density at 0.8678 g/cm³ at 26°C. Notably, UMPSA surfactant offers a cost-effective alternative, priced at RM 2.45 per liter, compared to the higher costs associated with Span 80 (RM 6.505 per liter) and Triton X-100 (RM 5.485 per liter), while maintaining comparable performance.

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