A NOVEL APPROACH TO FORMULATION OF EMULSIFIED ACID USING WASTE OIL

BY

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To my caring Father, loving Mother and my exceptionally wonderful Siblings

How blessed and fortunate I am to have you. Without YOU none of my success would be possible, I thank you, I appreciate you more than words can ever express. I pray that you be showered with grace and blessings abundantly.

-Ziad

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LIST OF ABBREVIATIONS

α_c : Relaxation time constant
A : Characteristic constant
B : Characteristic constant
˚C : Degree Celsius
CI : Corrosion Inhibitor
cP : Centipoise
d : Droplet diameter
e : Euler's number ≈ 2.71828
˚F : Degree Fahrenheit
FID : Flame Ionization Detector
GC : Gas Chromatography
G^* : Complex modulus
G' : Storage (elastic) modulus
G'' : Loss (viscous) modulus
HCl : Hydrochloric acid
HLB : Hydrophile-Lipophile Balance
hr : Hours
K : Consistency coefficient
L : Liter
min : Minutes
m : Dimensionless exponent
n : Dimensionless flow behavior index
η : Viscosity
η_a : Apparent viscosity
η_0 : Zero-shear viscosity
η_∞ : Infinite-shear viscosity
o/w : Oil-in-water
Pa : Pascal
T : Absolute temperature
τ : Shear stress
vol% : Volume percent
w/o : Water-in-oil
wt% : Weight percent
$\dot{\gamma}$: Shear rate

ABSTRACT

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The demand for petroleum energy is increasing worldwide. With this increase, research in recovering maximum amount of hydrocarbon becomes necessary as well as inevitable. Therefore, research on stimulation practices turn out to be a promising field of study. In carbonate reservoirs, hydrochloric acid (HCl) is commonly used for stimulation purposes. The main reason for using HCl is its high and rapid reactivity. However, HCl may react with the tubing causing severe corrosion and damages. These damages can be avoided by using emulsified acid, in which the reaction is retarded. Such retardation helps the emulsified acid reach deep in the formation; hence deeper penetration.

Generally, it is the practice in the industry to emulsify HCl with the use of diesel as the oil phase. However, in this work, diesel is replaced by a less-costly, environmentally friendly oil -referred to as waste oil. The HCl emulsion with waste oil is prepared using a cationic emulsifier. Furthermore, a concentration of HCl of 15 wt% is used. The ratio of acid-to-oil is 70:30. Moreover, thermal stability and rheology of both diesel and waste oil emulsified acids are addressed (up to 120ºC). In both systems, the influence on thermal stability and rheology of emulsifier concentration, mixing speed, addition rate of acid phase to oil phase and temperature are studied extensively. These data are correlated to droplet size distribution in order to better understand them.

Results showed the high potential use of waste oil to prepare high temperature emulsified acid. It is noteworthy to mention that waste oil emulsified acid is a fit-for-purpose system. That being said, to increase the stability time for the system; emulsifier concertation, mixing speed should be manipulated to reach the targeted time.

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ملخص الرسالة

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التخصص : هندسة بترول
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يوماً بعد يوم و مع التطور الصناعي و النمو الاقتصادي ، ازدادت الحاجة السنوية للنفط ومشتقاته حول العالم. و بسبب هذه الزيادة اضطرت الشركات العالمية المنقبة عن النفط لزيادة الإنتاج السنوي ، إلا أنّ هذه الزيادة تعد تحديا كبيراً بإستخدام طرق الحفر والإنتاج التقليدية. ولهذا فإن الدراسات والبحوث في مجال تحفيز إنتاج الحقول النفطية تُعد أرضاً خصبة للباحثين و العلماء ؛ لما لها من أهمية بالغة وتأثير كبير في وقتنا الحالي و في المستقبل.

ومن الطرق المتبعة حالياً لتحفيز الإنتاج النفطي في الحقول ، ضخ حمض الكلور في مكامن النفط الكربونية مما يؤدي الى توسع الشقوق الحجرية وزيادة كمية النفط المتسربة منها ليتم إنتاجها. بيد أن إستخدام حمض الكلور يؤدي الى تآكل و صدأ الأنابيب المستخدمة في ضخه. لذلك ، فإن الإجراء المُتبع في هذه الحالات لجعل الحمض يصل إلى مناطق أبعد و أعمق في المكامن النفطية هو تخفيف الحمض عن طريق ما يسمى بالإستحلاب (Emulsification).

في الصناعة النفطية يقام غالباً بإستحلاب حمض الكلور مع الديزل. أما في هذا البحث فقد تم دراسة أثر استبدال الديزل بزيت آخر أقل كلفة وأكثر وفرة ومحافظ للبيئة ، يطلق عليه بالزيت المُهمل. لقد تم استعمال – في هذا البحث – محلول حمض الكلور بتركيز ١٥٪ وبنسبة الحمض إلى الزيت

بمقدار ٧٠ إلى ٣٠٪. وتم استحلاب الحمض مع الزيت المُهمل بإستخدام مستحلِب ذو شحنة موجبة.

لقد قام البحث بدراسة الإستقرار الحراري والريولوجيا لكلا المستحلَبيْن (مستحلَب الديزل و مستحلَب الزيت المُهمل) وتمت مقارنة النتائج حتى درجة حرارة ١٢٠ درجة مئوية. وتمت أيضاً دراسة تأثير كل من : تركيز المستحلِب ، معدل إضافة الحمض للزيت ، سرعة المزج و أخيراً تغيُر الحرارة على الإستقرار الحراري والريولوجيا للمزيج. لقد تم ربط تلك البيانات مع توزيع حجم القطرات من المستحلَب.

تُظهر النتائج الإمكانية العالية لإستبدال الديزل بالزيت المُهمل في تحضير مستحلَب حمض الكلور حتى درجات حرارة عالية. ومن الجدير بالذكر أن الحمض المستحلَب بالزيت المُهمل ذو إمكانية لتغيير خصائصه طبقاً للغرض المستخدم إليه. على سبيل المثال، يمكن زيادة كمية المستحلِب وسرعة المزج من أجل ديمومة إستقرار المستحلَب لفترة أطول.

درجة الماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

المملكة العربية السعودية – الظهران - ٣١٢٦١

CHAPTER 1

INTRODUCTION

In petroleum industry, producing the maximum amount of hydrocarbon is essential. Hence, trying to invent new methods and means to maximize the production is inevitable. Well stimulation is one way to go about maximizing the hydrocarbon production. For well stimulation purposes, matrix acidizing is commonly used. And, in carbonate reservoirs, hydrochloric acid (HCl) is the one in common use for acidizing. In acidizing, solids and sediments in the pores are dissolved by the acids resulting in a better conduit i.e. increasing the permeability of the rock. Ultimately, permeability increase means more hydrocarbon production. However, ordinary acids are corrosive by nature and harmful to well tubings. Therefore, emulsified acids are widely used to avoid the potential damages that could be caused by ordinary acids.

The aim of this introductory chapter is to brief the reader about the necessary fundamentals to better understand this work. This is accomplished through seven distinctive sections. The first section addresses stimulation. The second one, briefs on emulsions and their types. The third one, explains emulsion stability. Further, the fourth section refers to emulsifiers and their applications. The fifth, discuses specifically emulsified HCl. Moreover, the sixth section describes rheology of emulsions. Finally, the seventh section provides a basic grounding in the particle size characterization techniques.

1.1 Stimulation

In oil and gas industry, stimulation is mainly meant to increase ultimate economic recovery by faster delivery of the petroleum fluids (Economides Michael et al., 2000). That being said, the productivity of a well is going to be enhanced. This enhancement could be by matrix stimulation and/or hydraulic fracturing.

As far as matrix stimulation is concerned, mainly acidizing is meant when describing matrix stimulation. In acidizing, solids and sediments in the pores are dissolved by the acids resulting in a better conduit which increases the connectivity between the pores. Thus, increasing the permeability of the rock.

Usually, when there exists a formation damage in a well caused by drilling, completion or even workover; acidizing is applied primarily to remove that damage. This damage could be due to pores plugging, hence removal of severe plugging can result in a better enhancement in well productivity. On the contrary, if no damage exists, the enhancement of the well productivity due to acidizing is occasionally over 50%. It, however, depends on other factors such as the depth of penetration and treatment size (McLeod, 1986).

With regards to hydraulic fracturing in carbonate reservoirs, it is best applied to those of low temperatures and shallow depth. HCl of 15 wt% is the common fluid used in fracturing. However, sometimes, HCl of 28 wt% is preferred in order to attain more penetration as well as more etching. Besides the concentration of HCl, other factors may affect the penetration depth. Such as temperature of the reservoir, width of the fracture, viscosity of HCl and the rate of injection (Williams et al., 1979).

1.2 Emulsions

An emulsion is defined as a dispersion of one immiscible liquid into another through the use of a chemical that reduces the interfacial tension between the two liquids to achieve stability. One of these two liquids is found in the form of finely distributed spherical droplets in the second one-the continuous phase. If oil is dispersed in water, the emulsion is considered an oil-in-water (o/w) emulsion and vice versa for water-in-oil (w/o) emulsion (Mollet et al., 2008). **Figure 1.1** depicts a w/o emulsion and the emulsifier molecules are holding the two phases together. There are several properties of emulsions. However, the most important ones are: stability, viscosity, particle size and concentration. Usually, these properties depend on each other; concentrated emulsions are very viscous and have smaller droplet size (Gopal, 1963). **Figure 1.2** shows the particle size ranges in which liquid-liquid dispersion appear. In general, for a stable emulsion to be formed, three basic conditions must be met (Chen et al., 2005):

1- The two liquids must be mutually insoluble in each other
2- Addition of emulsifying agent to reduce the interfacial tension
3- A sufficient agitation in order to disperse one liquid into the other

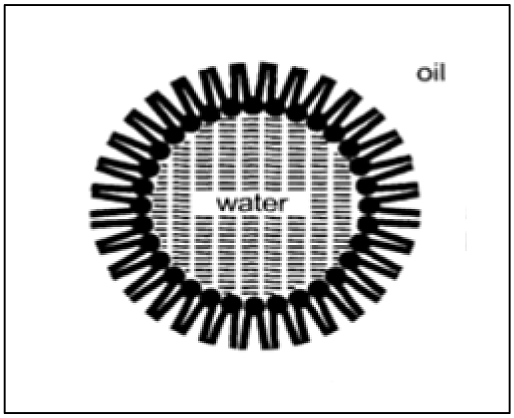


Figure 1.1: Water in oil emulsion with emulsifier (Mollet et al., 2008)

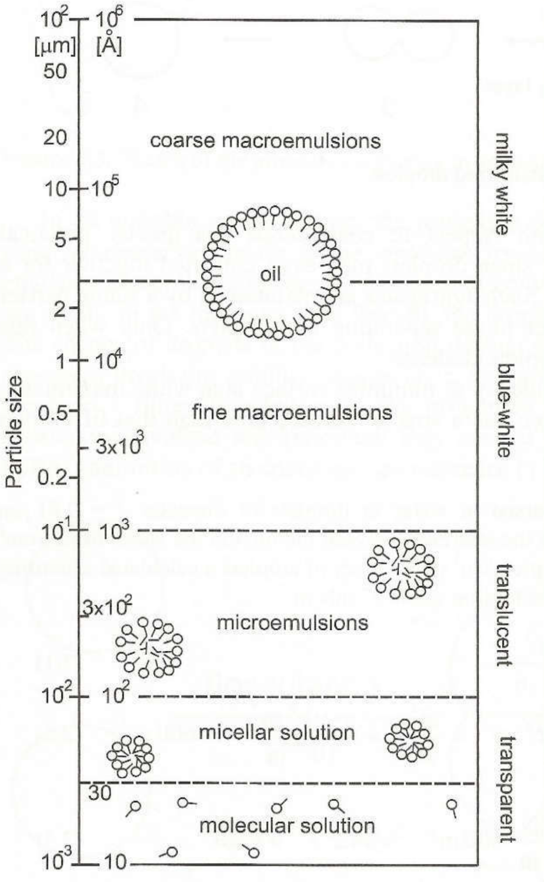


Figure 1.2: Droplet size ranges of emulsions (Mollet et al., 2008)

1.3 Emulsion Stability

When doing an acidizing job, it is essential for the emulsion to reach the formation with no separation of the acid phase. Otherwise, no retardation could occur. Hence, the stability of emulsions is very critical for field applications (Al-Anazi et al., 1998). There are three distinct processes in which an emulsion can break. These processes are: creaming, breaking and flocculation. Any or all of them can occur after the preparation of the emulsion as depicted in **Figure 1.3**. Creaming is the rise of the dispersion phase while the droplets are touching each other without bursting. Creaming could be upward or downward, deepening on the density of the fluids and it is not considered as instability. On the other hand, breaking is the natural joining of two small droplets or more to form bigger ones in the emulsion, also known as coalescence which leads to destroying the emulsion as shown in **Figure 1.4**. However, flocculation of aggregation is when droplets stick together but without the droplets coalesce. In flocculation, as long as the individual droplets are there, the emulsion is still stable (Kitchener et al., 1968). The droplet formed by coalescence has a smaller surface area compared to its two parent droplets together. Hence, it is known that the tendency of maximizing the volume while minimizing the surface area is the reason behind coalescence (Mollet et al., 2008). Nevertheless, emulsion instability is designated by the separation of water phase or by the complete separation of the two phases (Opawale et al., 1998).

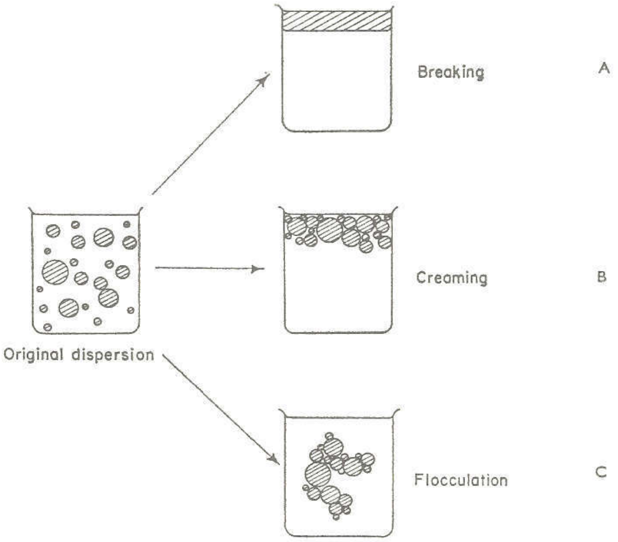


Figure 1.3: Diagrammatic representation of types of instable emulsions (Kitchener et al., 1968)

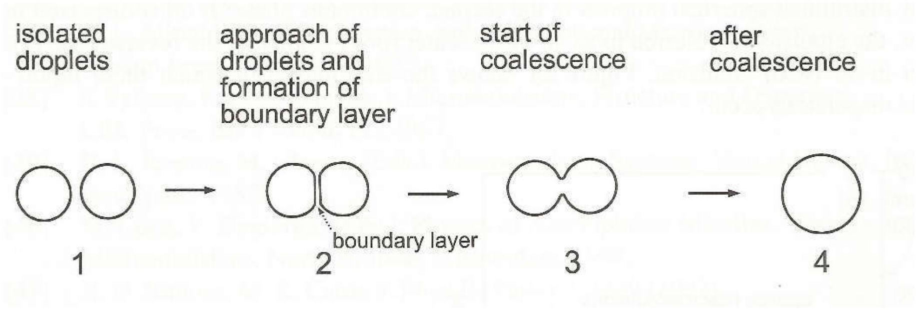


Figure 1.4: Coalescence of two droplets (Mollet et al., 2008)

1.4 Emulsifiers (Emulsifying Agents)

The emulsifier determines the stability of the emulsion as well as it decides its type, w/o or o/w. An emulsifier is composed of two parts: head and tail. Where the head is hydrophilic and the tail is lipophilic (hydrophobic). The tail is a hydrocarbon chain which is soluble in oil and the head has affinity for water. When the emulsifier molecules are added to oil and water interface, the hydrophilic head will be submerged in the water phase. Whereas, the lipophilic hydrocarbon tail will be extended into the oil phase (Mollet et al., 2008). **Figure 1.5** portrays a typical hydrophilic-lipophilic molecule.

To know what type of emulsion will be formed, the hydrophile-lipophile balance (HLB) number is used. The HLB number characterizes the emulsifiers from 1 to 20. An emulsifier with an HLB number ranges from 3 to 6 produces w/o emulsions (Griffin, 1946). **TABLE 1.1** summarizes the HLB numbers and their applications.

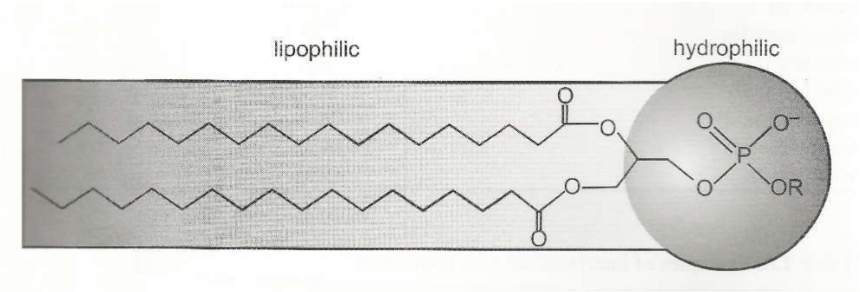


Figure 1.5: A typical hydrophilic-lipophilic molecule (Mollet et al., 2008)

TABLE 1.1: HLB values of emulsifiers and their applications (Mollet et al., 2008)

	HLB value	Application
lipophilic	0 - 3	Defoamers
↓	3 – 8	W/O emulsions
	7 – 9	Wetting agents
	8 – 18	O/W emulsions
	11 – 15	Detergents
hydrophilic	15 – 18	Solubilizes

1.5 Emulsified HCl

Diluted HCl of 15 wt% is commonly used. Emulsifying acid could be done with the aid of an emulsifier and a hydrocarbon phase such as diesel. Diesel is the commonly used as the hydrocarbon (continuous) phase (Al-Mutairi et al., 2008).

At high temperature, both reaction and corrosion rates become very high and regular HCl loses its advantages. There are many advantages associated with emulsified acids over ordinary ones. The main advantage is to achieve deep penetration due to the barrier caused by the hydrocarbon phase. Another reason is that minimum additives (iron control agents and Corrosion Inhibitor (CI)) are needed due to minimum contact with the well tubing. Also, the relatively high viscosity resulting in better sweep efficiency (Al-Mutairi et al., 2008).

Hence, the development of greater performing emulsification systems has permitted a significant improvement in the performance, stability, and properties of emulsion fluids (Young, 2011).

1.6 Rheology of Emulsions

Rheology is defined as the study of flow of matter and the deformation (Morrison, 2001). An important part of rheology is viscosity. Viscosity describes the tendency of fluid to resist an external force by internal friction. In Newtonian fluids, the shear stress (τ) in Pa, is proportional to the shear rate ($\dot{\gamma}$) in s^{-1}. And viscosity (η) in Pa.s, is the proportionality factor, (Equation 1.1).

$$\tau = \eta \, . \, \dot{\gamma} \tag{1.1}$$

Fluids that obey the Newtonian law of laminar friction, hence obeys Equation 1.1 are called Newtonian fluids. However, fluids for which the viscosity depends on shearing or time are known as non-Newtonian fluids. Viscosity of non-Newtonian fluids is referred to as apparent viscosity. Non-Newtonian fluids are classified into shear-thickening, shear-thinning, rheopectic and thixotropic. In shear-thinning fluids, the apparent viscosity decreases with increasing shear stress. Unlike shear thickening fluids, the apparent viscosity increases with increasing shear stress (Mollet et al., 2008).

Another important part of rheology is the viscoelasticity which is observed in emulsion. That being said, emulsions show both elastic and viscous behavior (Mollet et al., 2008). Viscoelastic behavior is measured by both oscillating and dynamic loading. The relevant parameters are the complex shear modulus G*, the loss (viscous) modulus G″ and the storage (elastic) modulus G′ where all three of these moduli have the SI units of Pa (Laba, 1993). Equation 1.2 shows the relationship between G′ and G″.

$$G^* = G' + \boldsymbol{i}\, G'' \tag{1.2}$$

There are some models used to predict the apparent viscosity of emulsified acids (pseudo-plastic fluids). For intermediate shear rates, power-law model which graphs on log-log scale a straight line, is represented by Equation 1.3.

$$\eta_a = K \, \dot{\gamma}^{n-1} \tag{1.3}$$

Where η_a is the apparent viscosity with Pa.s unit, K is the consistency coefficient with Pa.s^n unit, $\dot{\gamma}$ is the shear rate with s^{-1} unit and n is the dimensionless flow behavior index which represents the nearness of Newtonian flow. The fluid is shear-thinning, if the index n < 1 and shear thickening if n > 1. A plot of apparent viscosity over a wide range of shear rate data on log-log scale shows three discrete regions. Infinite-shear viscosity η_∞ occurs at high shear rate and zero-shear viscosity η_0 at low shear rate. Also, intermediate shear rate depicts power-law region. **Figure 1.6** illustrates the three regions.

Furthermore, for a wide range of shear rate, cross model becomes very handy. However, it uses five parameters which makes it harder to be used compared to power-law model. Cross model is presented in Equation 1.4

$$\eta_a = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1+(\alpha_c \dot{\gamma})^m} \tag{1.4}$$

Where α_c is a constant related to the relaxation time of the fluid, m is a dimensionless exponent (Rao, 2014)

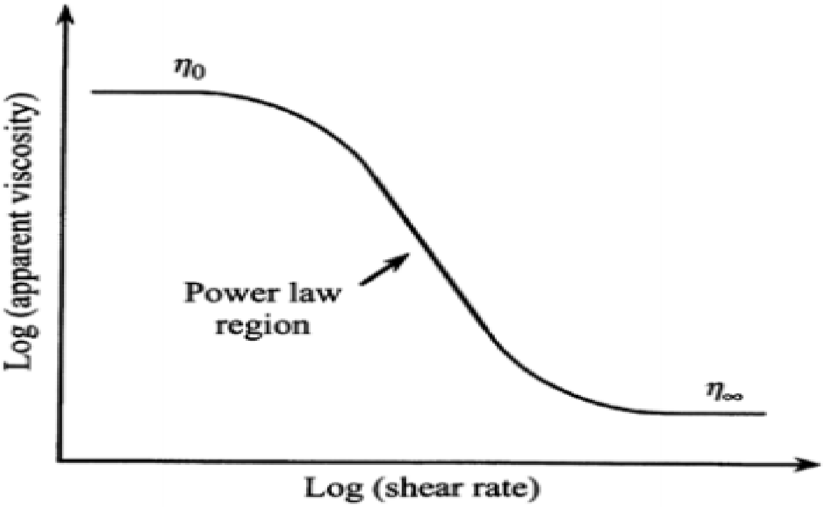


Figure 1.6: Three regions for apparent viscosity of wide range of shear rates (Rao, 2014)

Furthermore, the apparent viscosity has an inverse relationship with temperature. That being said, an increase in temperature results in decreasing the apparent viscosity. There are many models to describe said relationship, however, the most common one for emulsions is Arrhenius equation. Arrhenius stated that the viscosity is exponentially related to the inverse of the absolute temperature as depicted in Equation 1.5 (Arrhenius, 1889).

$$\eta = A\, e^{(B/T)} \tag{1.5}$$

Where η is the viscosity, A and B are characteristic constants and T is the absolute temperature.

1.7 Characterization Techniques of Particle Size

Measuring particle size is essential to emulsion quality. In addition, it is essential to understanding how these particles affect the emulsion and its stability. It is common to represent the distribution of particle size in the form of frequency distribution. In which, there is a range of statistical parameters that can be reported such as mean, median, mode and percentiles. These parameters will help in comparison and understanding of the data. Median is the size in which 50% of population is above/below, whereas, mode is the size with the highest frequency. Mean is the average size of a population. There are several methods to calculate the mean, however, for the scope of this work only the most common will be discussed. The number-length mean D[1,0], otherwise known as the arithmetic mean defined in Equation 1.6 as:

$$\mathrm{D}[1,0] = \frac{\sum d}{n} \tag{1.6}$$

Where d is the diameter of the droplet and n is the number of the droplets. It is called D[1,0] because it has d^1 in the numerator and d^0 in the dominator. The arithmetic mean is dependent on the number of droplets in the sample. However, there are other means which are independent on the number of droplets in the sample, known as moment means. The most common of moment means are the surface area moment mean or Sauter Mean Diameter, D[3,2], and the volume moment mean or De Brouckere Mean Diameter, D[4,3]. Sauter Mean Diameter is most relevant where specific surface area is important and is most sensitive to the existence of fine particles in the distribution. It is defined as in Equation 1.7:

$$\mathrm{D}[3,2] = \frac{\sum d^3}{\sum d^2} \tag{1.7}$$

And for the same mathematical logic, it is called D[3,2]. As for the volume moment mean, D[4,3], often referred to as De Brouckere Mean Diameter. It reflects the size of those particles which constitute the bulk of the sample volume and it is most sensitive to the existence of large particles in the distribution. It is given in Equation 1.8:

$$\mathrm{D}[4,3] = \frac{\sum d^4}{\sum d^3} \tag{1.8}$$

Laser diffraction calculates the distribution based on the volume and this is why it is reported using D[4,3].

Also, for volume weighted particles, percentiles are used. It is convenient to report data based on the maximum particle size for a given percentage volume of the sample. For example, the 10th percentile of a sample means the maximum particle diameter below which 10% of the sample volume exists. The most common reported percentiles are 10th, 50th and 90th; because by observing them, it would be possible to see if there are substantial changes in the overall particle size. As well as changes at the extremes of the distribution, which could be due to the presences of very fine or oversized particles.

CHAPTER 2

LITERATURE REVIEW

In 1975, (Bergstrom et al.) used a 70:30 acid-to-diesel ratio of HCl of 15 wt% with 1% surfactant and they found out that 50% of the emulsion broke out at 250˚F (121˚C) within 1 hour and within 15 minutes at 300˚F (149˚C). **TABLE 2.1** summarizes the static stability results at different temperatures. Also, for the same emulsion they measured the fann viscosity at 200˚F (93˚C) which was 53 cP and 32 cP at 100 RPM and 300 RPM, respectively. **TABLE 2.2** sums up the viscosity results.

TABLE 2.1: Stability results at different temperatures (Bergstrom et al., 1975)

TEMPERATURE, ˚F	TIME REQUIRED FOR 50% EMULSION BREAKOUT
75	Over three days
150	Over three days
200	Two days
250	One Hour
300	15 Minutes

TABLE 2.2: Viscosity results at different temperatures (Bergstrom et al., 1975)

TEMPERATURE, ˚F	FANN VISCOSITY, cP	
	100 RPM	300 RPM
80	96	58.3
100	90	56
125	85	50
150	80	48
175	71	43
200	53	32

Al-Anazi et al. (1998) studied the effect of emulsified acid in a tight carbonate reservoir where they tried to stimulate a dead well. They used acid-in-diesel emulsion, 70 vol% HCl (15 wt%): 30 vol% diesel. They found out that the stability of the acid decreased as temperature increased. Also, the stability decreased in the presence of the reservoir rock and the emulsified acid was stable for more than 72 hours at 24˚C, but when reservoir conditions (T= 96˚C and P =2500 psig) were used, the emulsified acid started to separate after 85 minutes. Then, gradually the acid phase started to increase (separate) until complete separation occurred after 219 minutes. Further, they measured the apparent viscosity at three temperatures, namely 24, 35 and 45 ˚C as a function of shear rate. They concluded that the apparent viscosity decreased with increase of temperature.

Navarrete et al. (1998) conducted experiments on emulsified acid with different strength at high temperature. The ratio they used was 70:30 HCl-to-diesel using three different HCl strengths 15 wt%, 20 wt% and 28 wt%. They reported that for more than 2 hours this emulsified acid was stable at 225˚F (107˚C) and for more than 1 hour at 300˚F (149˚C). In addition, the rheological behavior of the emulsified acid was measured for three different HCl strengths. Their finding was that the apparent viscosity decreased with temperature increase. Moreover, at a constant temperature, the increase of HCl strength resulted in an increase in the apparent viscosity.

Buijse et al. (1998) studied the apparent viscosity of the emulsified acid as a function of temperature. They first optimized the acid/diesel ratio to 70:30. They used 15 wt% of HCl and 1 vol% of emulsifier. The emulsion broke at 145˚C. Moreover, at shear rate of 170 s^{-1} at 25˚C, the apparent viscosity was 276 cP. Other data pertinent to viscosity measurements are summarized in **TABLE 2.3**.

TABLE 2.3: Summary of apparent viscosity of emulsified acids (Buijse et al., 1998)

			Apparent Viscosity, cP	
Temperature, ˚C	n	K	40 s^{-1}	170 s^{-1}
25	0.74	0.023	406	276
85	0.76	0.007	142	101
115	1.35	0.001	55	52
145*	0.69	0.000	<1	<1

*Broken emulsion

Nasr-El-Din et al. (2000) prepared an acid-to-diesel emulsion with 70:30 ratio and emulsifier concentration ranging from 0.2 to 2 vol% with some additives. They used 15wt% of HCl. They studied the thermal stability by pouring the emulsion in a graduated cylinder and then placing it in an oil bath at 130˚F (54˚C). Further, the volume of the acid separated was monitored with time. Results showed that the emulsion was more stable for higher emulsifier concentrations. Moreover, they measured the apparent viscosity at 75˚F (24˚C) as a function of shear rate. They concluded that the emulsion is a shear-thinning fluid. **Figure 2.1** shows the apparent viscosity results.

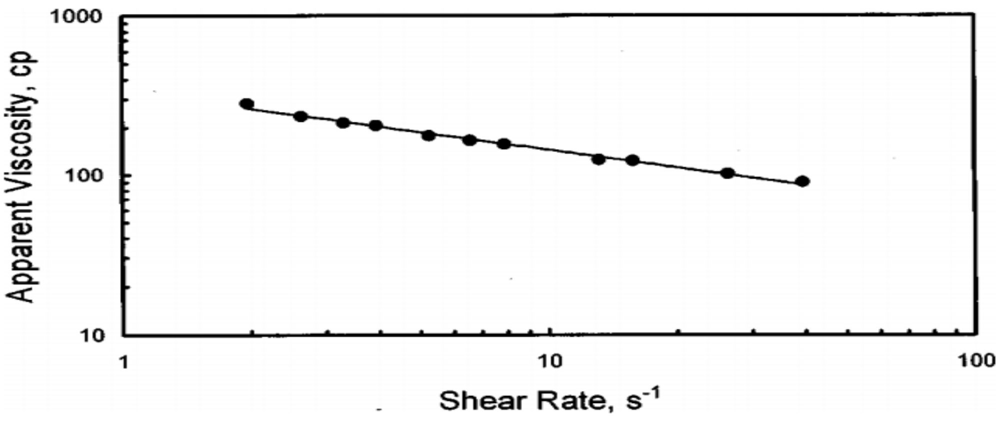


Figure 2.1: Apparent viscosity of emulsified acid at 75˚F(24˚C) (Nasr-El-Din et al., 2000)

Nasr-El-Din et al. (2001) used emulsified acid of 28 wt% HCl with 70:30 acid to diesel volume ratio with cationic emulsifier to stimulate deep sour, gas wells. The laboratory results showed that the emulsion at ambient condition was stable for over 2 days. But, at 250˚F (121˚C) the emulsion was stable for more than 4 hours. Moreover, the study confirmed that the emulsified acid was a shear-thinning fluid with a value of 300 mPa.s of apparent viscosity at 76˚F (24˚C) and 10 s^{-1} of shear rate. **Figure 2.2** represents the apparent viscosity at different shear rates at 76˚F (24˚C).

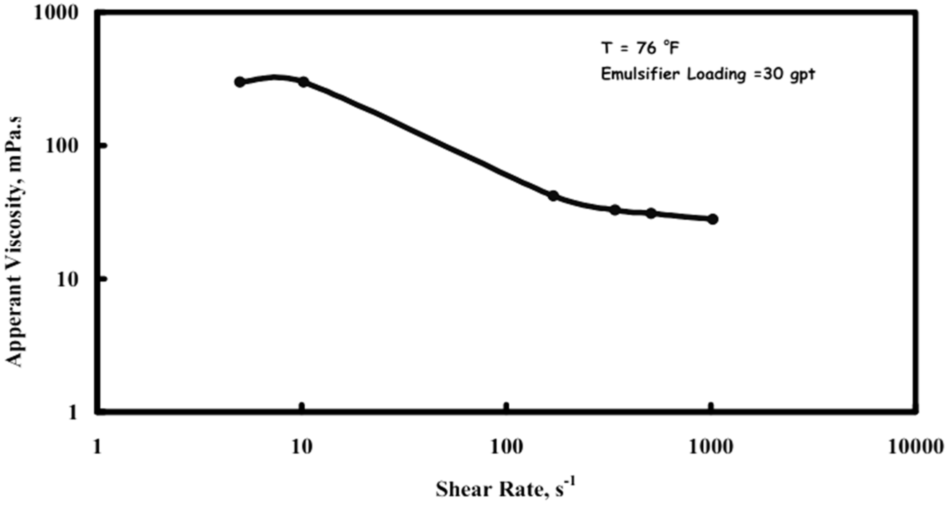


Figure 2.2: Apparent viscosity of emulsified acid at different shear rates at 76˚F (24˚C) (Nasr-El-Din et al., 2001)

Lynn et al. (2001) developed an emulsified acid system with 28 wt% of HCl of 70:30 ratio. They added corrosion inhibitor of 0.3 vol% and a volume percentage of 1.5 of cationic emulsifier. They found out their emulsion was stable for more than 5 hours at 250˚F (121˚C) with 300 psi of pressure applied.

In 2006, (Kasza et al.) conducted a study to select the best acidizing fluid to stimulate production wells of a reservoir in Poland. The reservoir had a high temperature of 120˚C.

They found out the best practice was to emulsify 15 wt% of HCl with crude oil in a 50:50 acid-to-oil ratio along with 2 vol% of emulsifier. This emulsion was stable for 180 minutes at 120˚C. Further, the apparent viscosity data are summarized in **TABLE 2.4**.

TABLE 2.4: Apparent viscosity data of 50:50 emulsified acid with crude oil (Kasza et al., 2006)

Temperature, ˚C	n	K, $lb*s^{n'}/ft^2$
20	0.4279	0.0453
30	0.5093	0.0144
40	0.5093	0.0144
50	0.3859	0.0144
60	0.3962	0.0181
80	0.3623	0.0147

Al-Mutairi et al. (2008) studied the effect of emulsifier concentration and acid volume fraction on the rheological properties and stability of emulsified acids. They ranged the temperature form 25 to 80˚C and they used three different emulsifier concentration 1, 5 and 10 gpt (0.1, 0.5 & 1 vol%, respectively). They used HCl of 15 wt% diluted with distilled water and the continuous phase was diesel. They reported that acid volume fractions close to 0.7 were more stable than others. Also, they found out that the viscosity of emulsified acid increased with acid volume fraction at high emulsifier concentration, 10 gpt (1 vol%). But, at low concentration 1 gpt (0.1 vol%), the viscosity increased as the acid volume fraction was increased from 0.4 to 0.6. Furthermore, they went on and studied the effect of mixing the two phases on the droplet size. **Figure 2.3** shows the resulted emulsion of different mixing methods. **Figure 2.3A**, shows an emulsion resulted from a few minutes of hand shaking, whereas, **Figure 2.3C** shows an emulsion resulted by atomizing the acid phase to diesel with the aid of a pressure nozzle. However, the emulsion in **Figure 2.3B** is the result of mixing both of the two previous emulsions i.e **Figure 2.3A** & **Figure 2.3C**. Also, the apparent viscosity decreased as the temperature increased from 25 to 80˚C. They concluded their study stating that fine emulsions tend to have higher apparent viscosity compared to the coarse ones. That being said, an increase of droplet size dedicated a decrease in apparent viscosity.

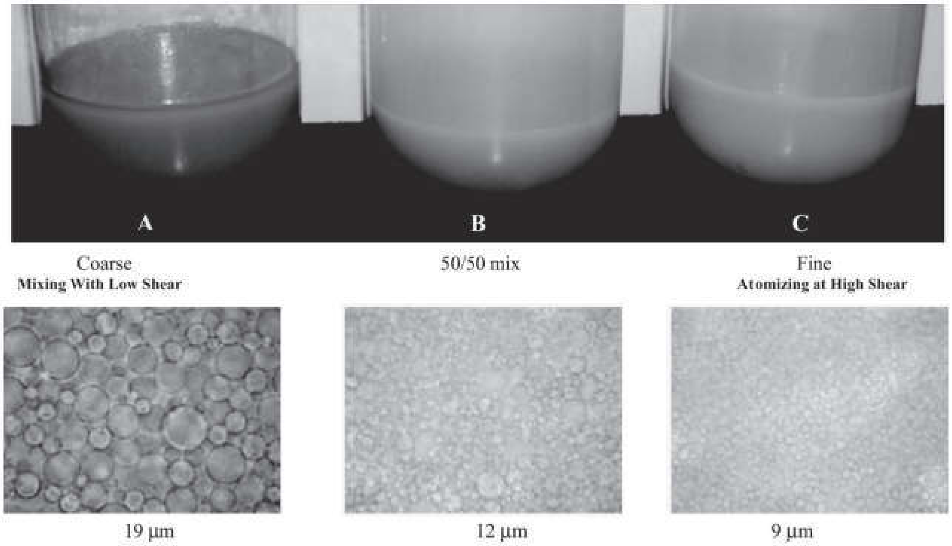


Figure 2.3: Effect of mixing on droplet size (Al-Mutairi et al., 2008)

Nasr-El-Din et al. (2008a) optimized the acid to diesel ratio and reported that 70:30 is the optimum one.

Al-Mutairi et al. (2009) formed HCl emulsions with 70:30 acid to diesel ratio of 15 wt% HCl at different temperatures: 25, 50 and 85˚C and at varied emulsifier concentration from 1 to 10 gpt. They noted that the addition of the acid phase to oil phase was of critical importance. Hence, they fixed the addition rate at 14 mL/min in order to ensure reproducible data. At different temperatures, apparent viscosity measurements were conducted, over a range of shear rates of 10 to 750 s^{-1}. At high temperatures, a pressure of 300 psi was applied to minimize evaporation. The results of apparent viscosity measurements were fitted perfectly in the power-law model. Apart from that, the increase of emulsifier concentration resulted in a decrease in average droplet size. The average droplet size was found to be 12.4, 8.4 and 6.0 µm for 0.1, 0.5 and 1 vol%, of emulsifier concentration, respectively. Additionally, they mentioned that increasing the temperature resulted in decreasing the apparent viscosity for the same emulsifier concentration. **TABLE 2.5** lists the findings of the results. In addition, **Figure 2.4** displays their data of apparent viscosity.

Appicciutoli et al. (2010) used 70:30 ratio of 15 wt% HCl to diesel with 2.5 vol% of emulsifier and mixed it at 3,000 rpm. The addition time of acid to diesel was 2 minutes which resulted in a stable emulsion at 70˚C for more than 2 hours.

TABLE 2.5: Summary of the findings of the experiments (Al-Mutairi et al., 2009)

	Set 1	Set 2	Set 3	Set 4	Set 5
Temperature, ˚C	25	25	25	50	85
Acid volume fraction	0.7	0.7	0.7	0.7	0.7
Corrosion concentration, gpt	5	5	5	5	5
Emulsifier concentration, gpt	1	5	10	10	10
Droplet size, µm	12.4	8.4	6.0	6.0	6.0
Power-law index	0.73	0.68	0.65	0.66	0.59
Power-law consistency index, g/(cm.s^{n-2})	1.145	3.129	3.347	2.363	1.030

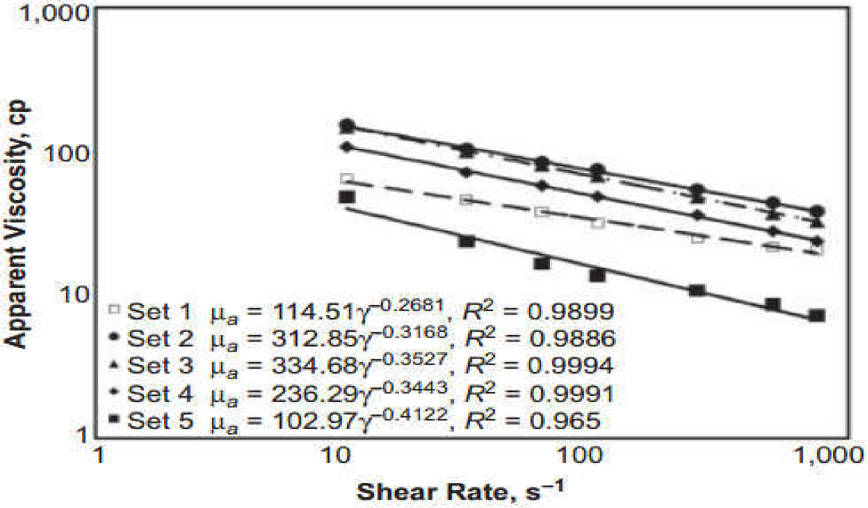
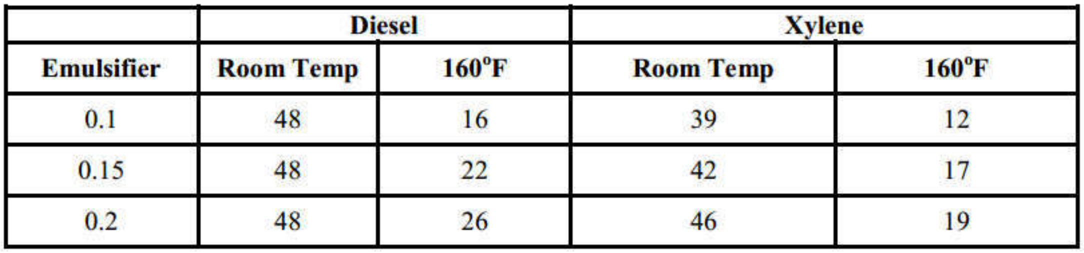


Figure 2.4: Viscosity data of the emulsified acid (Al-Mutairi et al., 2009)

Fattah et al. (2010) replaced diesel by xylene and studied its stability. They, also, used 70:30 ratio of 15 wt% HCl to diesel. The emulsifier concentration was varied from 0.1 to 0.2 vol%. Their experiments were conducted at room temperature and at 160˚F (71˚C). Results showed that the hydrocarbon phase (external phase) was of influence on stability and apparent viscosity for the emulsified acid. At 160˚F (71˚C) and emulsifier concentration of 0.1 vol%, the xylene emulsion was stable for 12 hours, whereas, the diesel emulsion was stable for 16 hours. As the concentration of emulsifier increased, the stability time increased. **TABLE 2.6** summarizes their stability findings. Further, the apparent viscosity of xylene emulsion was lower compared to diesel emulsion. They concluded that increasing the emulsifier concentration would result in an increase of the apparent viscosity and in turn meaning longer stability time for both xylene and diesel emulsions. **TABLE 2.7** summarizes the apparent viscosity results. Furthermore, increasing the emulsifier concentration resulted in generating smaller, yet more droplets.

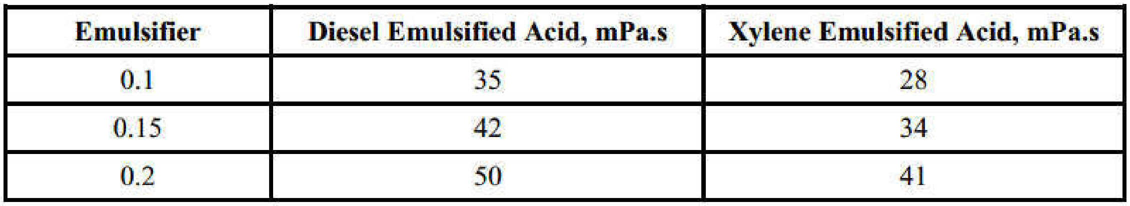
Thus, helping the emulsion to remain stable for longer periods. These findings were similar to the ones from Al-Mutairi et al. (2008, 2009) studies.

TABLE 2.6: Effect of emulsifier concentration on stability for xylene and diesel emulsified acid at room temperature and 160˚F (71˚C) in hours (Fattah et al., 2010)



	Diesel		Xylene	
Emulsifier	Room Temp	160°F	Room Temp	160°F
0.1	48	16	39	12
0.15	48	22	42	17
0.2	48	26	46	19

TABLE 2.7: Effect of emulsifier concnetraion on apparent viscosity for xylene and diesel emulsified acid (Fattah et al., 2010)



Emulsifier	Diesel Emulsified Acid, mPa.s	Xylene Emulsified Acid, mPa.s
0.1	35	28
0.15	42	34
0.2	50	41

Sayed et al. (2011) investigated the effect of emulsifier concentration and temperature on viscoelastic properties of emulsified acid. It is noteworthy to mention that their study was one of a kind, since the viscoelastic properties were not addressed before. In their study, they used varied emulsifier concentration, namely 0.5, 1.0, 2.0, 5.0 and 10.0 vol%. The HCl strength was 15 wt%. Moreover, the temperature was as high as 200˚F (93˚C). The results showed that changing the emulsifier concentration up to 2 vol% had no major effect on viscoelastic properties, however, a change in the emulsifier concentration above

2 vol% would increase the viscous modulus G″ but would have no effect on elastic modulus G′. Furthermore, above 2 vol% of emulsifier concentration G″ was always higher than G′. But, below 2 vol% of emulsifier concentration, G′ was higher than G″ only at higher frequencies. Generally, for higher emulsifier concentration, a slight increase of G′ would occur up to a temperature of 130˚F (54˚C); at higher temperatures, a decrease would occur. Moreover, at higher emulsifier concentrations a decrease of G″ with increasing temperature would be noted. **Figure 2.5**, **Figure 2.6**, **Figure 2.7** and **Figure 2.8** show the results of the viscoelastic properties at different temperatures and different emulsifier concentrations. **Figure 2.9** and **Figure 2.10** depict the temperature effect on elastic and viscoelastic moduli, respectively.

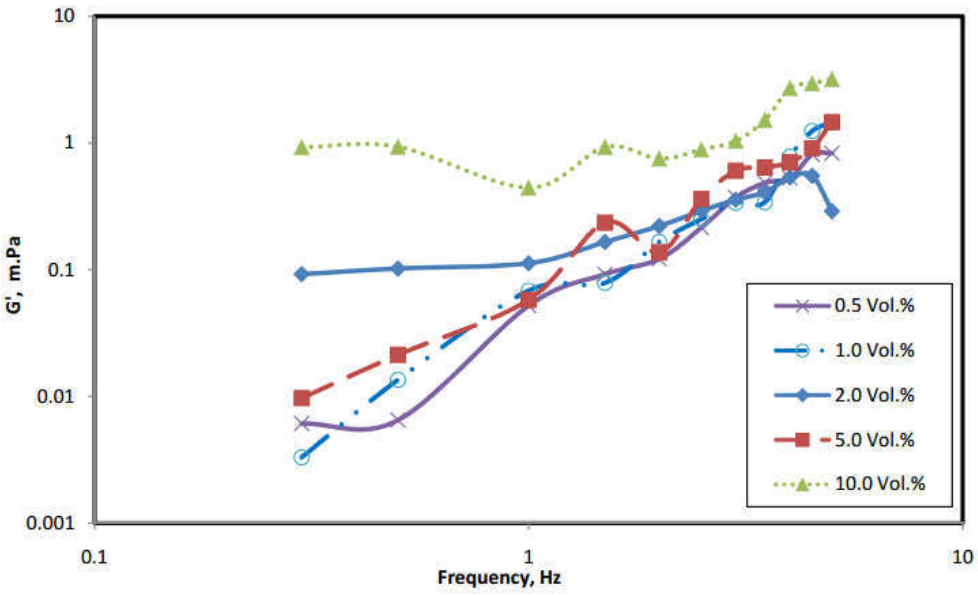


Figure 2.5: Effect of emulsifier concentration on elastic modulus at 130˚F (54˚C) (Sayed et al., 2011)

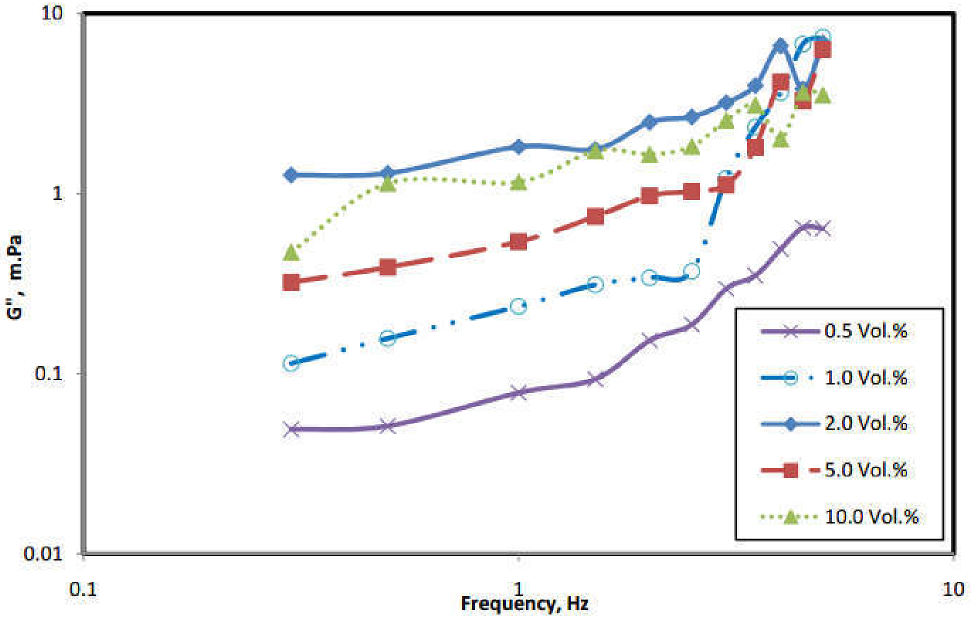


Figure 2.6: Effect of emulsifier concentration on viscous modulus at 130˚F (54˚C) (Sayed et al., 2011)

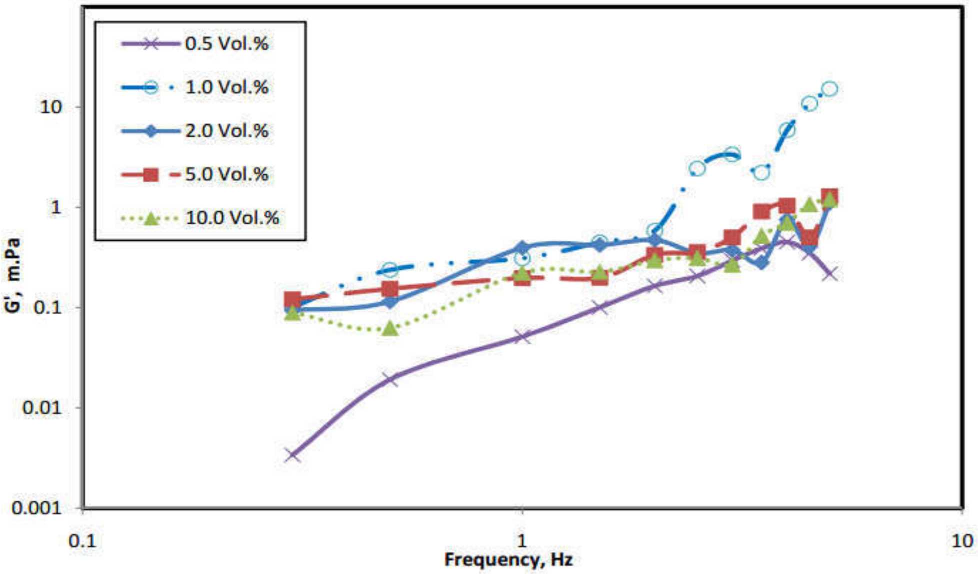


Figure 2.7: Effect of emulsifier concentration on elastic modulus at 200˚F (93˚C) (Sayed et al., 2011)

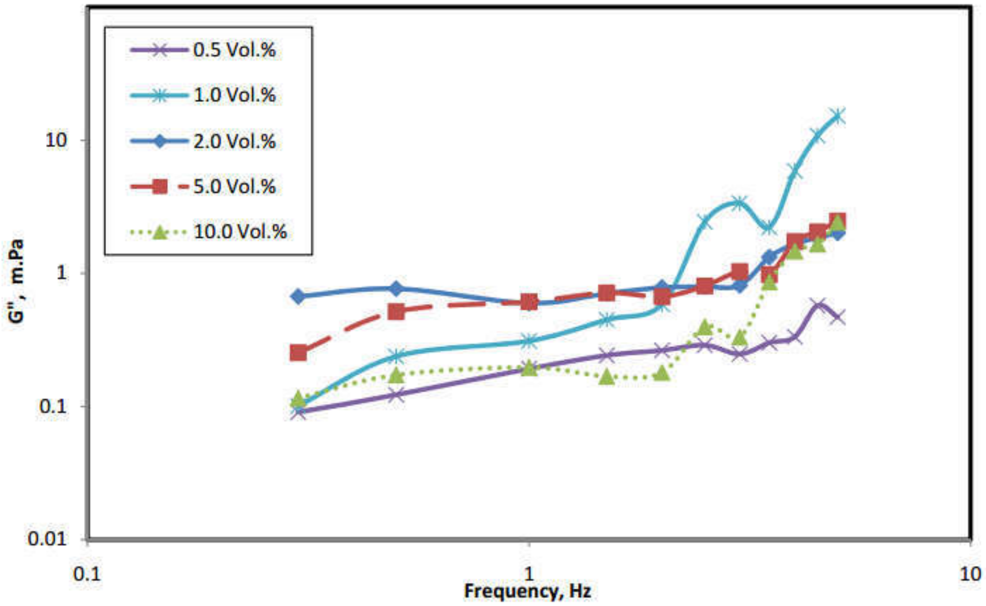


Figure 2.8: Effect of emulsifier concentration on viscous modulus at 200˚F (93˚C) (Sayed et al., 2011)

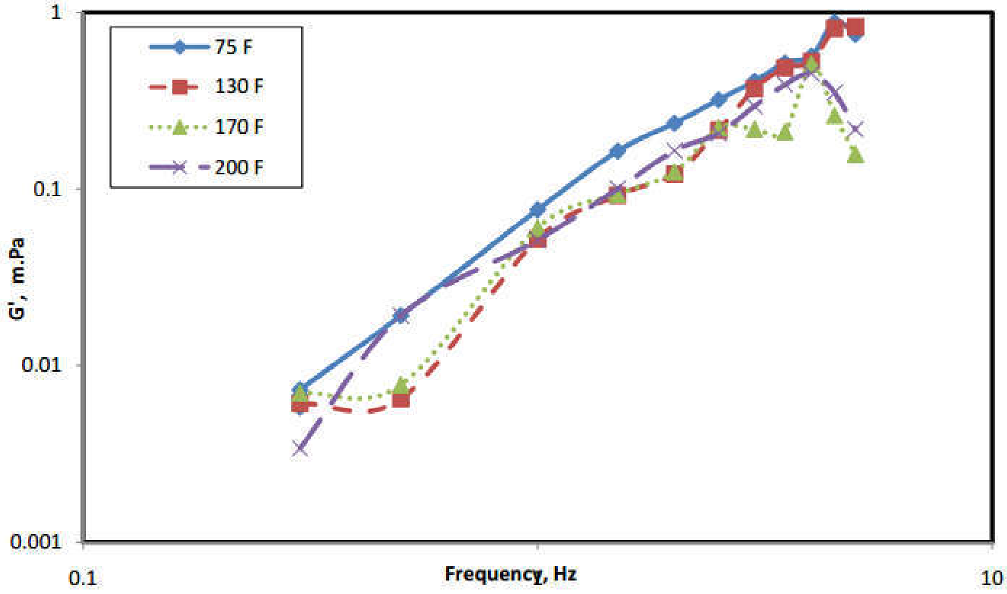


Figure 2.9: Effect of temperature on elastic modulus at emulsifier concentration of 0.5vol% (Sayed et al., 2011)

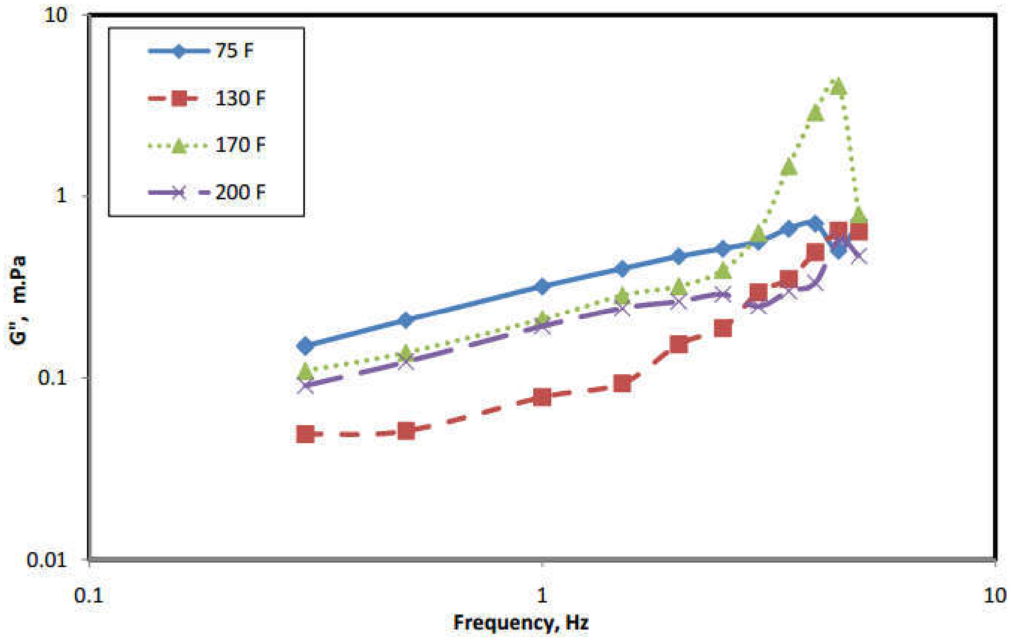


Figure 2.10: Effect of temperature on viscous modulus at emulsifier concentration of 0.5vol% (Sayed et al., 2011)

Sayed et al. (2012) prepared an emulsified acid system to stimulate deep wells in carbonate reservoirs. They used HCl acid with a ratio of 70:30 of acid-to-diesel. HCl was diluted with deionized water to concentrations of 5-28 wt%. The temperature was varied up to 300˚F (149˚C) as well as the emulsifier concentration from 0.5 to 2.0 vol%. For emulsion preparation, they added the acid phase to the diesel phase very slowly and then let it mix for 30 minutes. They reported that the samples prepared were stable at 24˚C for 48 hours. Further, they stated that temperature and emulsifier concentration have important effect on rheological behavior. Indicating that increasing the emulsifier concentration would increase the apparent viscosity at a constant shear rate, as shown in **Figure 2.11**. Likewise, increasing the emulsifier concentration would result in longer stability periods at high temperatures. **Figure 2.12**, **Figure 2.13** and **Figure 2.14** show the apparent viscosity data for different emulsifier concentration at different temperatures. Viscosity data were excellently fitted by power-law model. **TABLE 2.8** summarizes the results. This study was later expanded to include the effect of emulsifier concentration on droplet size by the same authors (Sayed et al., 2013). In the latter study, they reported that increasing the emulsifier concentration generated smaller droplet size. **Figure 2.15** shows the droplet size distribution at different emulsifier concentration.

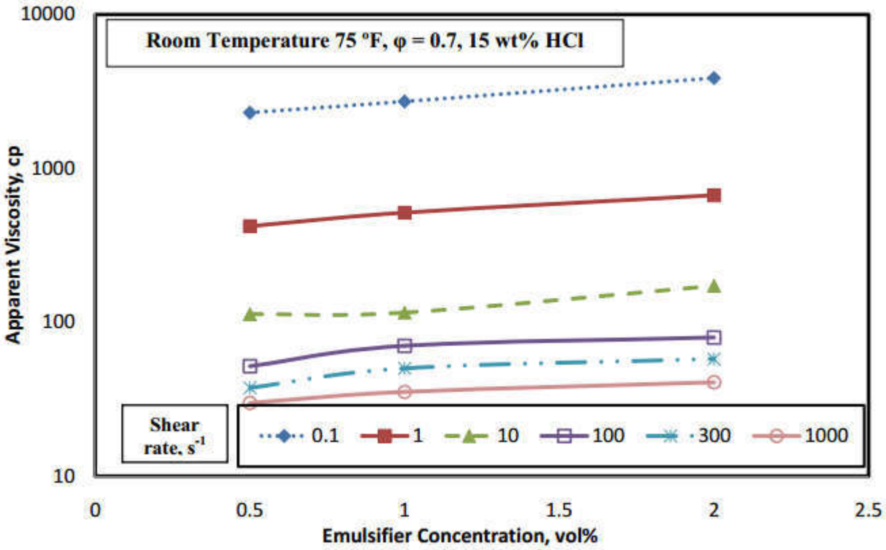


Figure 2.11: Effect of emulsifier concentration on apparent viscosity at different shear rates at 75˚F (24˚C) (Sayed et al., 2012)

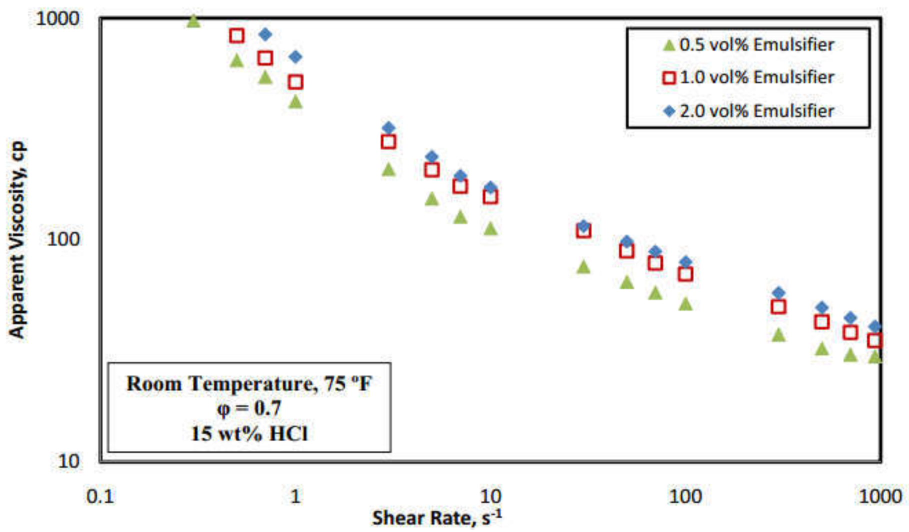


Figure 2.12: Effect of emulsifier concentration on apparent viscosity at 75˚F (24˚C) (Sayed et al., 2012)

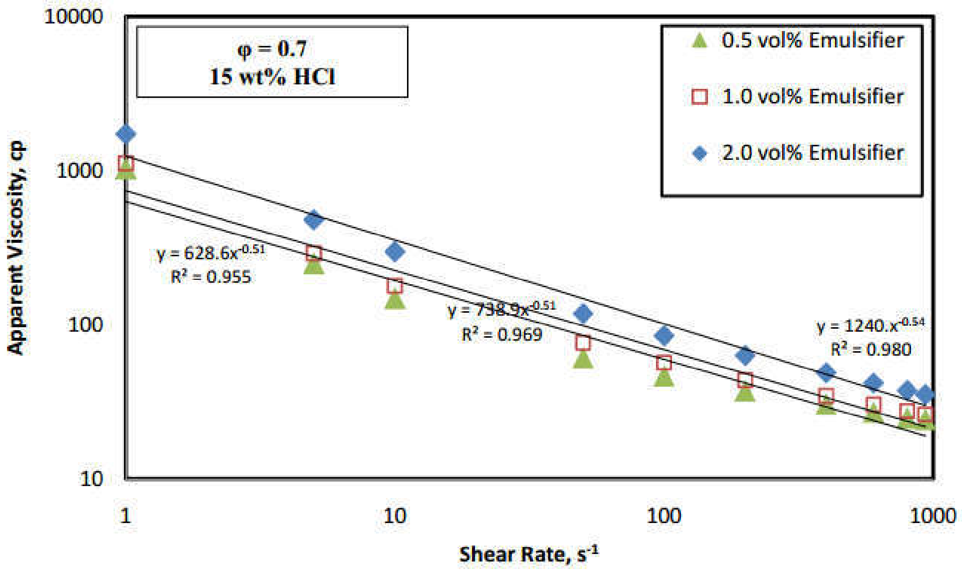


Figure 2.13: Effect of emulsifier concentration on apparent viscosity at 150˚F (66˚C) (Sayed et al., 2012)

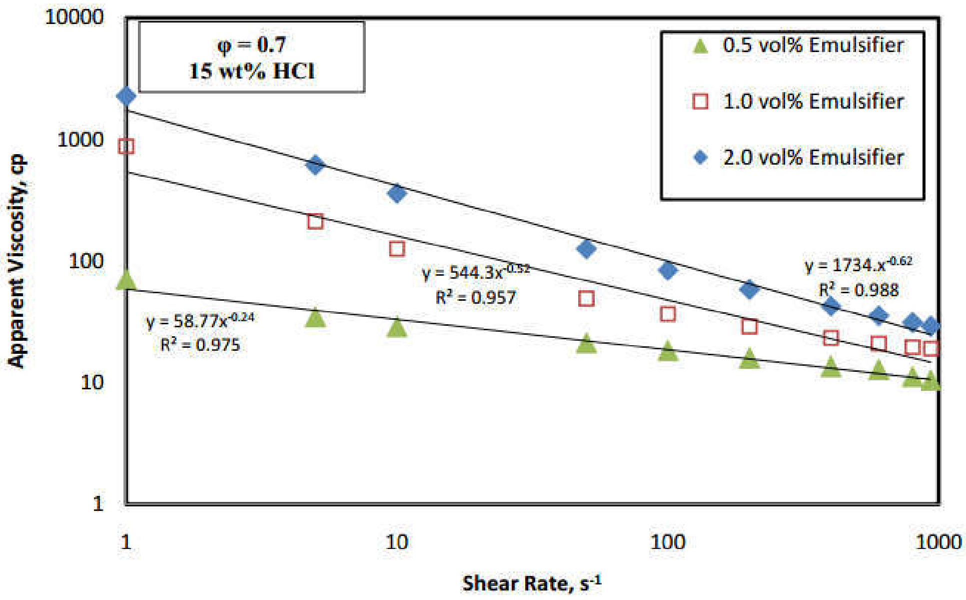


Figure 2.14: Effect of emulsifier concentration on apparent viscosity at 230˚F (110˚C) (Sayed et al., 2012)

TABLE 2.8: Summary of apparent viscosity at varied emulsifier concentrations and varied temperatures (Sayed et al., 2012)

Temperature	Emulsifier Concentration vol%	Power Law Constant, K mPa.s^n	Power Law Index, n	Correlating Coefficient
150˚F	0.5	628.6	0.488	0.955
	1	738.9	0.485	0.9699
	2	1240.1	0.456	0.9809
230˚F	0.5	58.77	0.751	0.9759
	1	544.39	0.472	0.9573
	2	1734.1	0.38	0.9887
300˚F	0.5	137.48	0.51	0.9518
	1	410.05	0.291	0.9532
	2	823.65	0.417	0.980

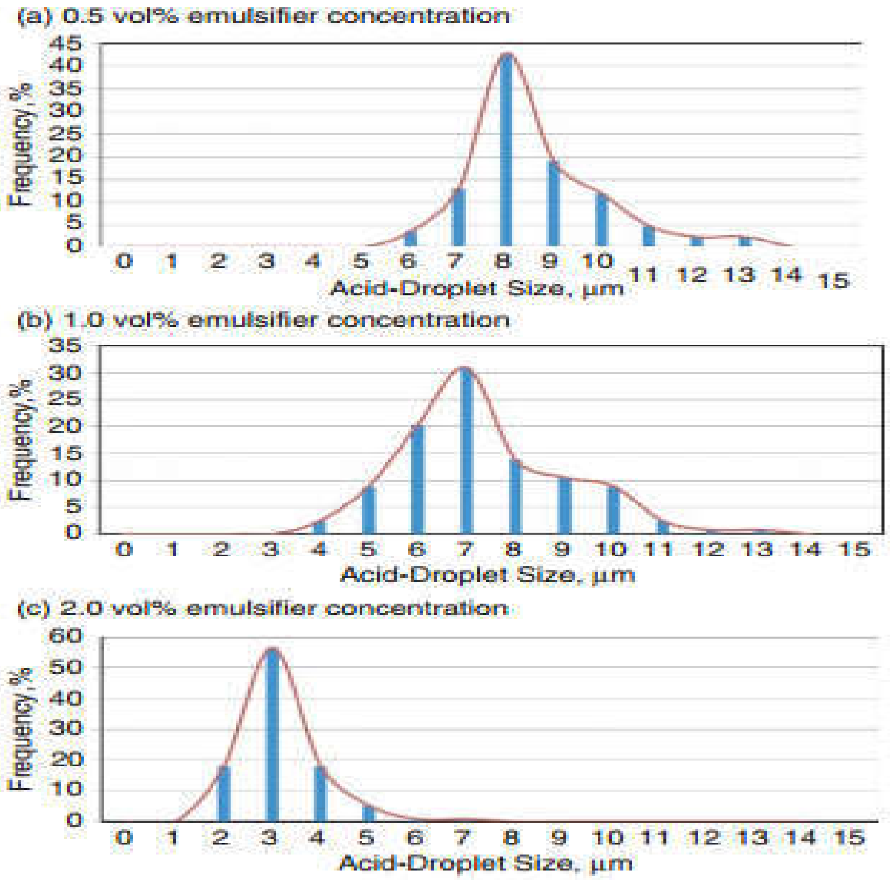


Figure 2.15: Effect of emulsifier concentration on droplet size distributions (Sayed et al., 2013)

Madyanova et al. (2012) studied rheology and stability of emulsified acid. They used 0.6 vol% of emulsifier concentration, 15 wt% of HCl and 70:30 acid-diesel ratio. The results showed that the emulsion had an apparent viscosity of 82 cP at a shear rate of 170 s^{-1} at 75˚F (24˚C). But, when heated to 200˚F (93˚C) for 50 minutes the apparent viscosity was 48 cP at 170 s^{-1} shear rate. Nevertheless, the emulsion was stable for 3 hours at 75˚F (24˚C) and for 1.5 hours at 200˚F (93˚C).

Zou et al. (2013) optimized the acid-to-oil ratio and reported that the ratio of 70:30 was the optimum one. Apart from that, they studied three different emulsifier concentrations: 2 vol%, 2.5 vol% and 3 vol%. They stated that the best performance was associated with 2.5 vol% of emulsifier. Their criteria for a good emulsion performance was when the emulsion is of uniform droplet size with small droplet diameter and tight placement of droplets. Further, they conducted experiments on three distinct HCl concentrations, namely, 15 wt%, 20 wt% and 28 wt%. Results showed that 15wt% of HCl with droplet size (5-25 µm) satisfied their criteria best.

Zakaria et al. (2015) prepared a polymer assisted emulsified acid to investigate the efficiency of acidizing. The emulsified acid system consisted of 15 wt% HCl, 4 gpt (0.4 vol%) of corrosion inhibitor, 1 vol% of cationic emulsifier and a varied concentration of polymer (0-2 vol%). The acid to diesel ratio was 70:30. The mixing speed was 500 rpm. The results showed that the emulsion with no polymer added generated a droplet size mean of 6.34 µm. The polymer assisted emulsion was stable for three days at room temperature. Moreover, they confirmed that the emulsion was a shear-thinning fluid.

CHAPTER 3

STATEMENT OF THE PROBLEM AND OBJECTIVES OF THE THESIS

The literature review chapter (Chapter 2), showed that there is a gap in emulsified acid systems and – to the author's best knowledge- this gap can be summarized as:

- Previous work did not show the effect of high temperature on the stability of emulsified acid for longer time. The best work done was an emulsified acid system that was stable for more than 4 days but at room temperature.
- Also, previous work showed the potential of replacing diesel by another oil phase.

The main objective of this thesis work is to study the possibility of replacing diesel by waste oil to formulate emulsified acid. Stability and rheology of waste oil emulsified acid are addressed.

The effect of emulsifier concentration on stability, apparent viscosity and elastic and viscous moduli are evaluated. Four different concentrations 0.5, 0.7, 1.0 and 1.5 vol% are used. Furthermore, the effect of mixing speed of emulsion preparation is investigated. And, four speeds are used to accomplish that, namely 600, 800, 1000 and 1400 rpm. Moreover, varying addition rate of acid phase to oil phase and mixing time of both oil and water phases are studied by relating them to stability results.

The significance of changing the temperature on both stability and rheology tests and up to 120ºC is also addressed. Further, the effect of corrosion inhibitor on stability is examined by relating it to the droplet size distribution.

Overall, the stability and rheology results are linked to better explain the waste oil emulsified acid behavior.

CHAPTER 4

DIESEL EMULSIFIED ACID

4.1 Abstract

HCl emulsion has been a popular means to stimulate carbonate reservoirs. Due to the various advantages that emulsified HCl has over straight HCl; including but not limited to deeper penetration and less corrosion damages. It is noteworthy to mention that a stable emulsion is essential to prevent tubular corrosion. Emulsified HCl has even more potential advantages if utilized properly. That being said, the way of preparation of emulsified HCl plays a significant role on unleashing some of these advantages. From stirring intensity all the way to mixing time, there are factors which affect the stability of the emulsion.

The aim of this chapter is to experimentally study the factors affecting the stability of emulsified HCl. The emulsion is prepared using 15wt% HCl and diesel with cationic emulsifier. Also, the acid-to-diesel ratio is 70:30. The studied variables are: mixing speed, concentration of the emulsifier, addition of corrosion inhibitor, effect of heating the emulsion, addition rate of acid phase to oil phase and mixing time of the emulsion. Mixing speed is varied from 600 to 1500 rpm. Emulsifier concentration ranges between 0.5 to 2 vol%. Heating temperature, to mimic reservoir condition, is as high as 120˚C.

The rate of adding acid phase to oil phase as well as the time of mixing the emulsion are also varied.

The results of studying the factors affecting the stability of emulsified HCl show that there is an optimum condition for emulsifier concentration and for mixing time of the emulsion. The optimum emulsifier concentration is found to be 1 vol% with 5 minutes of mixing time. As for the addition rate of acid phase to oil phase, 1.4 mL/min of drop-wise addition is found to give a very stable emulsion. The effect of mixing speed on the emulsion stability is proportional, the higher the rpm speed the better the stability. Corrosion inhibitor, on the other hand, plays a role as a destabilizer. With regards to heating temperature, it is found out that the higher the temperature, the faster the emulsion breaks.

The novelty of this study is the comprehensive knowledge it brings about the factors affecting the stability of HCl emulsion at high temperature i.e. 120˚C. It helps to better understand HCl emulsion and how it works. Hence, the production engineer can design and conduct acidizing jobs perfectly.

4.2 Introduction

For stimulation treatments, matrix acidizing is widely used in the petroleum industry in order to enhance the productivity or the injectivity of wells (Alghamdi et al., 2009). In acidizing, solids and sediments in the pores are dissolved by the acids resulting in a better conduit i.e. increasing the permeability of the rock. Ultimately, permeability increase means more hydrocarbon production. However, ordinary acids are corrosive by nature and harmful to well tubings. Therefore, emulsified acids are widely used to avoid the potential damages that could be caused by ordinary acids. Besides less corrosion, emulsified acid is also a means to retard the reaction with the formation, therefore, causing deep wormholes (Williams et al., 1972, Guidry et al., 1989, Navarrete et al., 1998). Moreover, emulsified acid has better sweep efficiency due to its high viscosity. In turn, this will improve acid distribution especially in heterogeneous reservoirs (Sayed et al., 2012). Furthermore, emulsified acids have no residue; hence, they cause no damage on the formation rock (Lynn et al., 2001).

Generally, when there exists a formation damage in a well caused by drilling, completion or even workover; acidizing is applied primarily to remove that damage. This damage could be due to pores plugging; therefore, removal of severe plugging can result in a better enhancement in well productivity. On the contrary, if no damage exists, the enhancement of the well productivity due to acidizing is occasionally over 50%. It, however, depends on other factors such as the depth of penetration and treatment size (McLeod, 1986).

Emulsified acid can be categorized into two types micro-emulsion (Hoefner et al., 1985) & macro-emulsion (Al-Anazi et al., 1998, Mohamed et al., 1999, Nasr-El-Din et al., 2000, Kasza et al., 2006, Nasr-El-Din et al., 2008a). Mollet et al. (2008) specified that micro-emulsions are composed of droplet size of (10^{-2} – 10^{-1}) μm, and macro-emulsions are composed of any size bigger than that.

Nasr-El-Din et al. (2000) prepared an acid-to-diesel emulsion with 70:30 ratio and emulsifier concentration ranging from 0.2 to 2 vol%. They used 15wt% of HCl. They showed that the emulsion was more stable for higher emulsifier concentration. Moreover, they concluded that the emulsion was a shear-thinning fluid.

Nasr-El-Din et al. (2001) used emulsified acid of 28wt% HCl with 70:30 acid to diesel volume ratio with cationic emulsifier to stimulate deep sour, gas wells. The laboratory results showed that the emulsion at ambient conditions was stable for over two days. However, at 250˚F (121˚C) the emulsion was stable for more than 4 hours. Moreover, the study confirmed that the emulsified acid was a shear-thinning fluid with a value of 300 mPa.s of apparent viscosity at 76˚F (24˚C) and 10 s^{-1} of shear rate.

Lynn et al. (2001) developed an emulsified acid system with 28 wt% of HCl of 70:30 ratio. They added corrosion inhibitor of 0.3 vol% and a volume percentage of 1.5 of cationic emulsifier. They found out their emulsion was stable for more than 5 hours at 250˚F (121˚C) with 300 psi of pressure applied.

In 2006, (Kasza et al.) conducted a study to select the best acidizing fluid to stimulate production wells of a reservoir in Poland. The reservoir had a high temperature of 120˚C. They found out the best practice was to emulsify 15 wt% of HCl with crude oil in a 50:50 acid-to-oil ratio along with 2 vol% of emulsifier. This emulsion was stable for 180 minutes at 120˚C.

Al-Mutairi et al. (2009) formed HCl emulsions with 70:30 acid to diesel ratio of 15 wt% HCl at different temperatures, 25, 50 and 85˚C and at varied emulsifier concentrations from 1 to 10 gpt. They noted that the addition of the acid phase to oil phase was of critical importance. Hence they fixed the addition rate at 14 mL/min in order to ensure reproducible data. At different temperatures, apparent viscosity measurements were conducted, over a range of shear rate of 10 - 750 s^{-1}. At high temperatures, a pressure of 300 psi was applied to minimize evaporation. The results of apparent viscosity measurements were fitted perfectly in the power-law model. Apart from that, the increase of emulsifier concentration resulted in a decrease in average droplet size. The average droplet size was found to be 12.4, 8.4 and 6.0 µm for 0.1, 0.5 and 1vol%, of emulsifier concentration, respectively. Additionally, they mentioned that increasing the temperature would decrease the apparent viscosity for the same emulsifier concentration.

Appicciutoli et al. (2010) used 70:30 ratio of 15 wt% HCl to diesel with 2.5vol% of emulsifier and mixed it at 3,000 rpm. The addition time of acid to diesel was 2 minutes, and they managed to get a stable emulsion at 70˚C for more than 2 hours.

Sayed et al. (2011), investigated the effect of viscoelastic properties on emulsified acid and found out that generally the viscous modulus G″ was always greater than the elastic modulus G′. Also, they reported that the viscous behavior became more dominant as the emulsifier concentration increased above 2 vol%. However, an increase in emulsifier concentration up to 2 vol% would have no major effect on both G′ and G″.

Madyanova et al. (2012) studied rheology and stability of emulsified acid. They used 0.6vol% of emulsifier concentration, 15wt% of HCl and 70:30 acid-diesel ratio. The results showed that the emulsion had an apparent viscosity of 82 cP at 75˚F (24˚C) and 170 s^{-1} shear rate. But, when heated to 200˚F (93˚C) for 50 minutes the apparent viscosity was 48 cP at 170 s^{-1} shear rate. Nevertheless, the emulsion was stable for 3 hours at 75˚F (24˚C) and for 1.5 hours at 200˚F (93˚C).

Before injecting emulsified acid into the reservoir, its stability and rheology should be checked (Sayed et al., 2012). Hence, a better understanding of the emulsion is essential to perform a successful stimulation job. Moreover, the type and concentration of the emulsifier are of the key parameters in formulating a stable emulsion. Also, temperature and emulsifier concentration play an important role in stability, therefore, they need to be addressed for characterizing the behavior of emulsions (Nasr-El-Din et al., 2008a, Sayed et al., 2011). Emulsion instability is designated by the separation of water phase or by the complete separation of the two phases (Opawale et al., 1998).

This work aims to comprehensively understand acid emulsions and the factors affecting its stability and rheology at high temperature, specifically at 120˚C.

4.3 Experimental Procedure

4.3.1 Materials

In this study both the cationic emulsifier (Armostim H-Mul) and the corrosion inhibitor (Sanjal AI-8) are supplied by AkzoNobel. The HCl of (ACS) grade is titrated using Sodium Hydroxide solution and its concentration is found out to be 36.9wt%. The HCl is diluted to 15wt% using distilled water. The diesel used in this study is a commercial type in Saudi Arabia which has a composition illustrated in **Figure 4.1**. A more detailed analysis of diesel is reported in **Appendix A**.

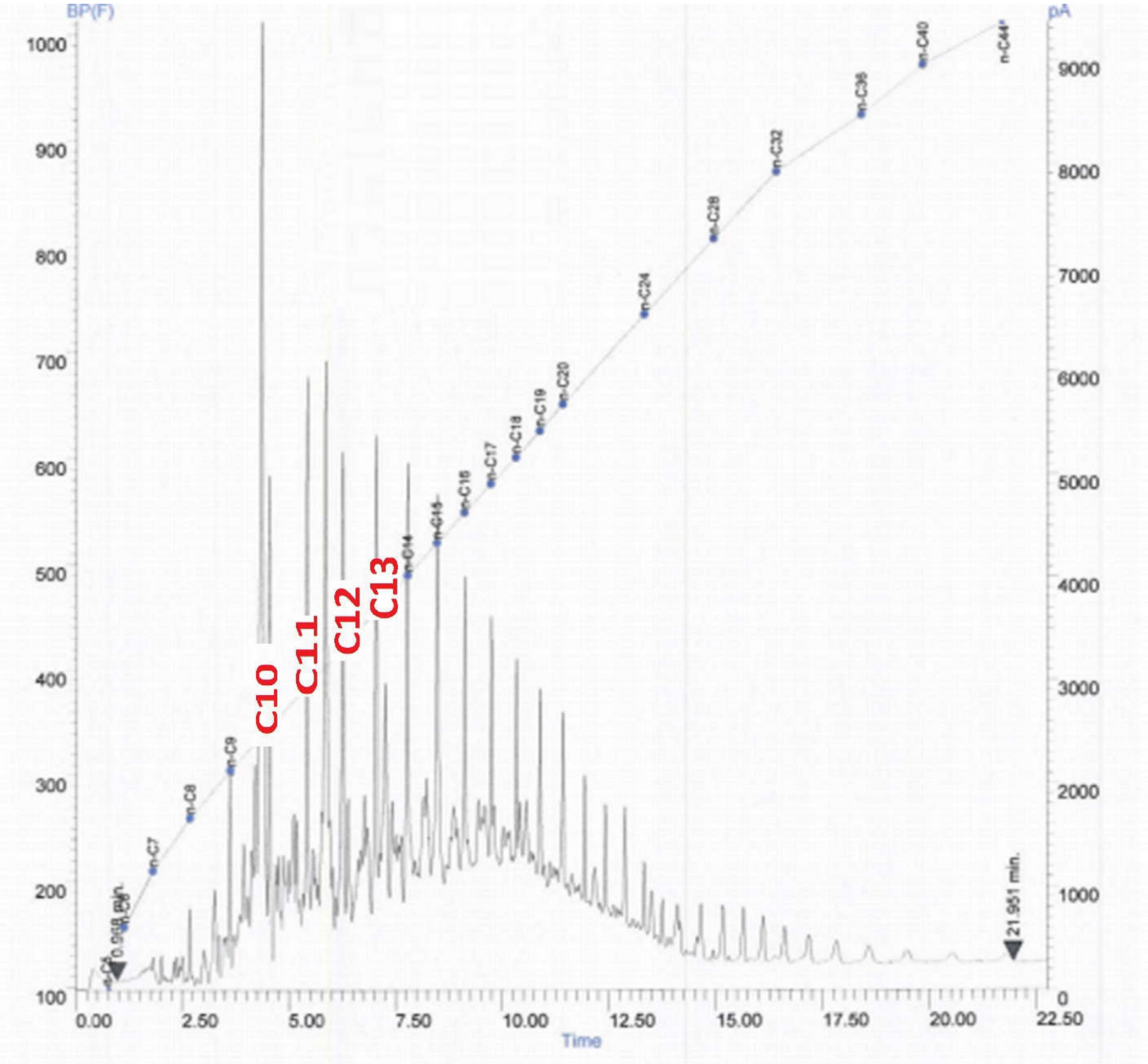


Figure 4.1: Diesel composition

4.3.2 Preparation

In the present study, the experiments are prepared at room temperature. The acid/oil ratio is 70:30 with 15 wt% of HCl. The oil phase (diesel + emulsifier) is prepared in one beaker and the water phase (15 wt% HCl + corrosion inhibitor) is prepared in a different beaker. A specific volume of emulsifier concentration is added to the diesel while mixing. Then, the oil phase is let to be mixed for 5 minutes at a specific mixing speed. In the water phase beaker, the 15 wt% HCl is added along with the corrosion inhibitor and mixed for 5 minutes at the same speed used for the oil phase. After finishing the mixing of the separate phases, the water phase is added to the oil phase drop-wise and uniformly at certain addition rate while mixing is taking place. This addition rate plays a very important role on reproducibility of the data, it should be consistent throughout the experiments. Once the last drop of water phase is added, the emulsion have already been formed and should be mixed for 5 minutes at the same speed. It should be noted that if the water phase is added to the oil phase at once coarse droplets would form, but finer ones would form if the addition is of drop-wise kind (Al-Mutairi et al., 2008).

4.3.3 Apparatus

In the present study, a high-power mixer of 1100 W of power input is used with a speed range of (600 - 10,000) rpm and the deviation of the speed is only 1%. This mixer is manufactured to be used with HCl acid. The mixer is delivered by IKA®, a German company and the model is T 50 digital ULTRA-TURRAX®. The rheological experiments in this study are done by the aid of an acid-resistant rheometer manufactured by REOLOGICA® and the model is STRESSTECH. It has a range of torque of 3.0×10^{-8} to 2.0×10^{-1} N.m and a range of temperature of -20 to 150˚C. The rheometer has many sets for different purposes and in this work the bob/cup set is used and it requires a volume of 15.9 mL of emulsion for testing. For droplet size distribution measurements, FRITSCH® ANALYSETTE 22 MicroTec plus of measuring range of 0.1-600 μm is used. This droplet analyzer works on diffraction of electromagnetic waves principle. And, the droplet size distribution is calculated using Lorenz-Mie or Fraunhofer theory.

4.3.4 Testing procedure

4.3.4.1 Emulsion type

The dilution test is done for identifying the emulsion type. Dilution test is grounded on the principle of emulsions will be diluted by the liquid that constitutes its external phase. That being said, adding small amounts of the emulsion into two separate beakers, one containing pure water and the other pure oil, would result in dispersion in only one beaker. If the dispersion occurs in the pure water beaker the emulsion is of oil-in-water type. In contrast, if the dispersion occurs in the pure oil beaker the emulsion is of water-in-oil type (Pal, 1993). **Figure 4.2** shows that the emulsion is dispersed in pure oil but not in pure water indicating the water-in-oil emulsion type. Also, to assess the quality of the emulsion, the electric conductivity is measured. If the conductivity reads a value near 0, then the emulsion is of good quality.

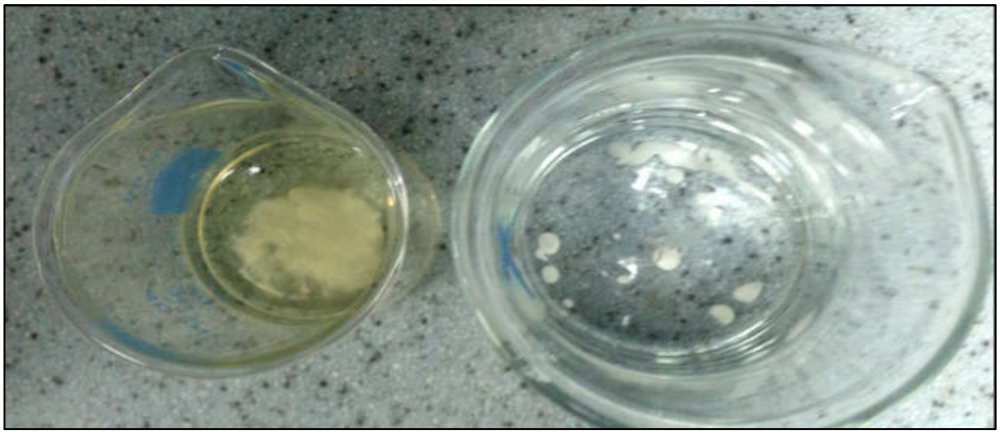


Figure 4.2: Top view of dilution test of diesel emulsion where a dispersion occurred in pure oil (left) but not in pure water (right) indicating a water in oil emulsion

4.3.4.2 Stability test

All of the stability tests in this work are presented in phase changes diagram. This diagram plots the relative volume versus time for the three phases (emulsion, water and oil phases). Initially, all samples are in emulsion phase with 0% of water phase as well as oil phase. But, with the effect of heating, the emulsion phase starts to decrease on the expense of increasing the other two phases. The volume change of the three phases over time keeps taking place until the emulsion is entirely separated. The thermal stability tests are carried out at 120˚C and for 6 hour period. During that period, a multiple recording of the three phases (emulsion, water and oil) volume is done.

4.3.4.3 Rheology test

In rheology tests, 15.9 mL of the emulsion is needed to measure the viscosity and oscillating properties at temperatures of 25, 60 and 100˚C. Due to limitation from the rheometer, reaching 120˚C is challenging. As the set-up does not have proper ventilation as well as the flash point of diesel is low.

4.3.4.4 Droplet size measurements

To get an indication of the emulsion quality, droplet measurements are done. Where, coarse droplets indicate a less stable emulsion compared to finer droplets (Al-Mutairi et al., 2008). The maximum temperature reached is 100˚C, due to equipment limitations.

4.4 Results and Discussion

This section presents the results and discussion of the aforementioned tests of diesel emulsified acid. It categorizes them into three: thermal stability, viscosity and oscillating measurements and droplet size distribution measurements.

4.4.1 Thermal stability

In this test, the effect of emulsifier concentration and the effect of mixing speed (rpm) are addressed at a temperature of 120˚C. First the emulsifier concentration is optimized and later the optimum concentration is used for mixing speed optimization.

Thermal stability tests are conducted on four experiments setups, A, B, C and D. The differences between these setups are: addition rate of acid phase to oil phase, using a syringe pump or a glass funnel for that addition, adding corrosion inhibitor and using a homogenizer or a magnetic stirrer for mixing.

In setup A, a magnetic stirrer is used for the mixing. The addition rate of acid phase to oil phase is 3.11 mL/min using a glass funnel. Also, a 0.3 vol% of corrosion inhibitor is added.

Moreover, setup B is similar to setup A and the only difference is the addition rate and the type of magnetic stirrer. Where setup B addition rate is 1.07 for emulsifier concentration experiments and 4.34 mL/min for mixing speed optimization. In addition, a more powerful magnetic stirrer is used. It is noteworthy to mention that, it is very difficult to control the addition rate in order to have consistent results because the glass funnel is used and this problem creates inconsistent results for emulsifier concentration and mixing speed optimizations.

In setup C, a syringe pump is used and hence the addition rate problem that is faced in the preceding setups is fixed. For this setup the addition rate is 1.33 mL/min. Also, a magnetic stirrer -same as in setup B- is used for mixing purposes. And, corrosion inhibitor of 0.3 vol% is added – as in setups A and B.

Setup D, a powerful homogenizer for mixing is used along with a syringe pump making the addition rate 3.5 mL/min and no corrosion inhibitor is added.

The reason for using these different setups is because data reproducibility is critical to ensure. Hence, an improvement form one setup to the succeeding one can be seen. Setup B has a slower addition rate compared to A, but still both addition rates are not controllable. Setup C, a syringe pump is used to eliminate the inconsistency of the addition rate problem that is encountered in setups A and B. Finally by setup D, all of the potential problems that could cause inconsistency of the results are eliminated. **TABLE 4.1** compares the four setups in terms of addition rate, the medium used for mixing, the medium used for adding the acid phase to oil phase and whether or not the corrosion inhibitor is added to the emulsion.

To study the effect of emulsifier concentration on the thermal stability, four different emulsifier concentrations are used namely, 0.5, 0.7, 1.0 and 1.5 vol%. The emulsion is prepared with those concentrations separately at a mixing speed of 600 rpm. Then, high-temperature-graduated test tubes are used to observe the stability behavior for 6 hours at

120˚C for these emulsions. The separation of the three phases is observed as a function of time and recorded. That is done for the four experiments setups.

TABLE 4.1: Summary of the setups used for diesel emulsion

SETUP	Oil Phase	Addition Rate, mL/minute	Corrosion Inhibitor (Yes/No)	Syringe Pump(SP) or Glass Funnel(GF)	Homogenizer(H) or Magnetic Stirrer(MS)
A	DIESEL	3.11	Yes	GF	MS1
B	DIESEL	1.07 & 4.34	Yes	GF	MS2
C	DIESEL	1.33	Yes	SP	MS2
D	DIESEL	3.5	No	SP	H

4.4.1.1 Setup A

For emulsifier concentration of setup A, increasing the emulsifier concentration results in forming more stable emulsion. Where at 3 hour period of heating at 120˚C, 1.5vol% has 98% of the emulsion phase, 1 and 0.5 vol% both have 96% and 0.7 vol% has 79%. **Figure 4.2**, **Figure 4.3** and **Figure 4.4** show a plot of the emulsion, water and oil phases, respectively, of the 4 concentrations as a function of time for 6 hour period at 120˚C. From these figures it can be concluded that at the end of the stability test (6 hours), 1.5 and 1 vol% have similar results, hence 1 vol% is used to optimize the rpm speed.

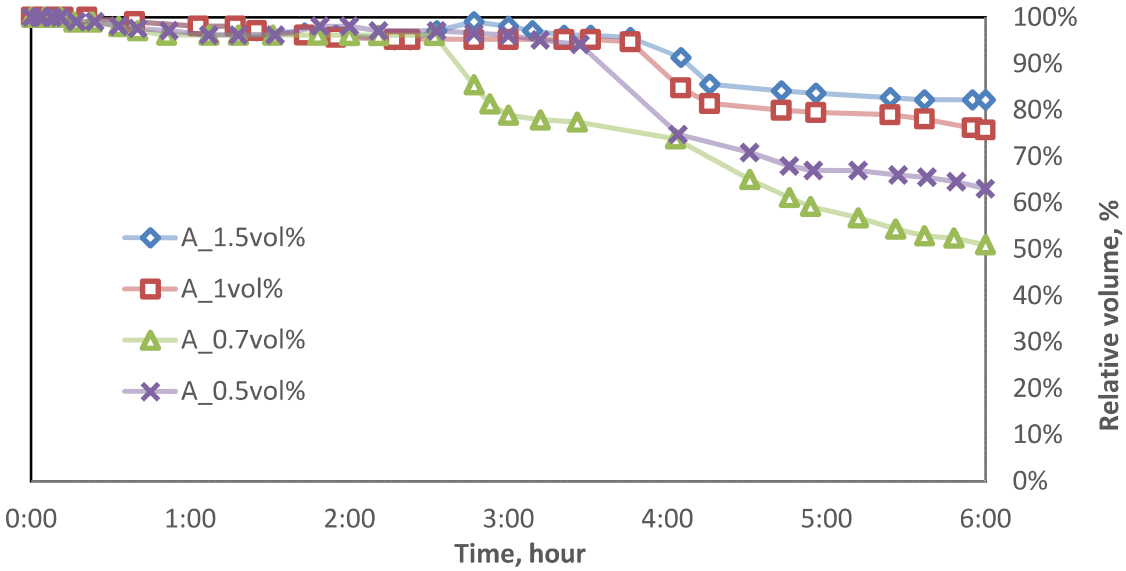


Figure 4.2: Emulsion phase of diesel emulsion of setup A at different emulsifier concentration at 120˚C

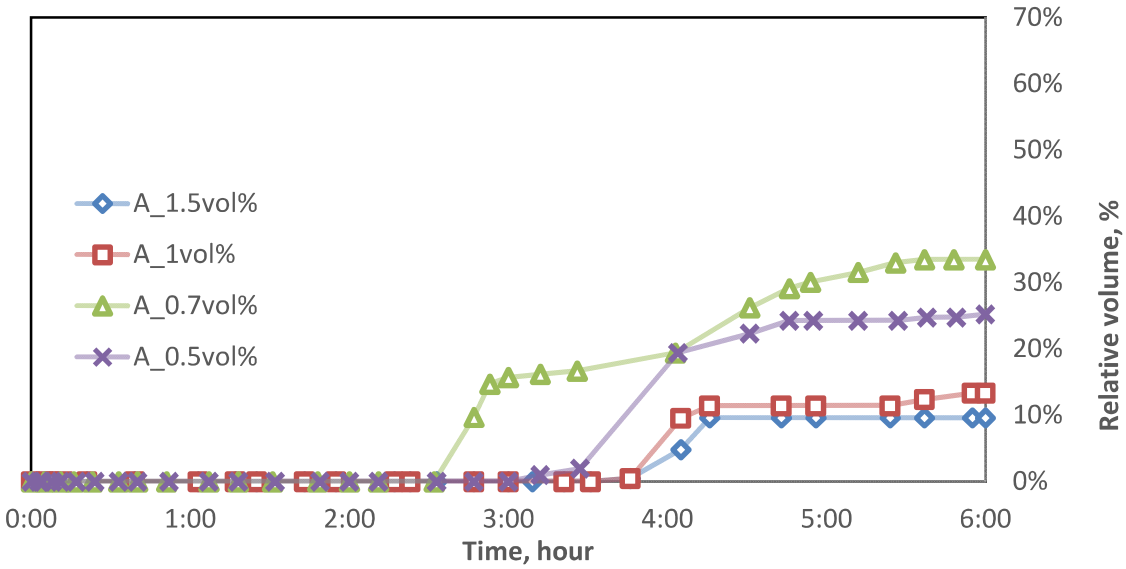


Figure 4.3: Water phase of diesel emulsion of setup A at different emulsifier concentration at 120˚C

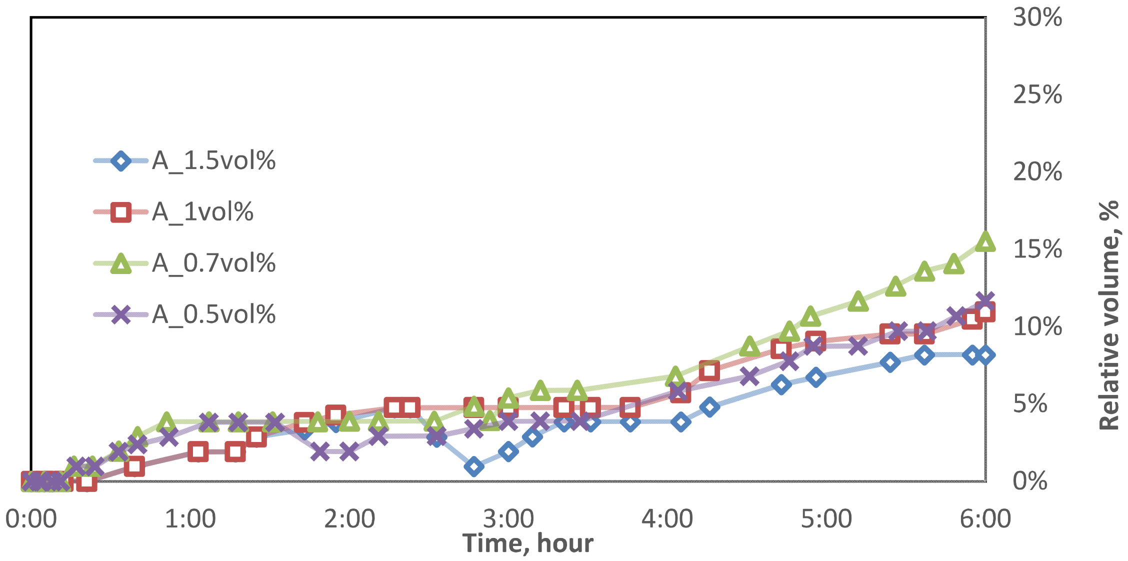


Figure 4.4: Oil phase of diesel emulsion of setup A at different emulsifier concentration at 120˚C

For mixing speed optimization, the rpm speed is varied: 600, 800, 1100, 1400 and 1500. These speeds are prepared at an emulsifier concentration of 1 vol%. **Figure 4.5**, **Figure 4.6** and **Figure 4.7** show the results of optimizing the rpm concentration. Emulsion prepared with 1100 rpm is the most stable one and succeeding to that is the emulsion of 1400 rpm and then 800, 600 and 1500 rpm, respectively. To make sure these data are reproducible, 1100 and 600 rpm samples are repeated at the same conditions except for the addition rate which is challenging to keep it the same since the glass funnel is used. Nonetheless, **Figure 4.8** and **Figure 4.9** show the reproducibility experiments of 600 and 1100 rpm, correspondingly. In both cases the data are not reproducible since the addition rate is different. Also, later, it is found out that the magnetic stirrer, which is used in this setup, at 1200 rpm and above does not work properly. Hence, a more reliable magnetic stirrer is used to perform the experiments in setup B.

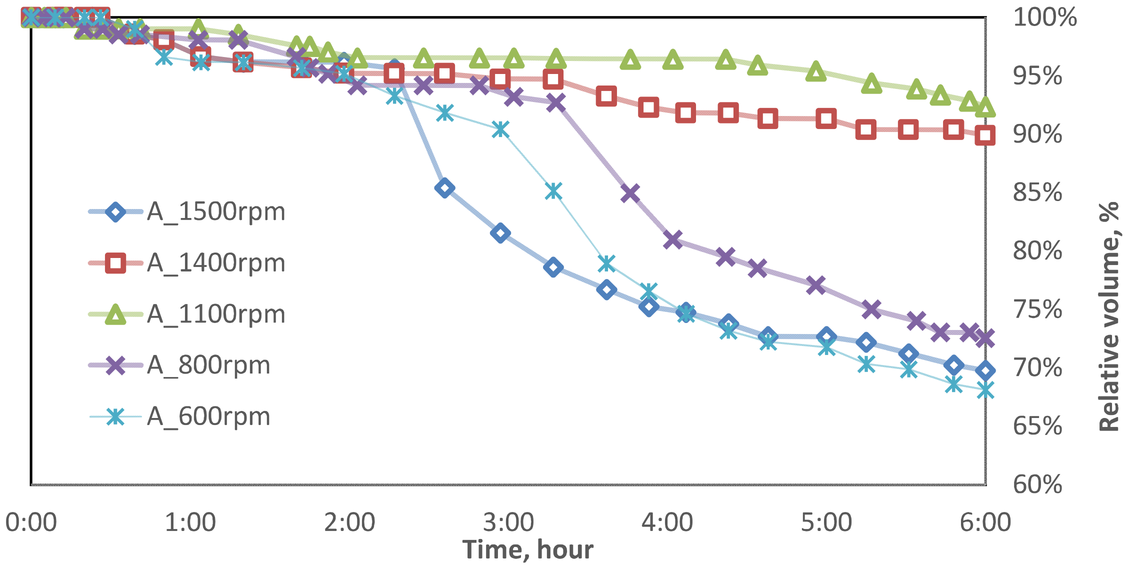


Figure 4.5: Emulsion phase of diesel emulsion of setup A at different mixing speed at 120˚C

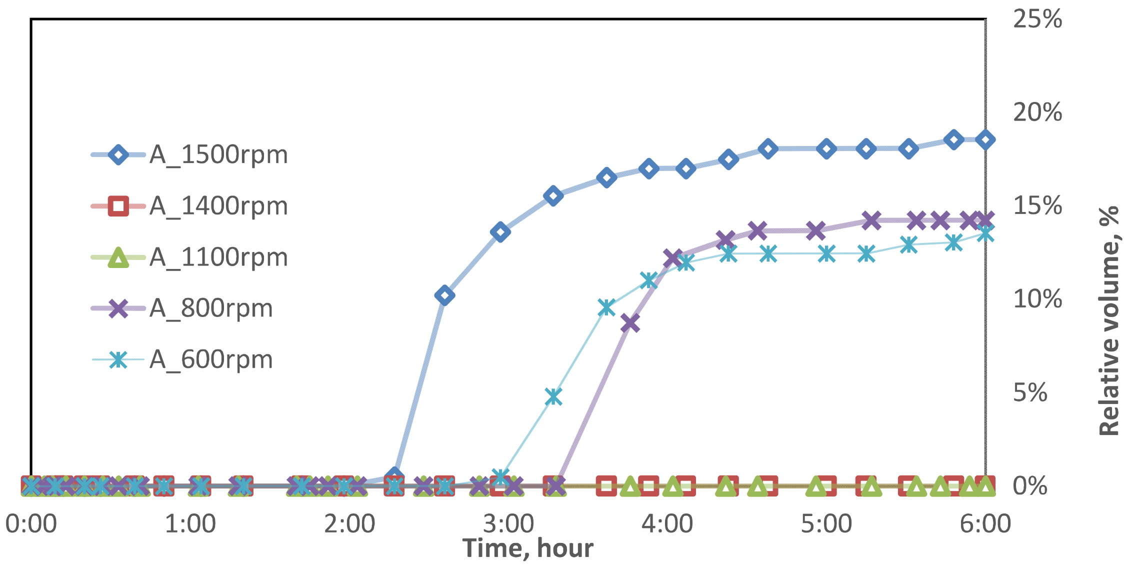


Figure 4.6: Water phase of diesel emulsion of setup A at different mixing speed at 120˚C

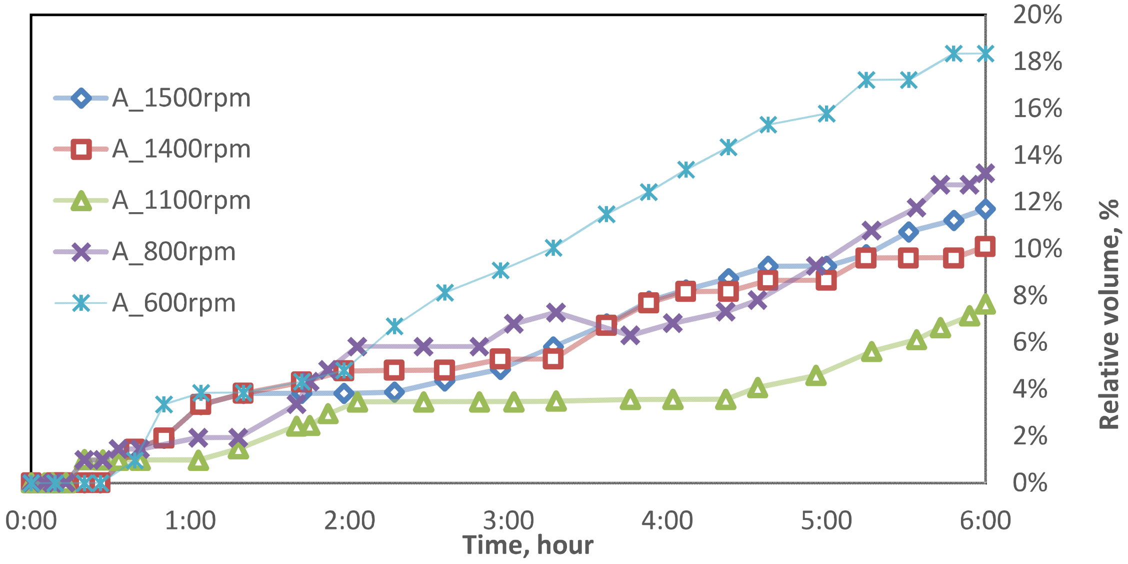


Figure 4.7: Oil phase of diesel emulsion of setup A at different mixing speed at 120˚C

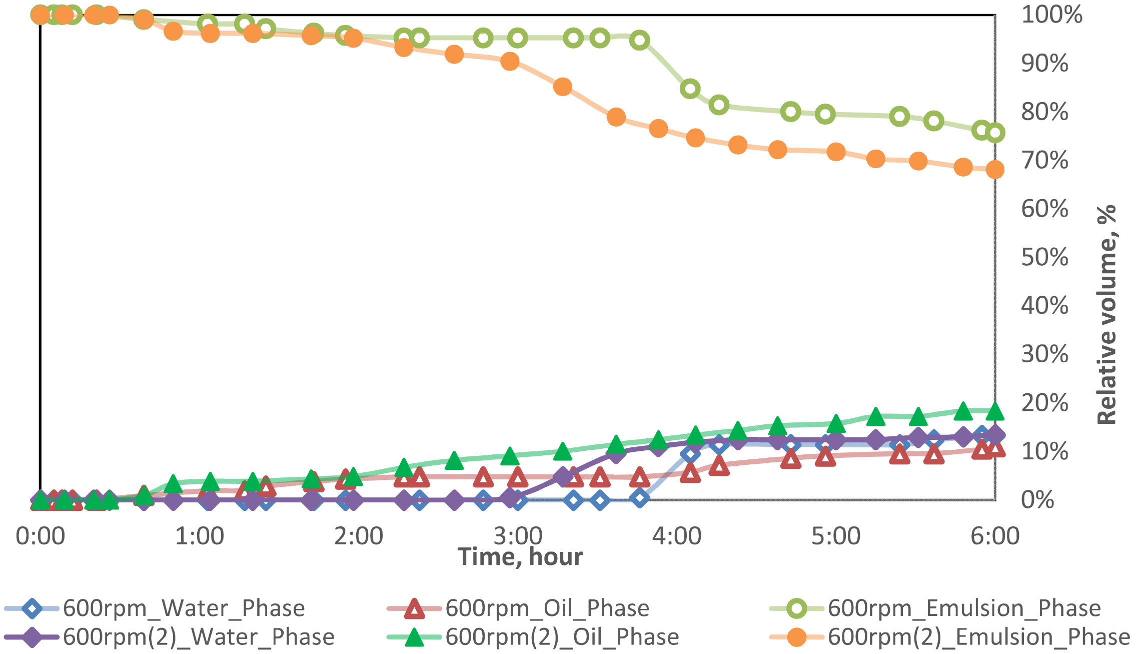


Figure 4.8: Reproducibility data for diesel emulsion of setup A at 600rpm at 120˚C

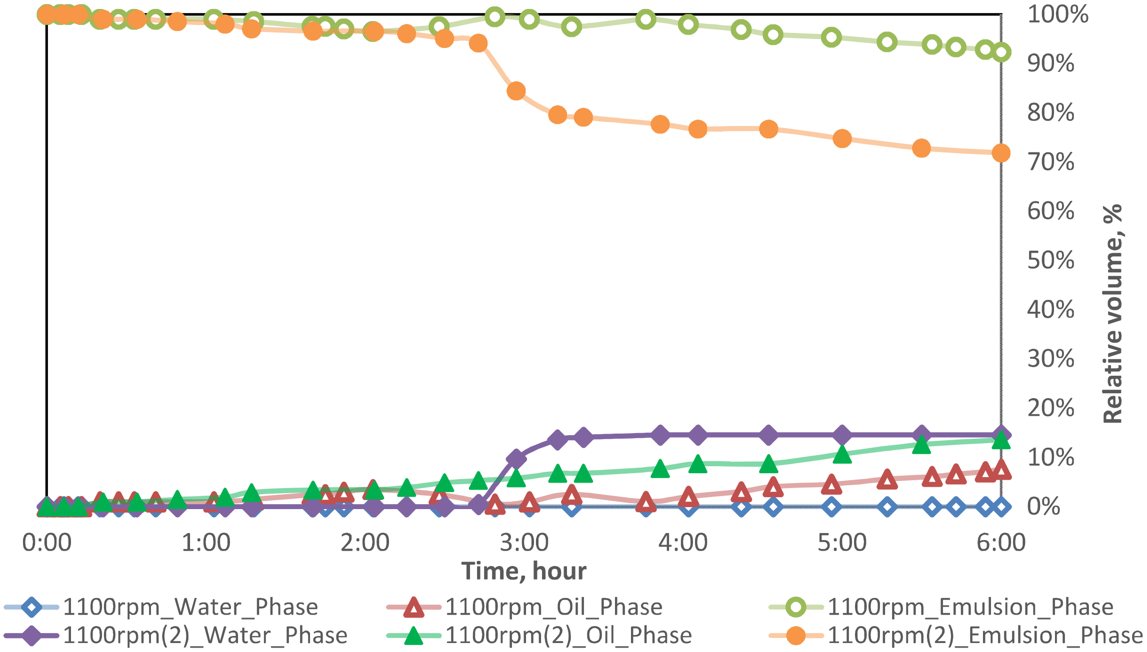


Figure 4.9: Reproducibility data for diesel emulsion of setup A at 1100rpm at 120˚C

4.4.1.2 Setup B

As far as setup B is concerned, for the 6 hour period of stability tests, increasing the emulsifier concentration results in more stable emulsion. However, both 1.5 and 1 vol% of emulsifier concentration have similar results which means increasing the emulsifier concentration above 1 vol% has little effect on the stability. These results are plotted in **Figure 4.10**, **Figure 4.11** and **Figure 4.12**. The addition rate of acid phase to oil phase is constant throughout the emulsifier optimization which is 1.07 mL/min. In this setup, the idea of having an optimum emulsifier concentration is when the emulsion starts to break after 3 hours of heating. Therefore, emulsifier concentration of 0.5 vol% is used as the optimum and it is carried out to mixing speed optimization.

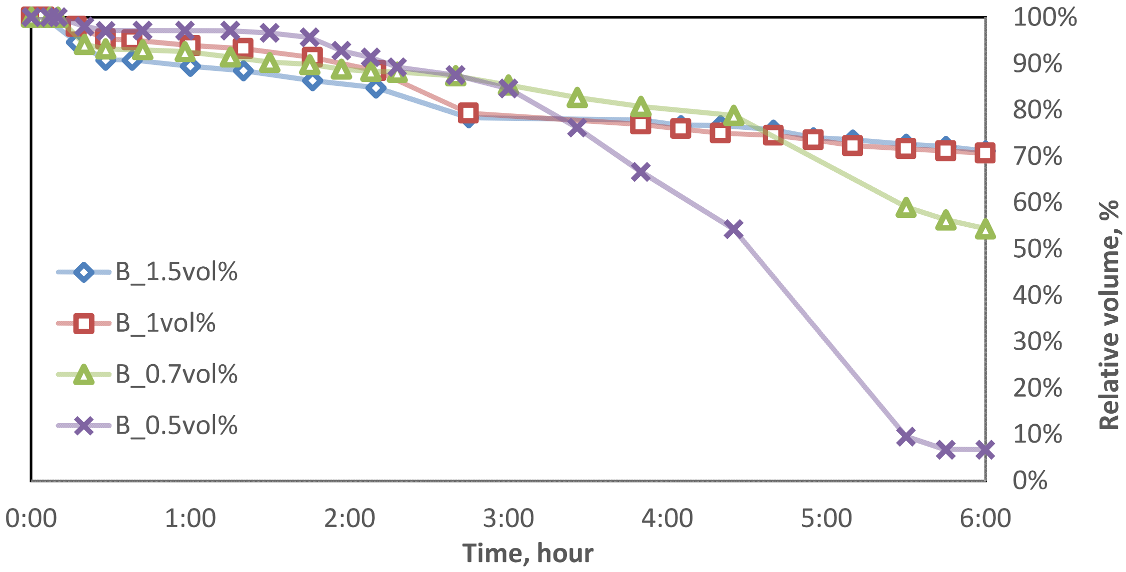


Figure 4.10: Emulsion phase of diesel emulsion of setup B at different emulsifier concentration at 120˚C

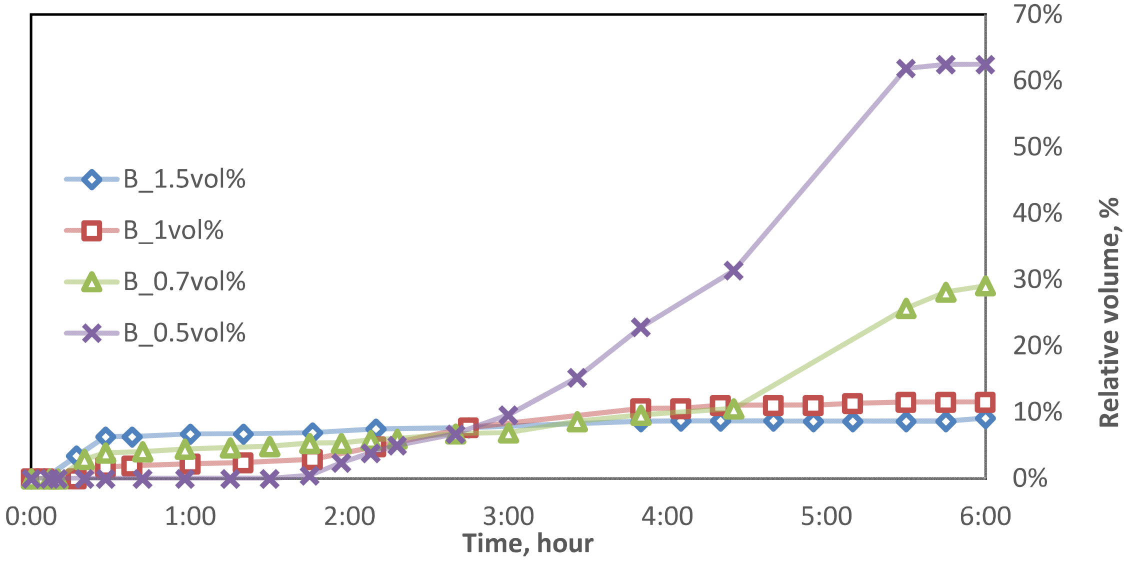


Figure 4.11: Water phase of diesel emulsion of setup B at different emulsifier concentration at 120˚C

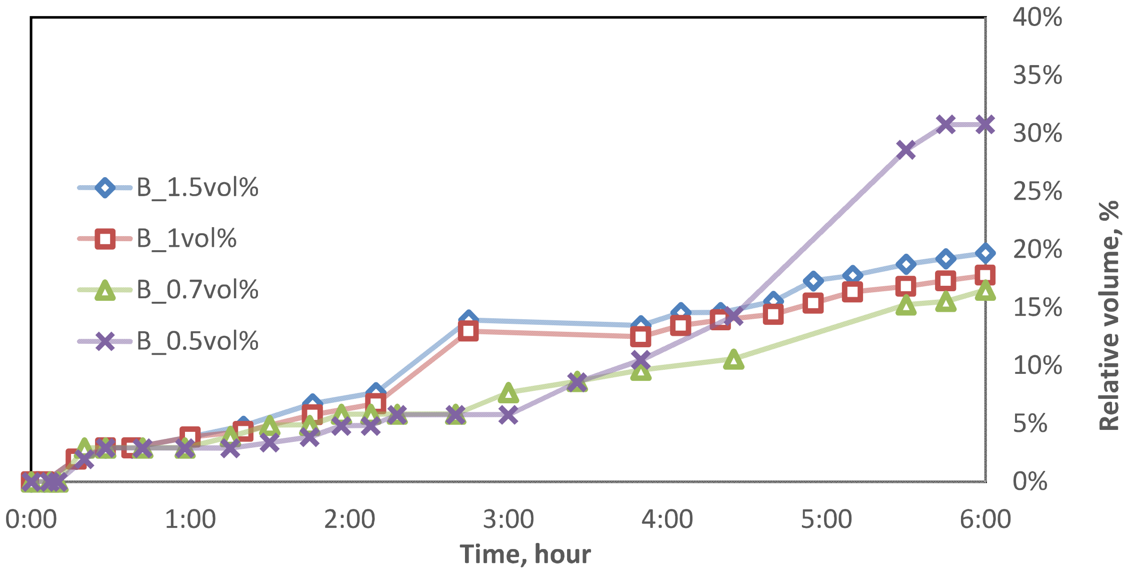


Figure 4.12: Oil phase of diesel emulsion of setup B at different emulsifier concentration at 120˚C

As for mixing speed optimization, a more reliable magnetic stirrer is used in this setup, therefore different mixing speed are employed in the experiments. The speeds are: 600, 800, 1000, 1200 and 1500. The emulsifier concentration is 0.5 vol%. Further, the results show that the emulsion prepared at 1000 rpm is the most stable and it does not break completely within the 6 hour-stability-test period, unlike the other four speeds. **Figure 4.13**, **Figure 4.14** and **Figure 4.15** represent the stability tests for those speeds. Also, the figures indicate that the second most stable emulsion is the one prepared with 1200 rpm but it completely breaks within 4.5 hours. Interestingly, if an observer were to look at the stability results for only the first 3 hours and discard the last 3, 1500 rpm would be the most stable emulsion followed by 1200 rpm and then 1000 rpm.

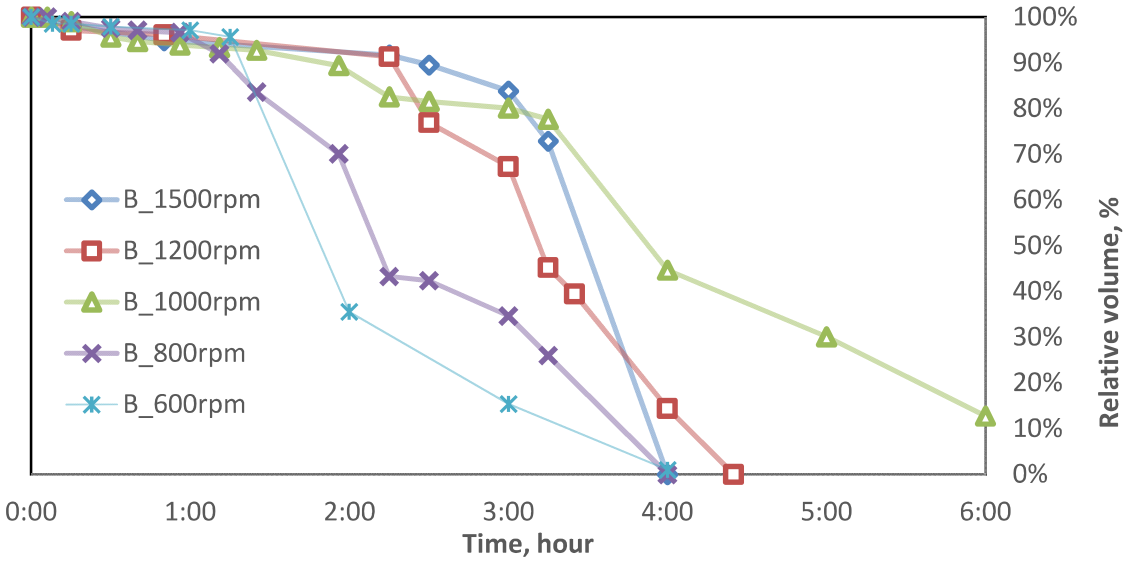


Figure 4.13: Emulsion phase of diesel emulsion of setup B at different mixing speed at 120˚C

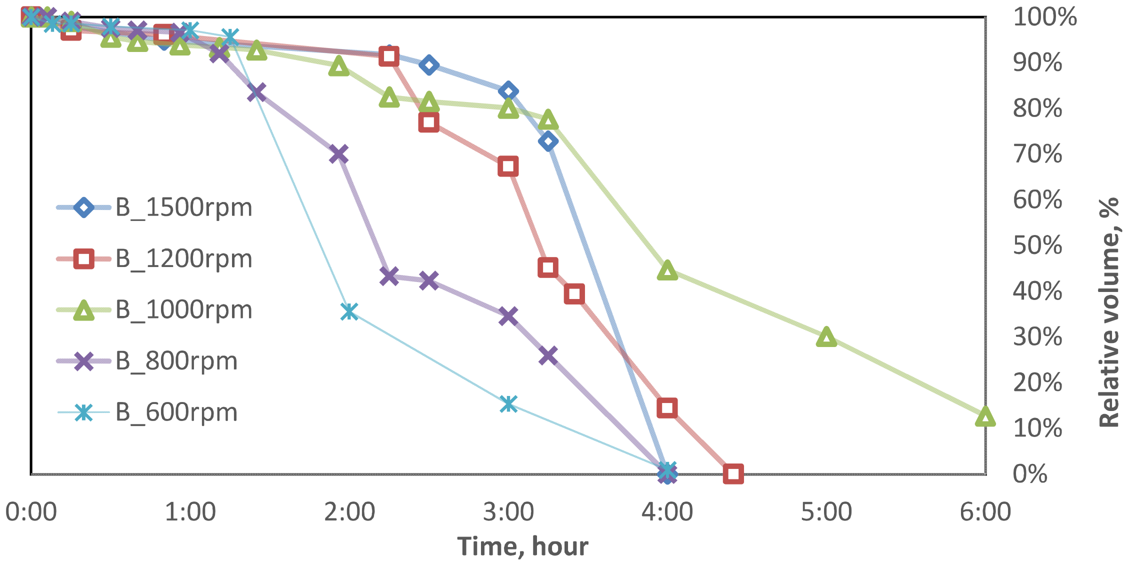


Figure 4.14: Water phase of diesel emulsion of setup B at different mixing speed at 120˚C

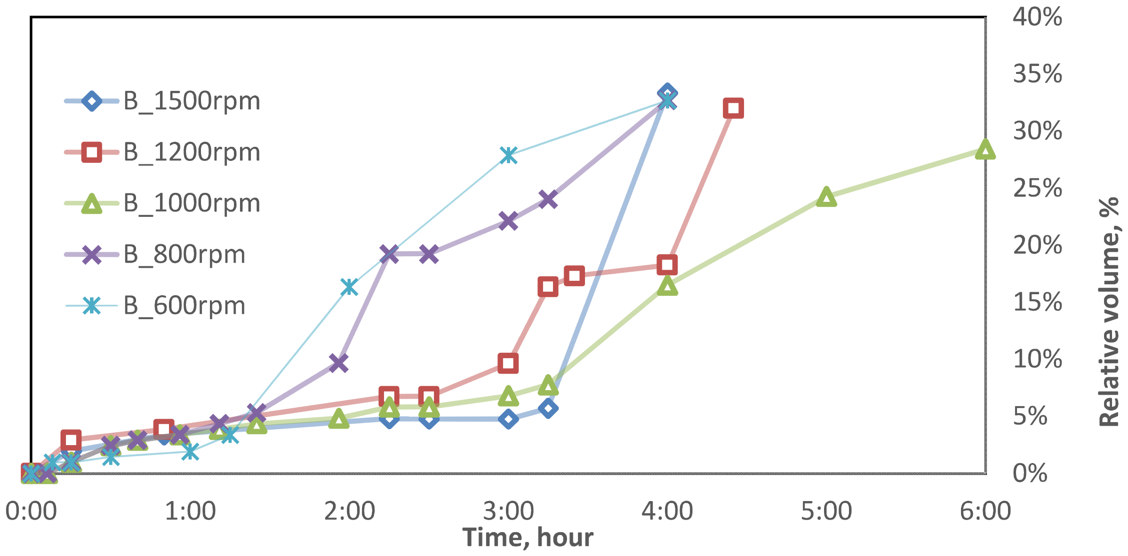


Figure 4.15: Oil phase of diesel emulsion of setup B at different mixing speed at 120˚C

The addition rate in mixing speed optimization for this setup is, unfortunately, not consistent with the emulsifier concentration experiments. Hence, obtaining reproducible data is challenging. This fact explains why emulsions prepared for mixing speed experiments completely break while the ones prepared for emulsifier concentration do not break as much. While the addition rate for emulsifier concentration experiments is of slower type (1.07 mL/min) - hence more stable-, the mixing speed experiments are prepared with faster addition rate of 4.34 mL/min. Also, the same fact explains the reproducibility experiment; is presented in **Figure 4.16**. Which, clearly, indicates the data are not reproducible.

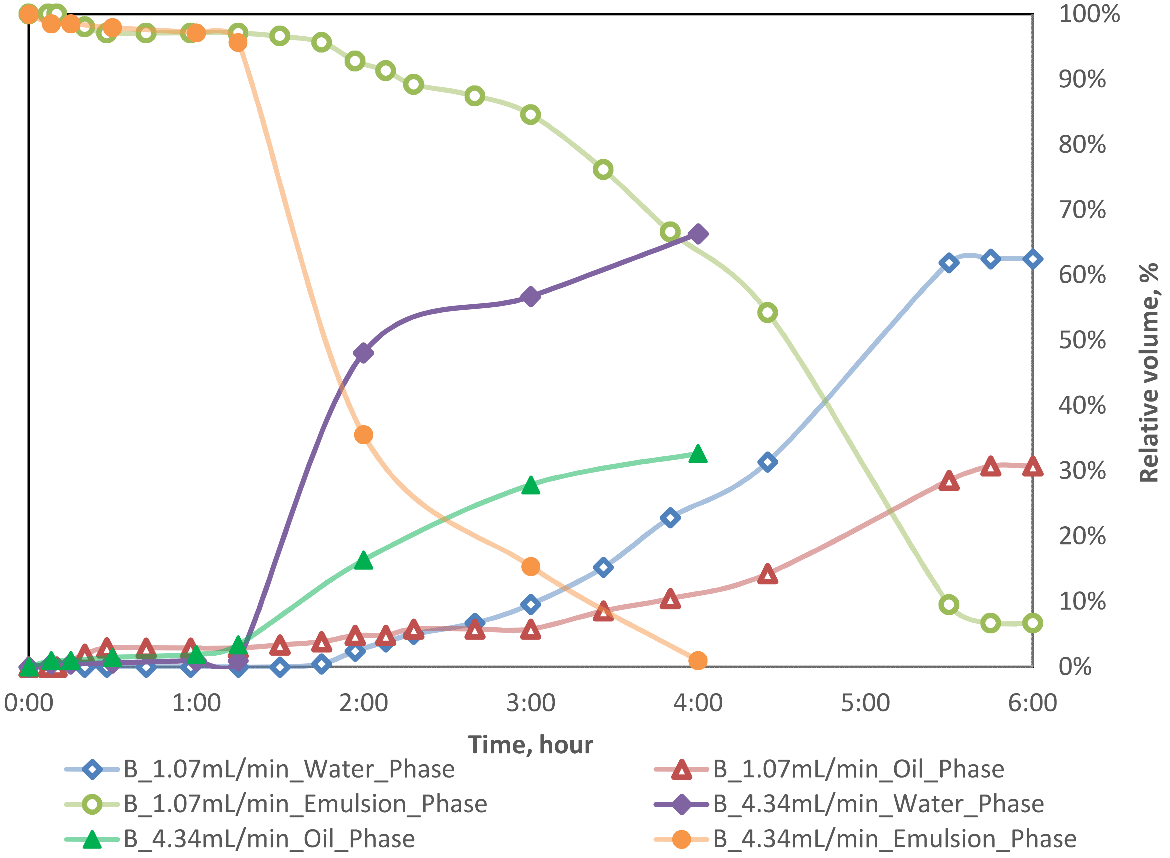


Figure 4.16: Reproducibility data for diesel emulsion setup B at 120˚C

4.4.1.3 Setup C

To overcome the addition rate problem that is faced in the previous setups, a syringe pump is used in this setup onwards. This syringe pump adds the required volume in a regulated time. The addition rate for both emulsifier concentration and mixing speed experiments is consistent of 1.33 mL/min, in this setup. Also, in this setup the same magnetic stirrer is used as in setup B.

In this setup 0.7 vol% is eliminated and not used. Moreover, the emulsifier concentration is optimized and the results are shown in **Figure 4.17**, **Figure 4.18** and **Figure 4.19** for emulsion, water and oil phases, respectively. The results show a contrary trend compared to the previous setups. In this setup, 0.5 vol% is the most stable one followed by 1 vol%; 1.5 vol% is the least stable one during the 6 hour period. Since these results are suspicious, the duration of the experiment is extended to 24 hour. **TABLE 4.2** summarizes the results of the effect of emulsifier concentration after 24 hours. These results are more in agreement with the previous setups. That being said, increasing the emulsifier concentration results in more stable emulsion.

After that, mixing speed optimization is done next. The mixing speed values are: 600, 800, 1000 and 1200 rpm. Overall, the results show that for the first 3 hours of the experiment, all of the speeds are the same. In the second 3 hour period, the trend starts to deviate. **Figure 4.20**, **Figure 4.21** and **Figure 4.22** depict the results of mixing speed for emulsion, water and oil phases, respectively. It can be seen that the four rpm speeds have almost close results especially for 1200 and 1000 rpm which are almost the same. To some extent, increasing the rpm speed has a minor effect on the stability.

TABLE 4.2: Diesel emulsion summary after 24 hours for setup C at 120˚C

Emulsifier Concentration, vol%	Emulsion Phase, %	Water Phase, %	Oil Phase, %
1.5	38	35	27
1.0	32	39	29
0.5	0	70	30

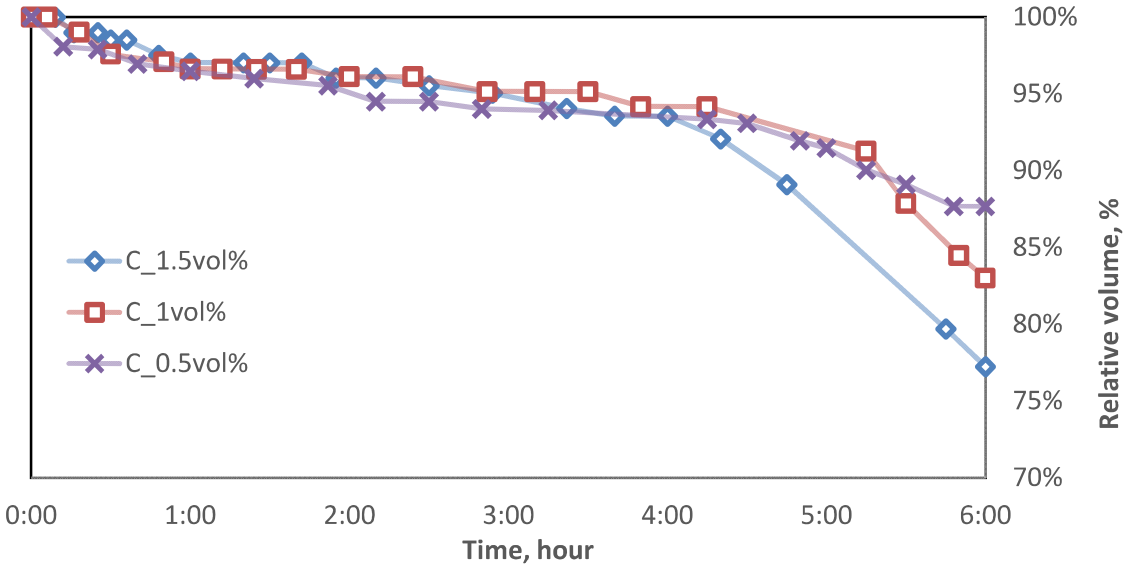


Figure 4.17: Emulsion phase of diesel emulsion of setup C at different emulsifier concentration at 120˚C

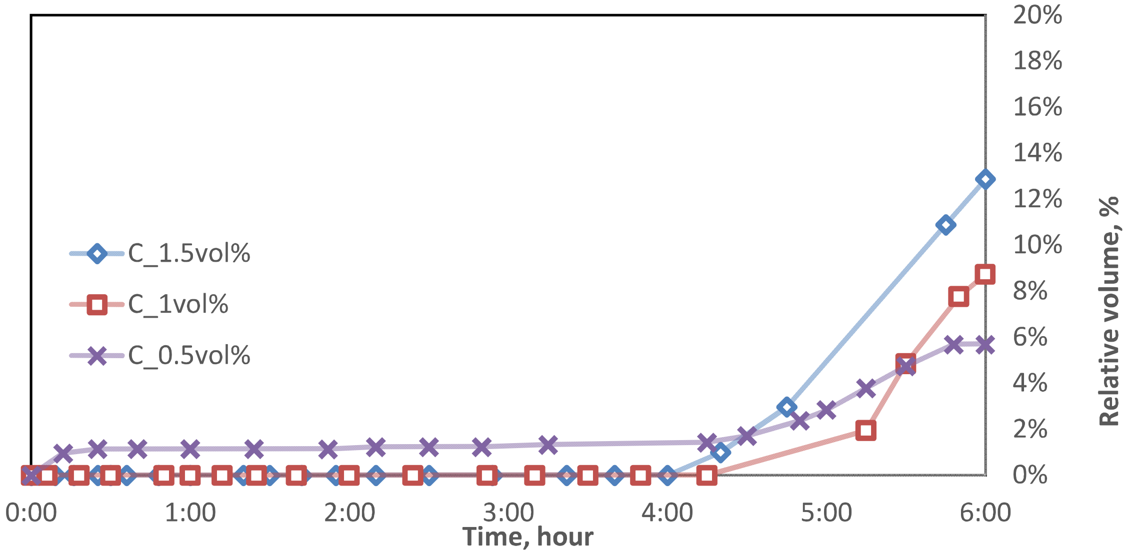


Figure 4.18: Water phase of diesel emulsion of setup C at different emulsifier concentration at 120˚C

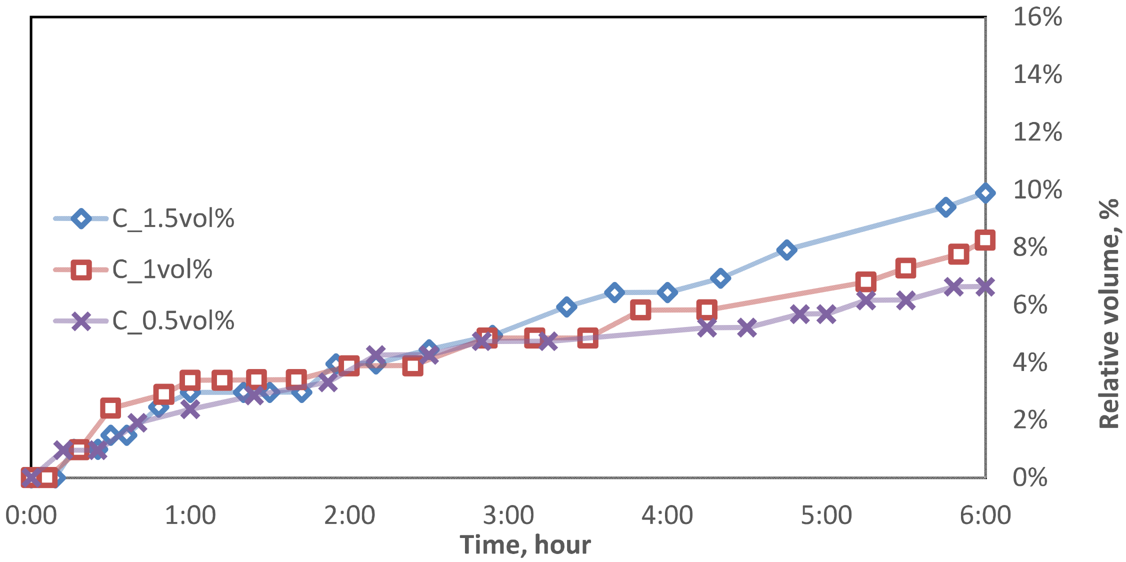


Figure 4.19: Oil phase of diesel emulsion of setup C at different emulsifier concentration at 120˚C

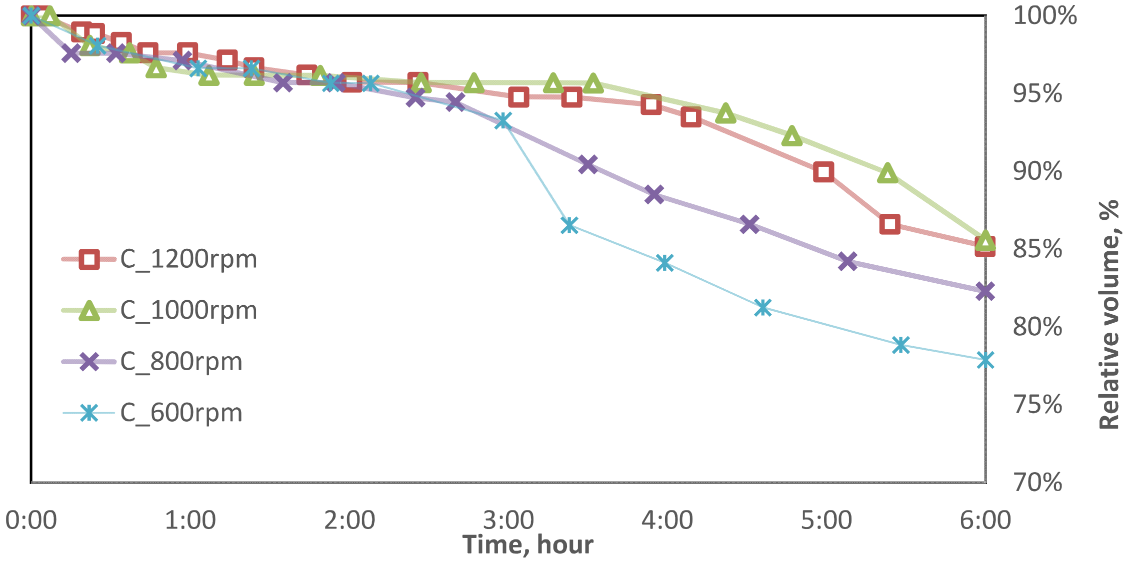


Figure 4.20: Emulsion phase of diesel emulsion of setup C at different mixing speed at 120˚C

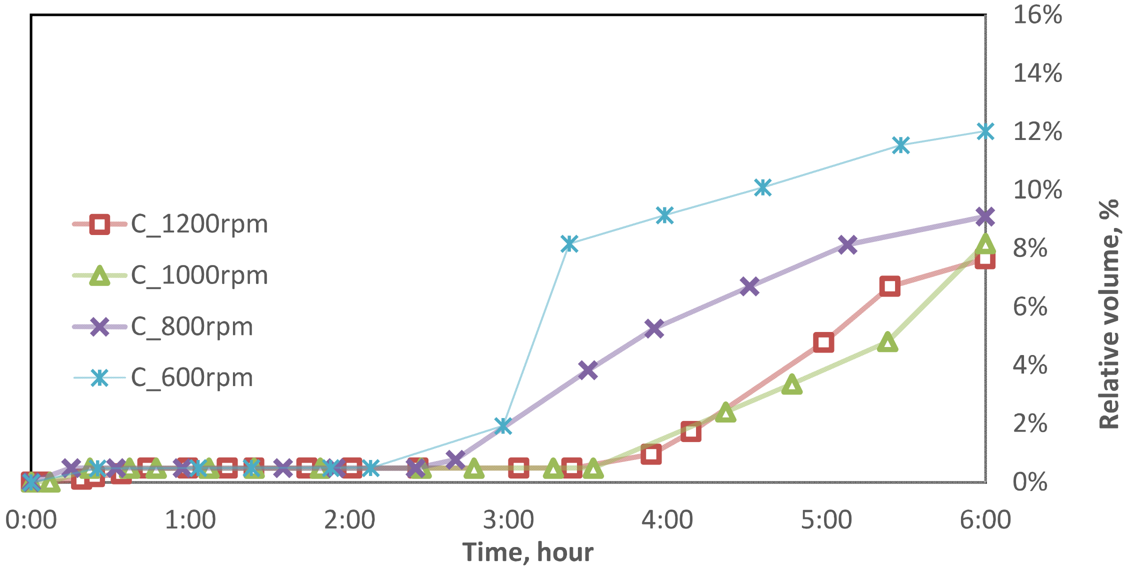


Figure 4.21: Water phase of diesel emulsion of setup C at different mixing speed at 120˚C

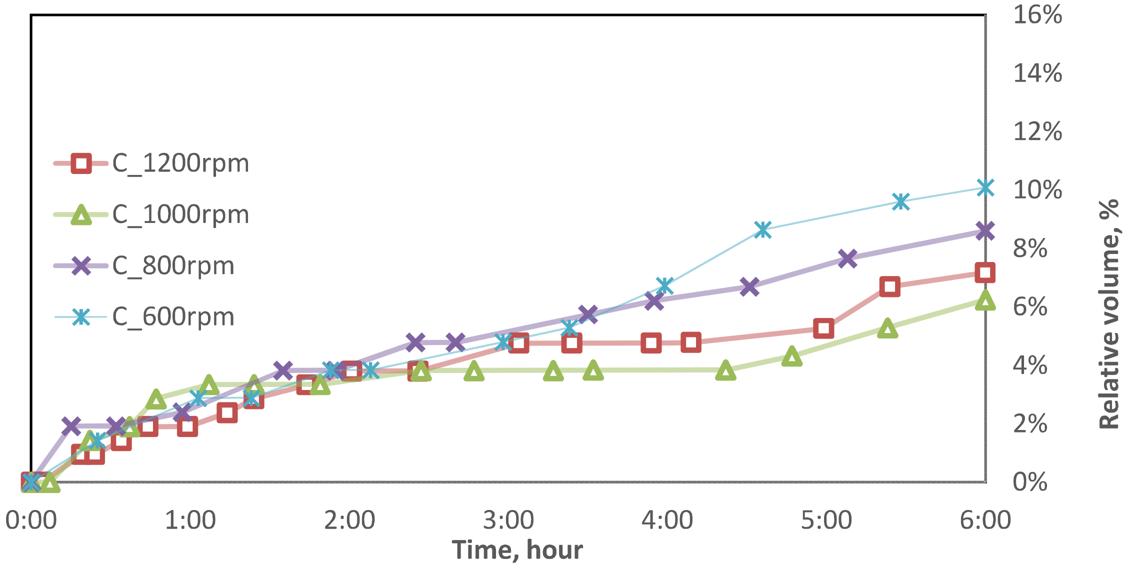


Figure 4.22: Oil phase of diesel emulsion of setup C at different mixing speed at 120˚C

In the previous two setups, data reproducibility is an issue. However, in this setup such an issue is vanished. **Figure 4.23** shows that the data are, reasonably, reproducible.

In all of the previous setups, corrosion inhibitor is added. In the next setup which is setup D, no corrosion inhibitor is added to the emulsion as well as a powerful homogenizer is used for mixing instead of the magnetic stirrer.

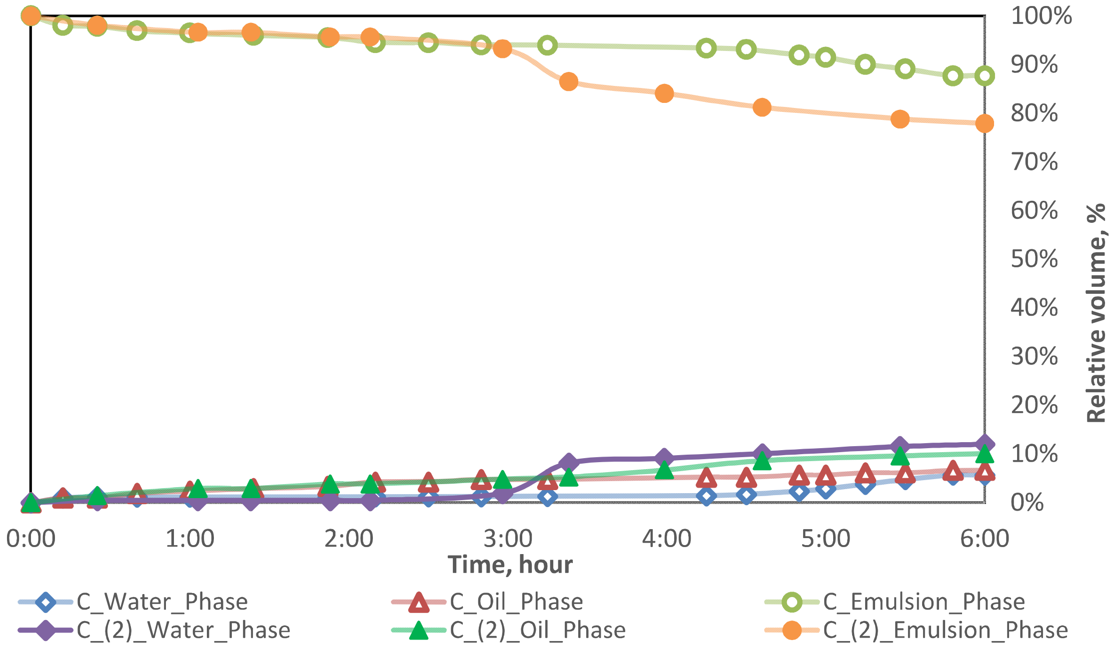


Figure 4.23: Reproducibility data for diesel emulsion of setup C at 120˚C

4.4.1.4 Setup D

Increasing the emulsifier concentration, in this setup, has a minor effect on the stability (same as setup C). **Figure 4.24**, **Figure 4.25** and **Figure 4.26** indicate that the emulsions prepared with the homogenizer are very stable; the heating for 6 hours at 120˚C results in a break in the emulsion phase of 12% only. Moreover, the difference between the highest and the lowest of the emulsion phases in **Figure 4.24**, is 1% only. For that particular reason, 0.5 vol% is chosen to continue the optimization for the mixing speed experiments.

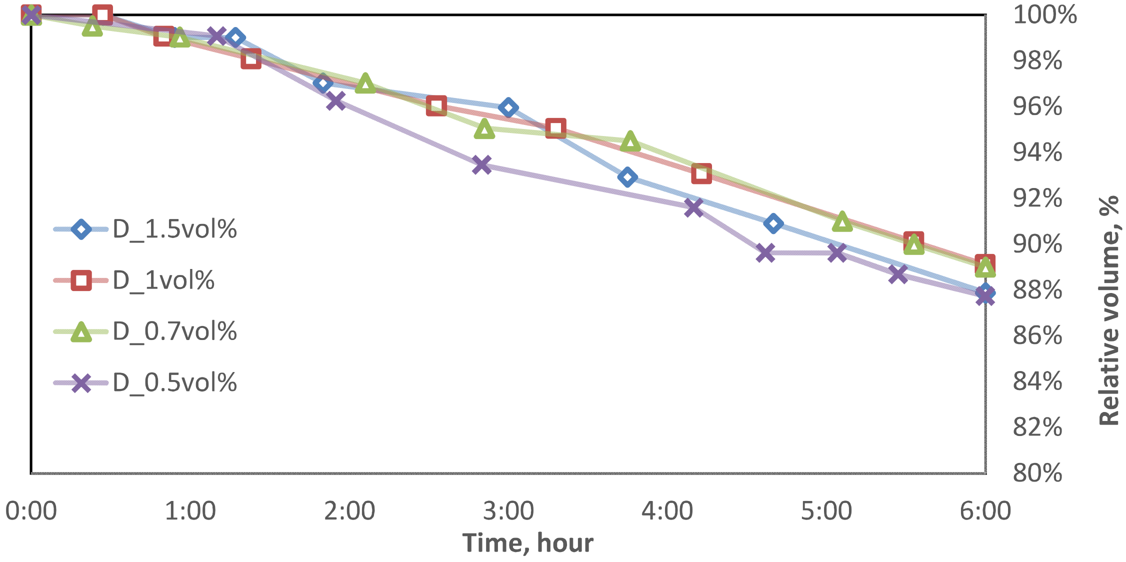


Figure 4.24: Emulsion phase of diesel emulsion of setup D at different emulsifier concentration at 120˚C

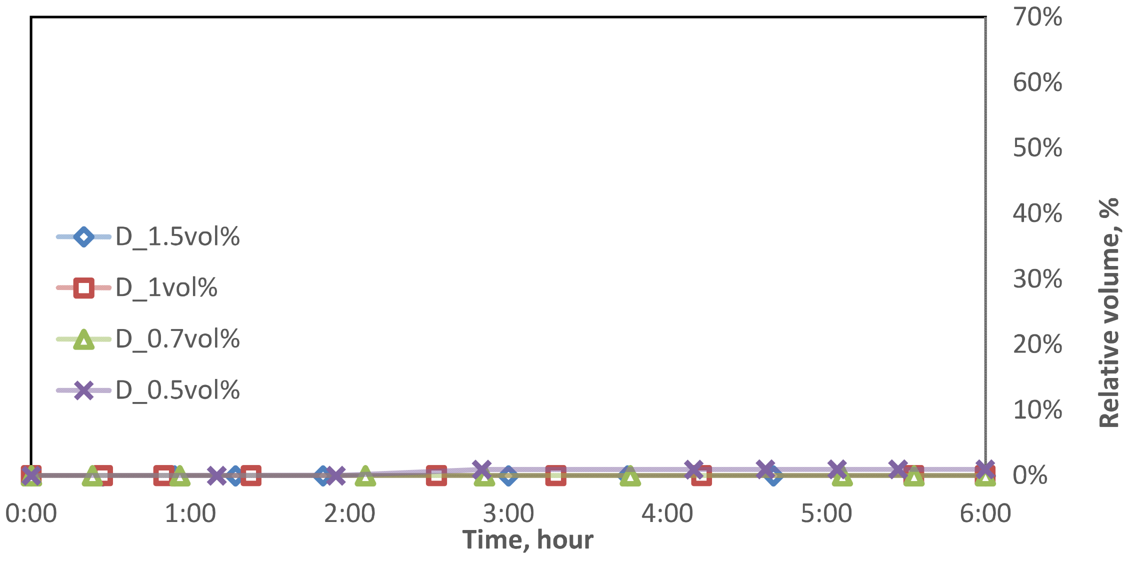


Figure 4.25: Water phase of diesel emulsion of setup D at different emulsifier concentration at 120˚C

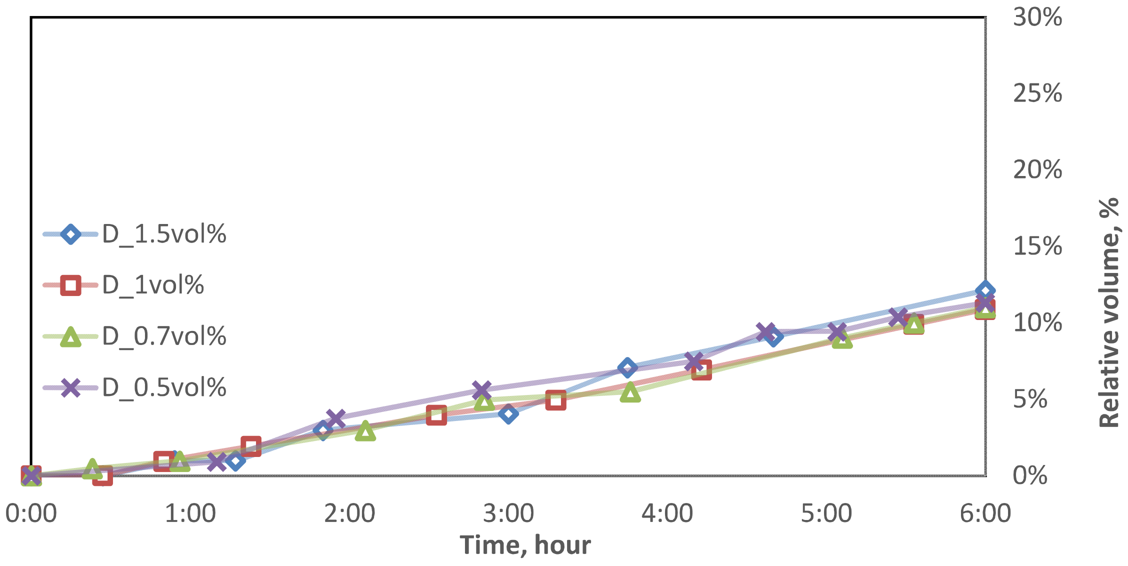


Figure 4.26: Oil phase of diesel emulsion of setup D at different emulsifier concentration at 120˚C

After the optimization of the emulsifier concentration (0.5vol %), four distinct mixing speeds (rpm) are used namely, 600, 800, 1000 and 1400 rpm. The emulsions are prepared with 0.5vol % of emulsifier concentration and at the four mixing speeds.

Then, the emulsions are heated at 120˚C to address the effect of mixing speed on it. **Figure 4.27**, **Figure 4.28** and **Figure 4.29** show the effect of mixing speed on emulsion, water and oil phases, respectively. These results show that the mixing speed has no major effect on the stability. Generally, the emulsions prepared in this setup are very stable because of the use of the homogenizer. **Figure 4.25** and **Figure 4.28** both show that there is no water phase coming out of the emulsion during the heating period for 6 hours at 120˚C.

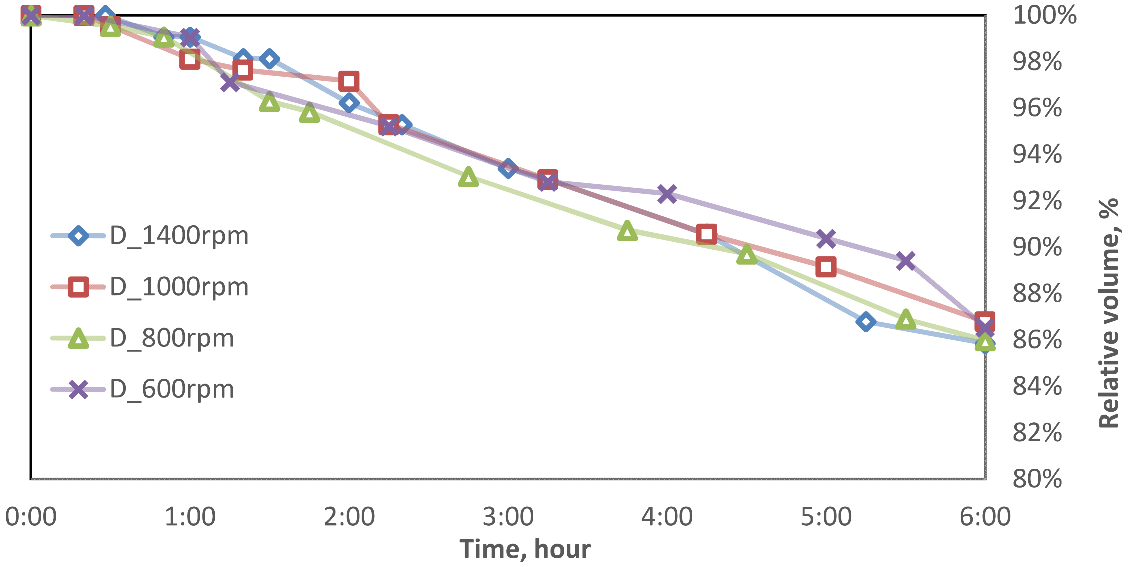


Figure 4.27: Emulsion phase of diesel emulsion of setup D at different mixing speed at 120˚C

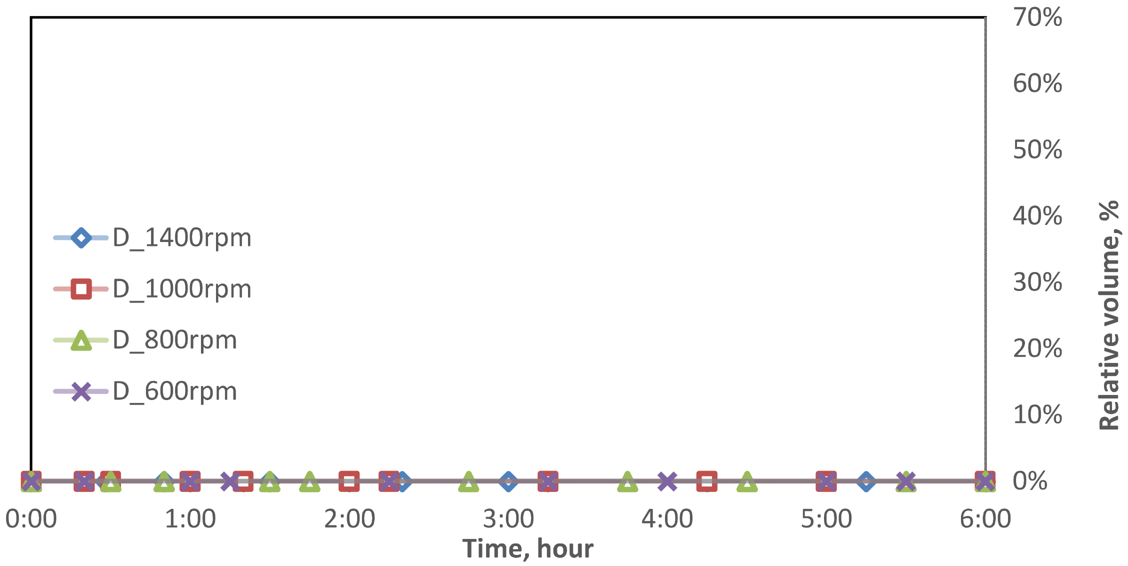


Figure 4.28: Water phase of diesel emulsion of setup D at different mixing speed at 120˚C

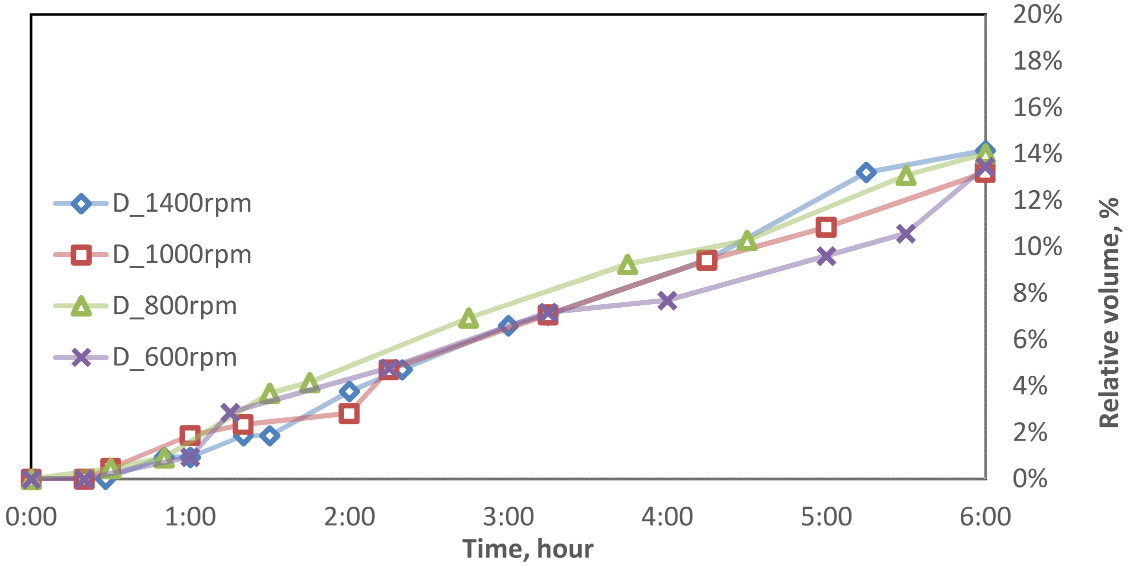


Figure 4.29: Oil phase of diesel emulsion of setup D at different mixing speed at 120˚C

Moreover, reproducibility of the data is not an issue in this setup as **Figure 4.30** confirms that. Therefore, setup D is the best of all setups used in this study, hence, it will be used to carry on the rheology tests. Because rheology tests need to have reproducible data in order for the study be consistent.

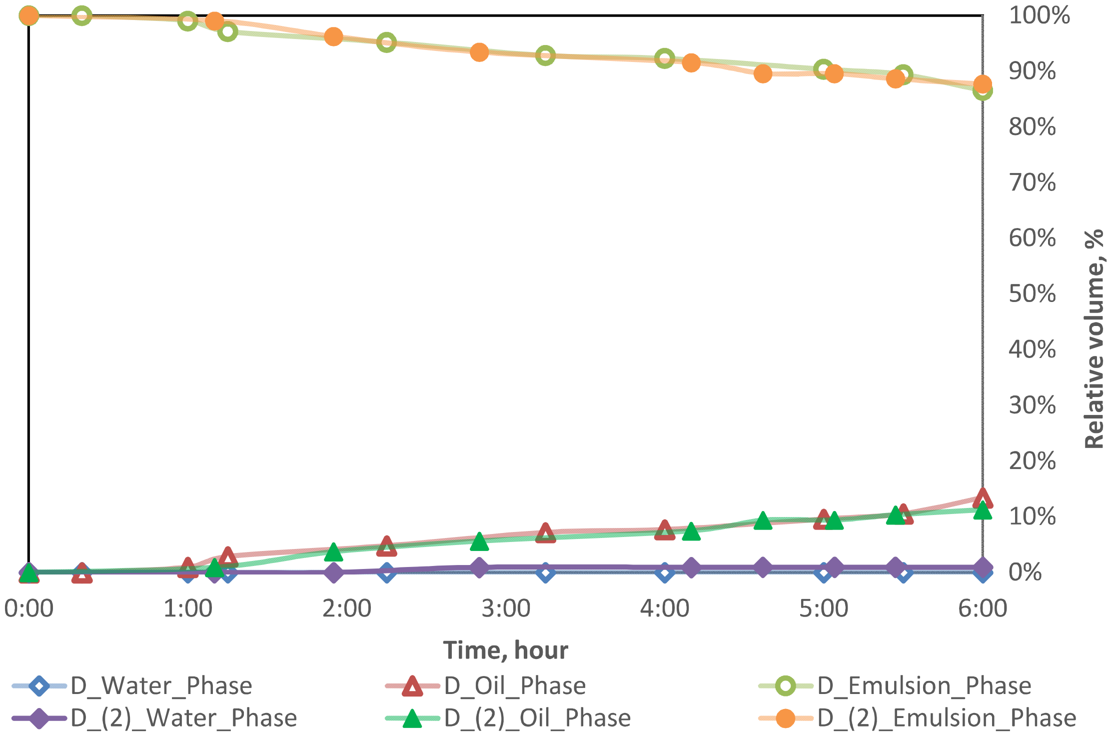


Figure 4.30: Reproducibility data for diesel emulsion of setup D at 120˚C

4.4.2 Viscosity and oscillating measurements

In order to conduct viscosity and oscillating measurements, assuring reproducibility of the data is essential. Therefore, setup D is the only setup used for these measurements. In this section, the effect of emulsifier concentration, mixing speed, temperature and aging on rheology are investigated.

4.4.2.1 Effect of emulsifier concentration

The emulsifier concentrations is varied in order to apprehend its effect on both apparent viscosity and viscoelastic properties. The emulsifier concentrations are: 0.5, 0.7, 1.0 and 1.5 vol%.

Figure 4.31, **Figure 4.32** and **Figure 4.33** show the four concentrations effect on apparent viscosity at 25, 60 and 100˚C, respectively. All of the data are fitted seamlessly using power-law model. In addition, the overall trend is that the increase of emulsifier concentration results in an increase in the apparent viscosity. However, that increase is not significant, but, it only is significant at 100˚C of 1.5 vol% especially at low shear rates. The parameters of the power-law model used to fit the variation of emulsifier concentration at different temperatures are summarized in **TABLE 4.3**. Overall, the data are seamlessly fitted in power-law model with the correlation coefficient ranging between 0.95 to 0.99. Moreover, at a given temperature, the emulsifier concertation is inversely related to power law index, n and directly related to power law constant, K. Increasing the emulsifier concertation dedicates an increase in the apparent viscosity which means more emulsifier, more molecules to work on reducing the interfacial tension resulting in more stable emulsion, hence more viscous. This trend is stunningly depicted in the inverse relation between the emulsifier concertation and n.

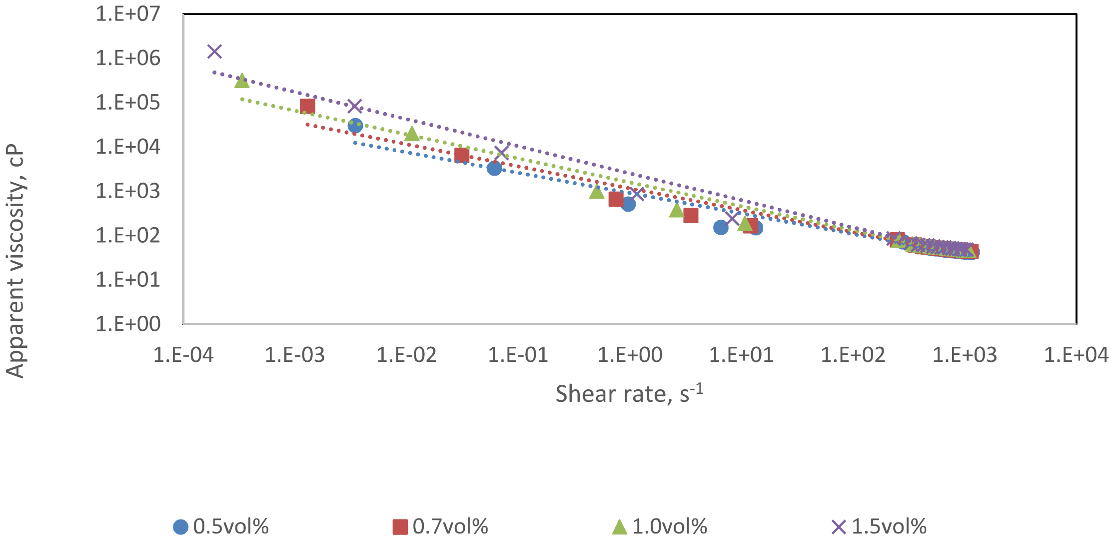


Figure 4.31: Effect of emulsifier concentration on apparent viscosity for diesel emulsion at 25˚C

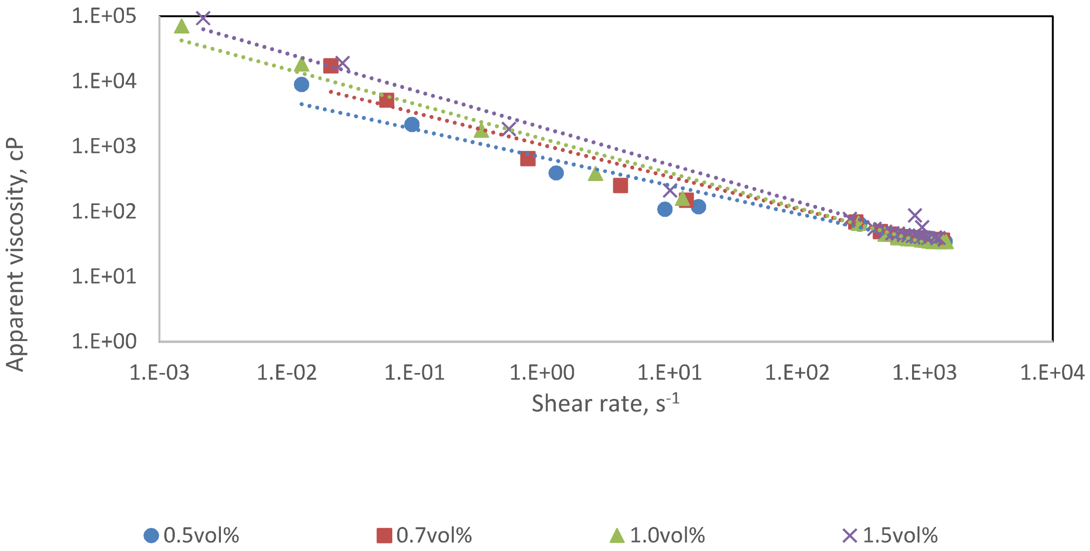


Figure 4.32: Effect of emulsifier concentration on apparent viscosity for diesel emulsion at 60˚C

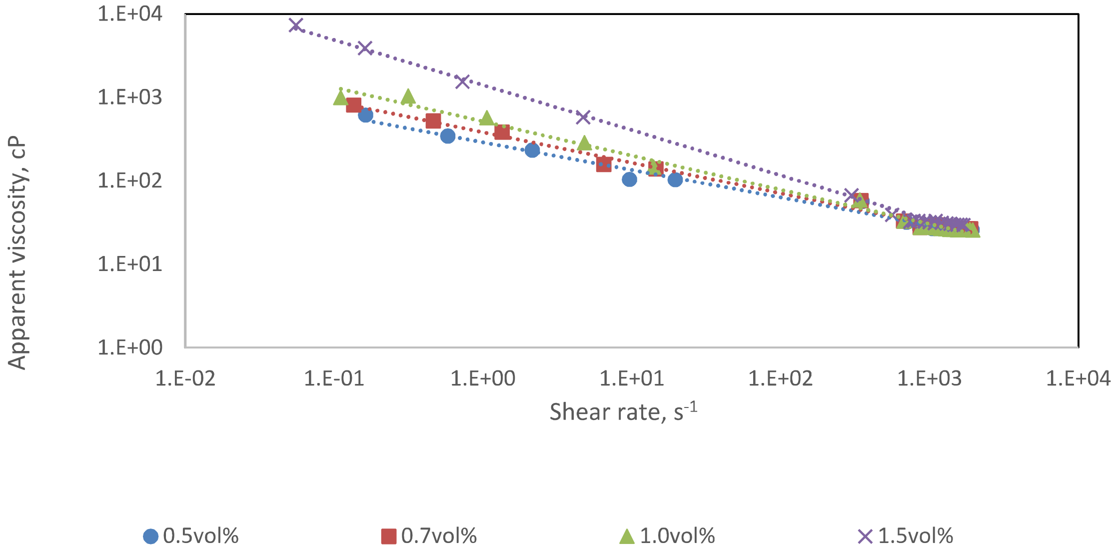


Figure 4.33: Effect of emulsifier concentration on apparent viscosity for diesel emulsion at 100˚C

TABLE 4.3: Summary of power-law model for emulsifier concentration for diesel emulsion

Temperature ˚C	Emulsifier Concentration vol%	Power Law Constant, K mPa.s^n	Power Law Index, n	Correlating Coefficient, R^2
25	0.5	913.9	0.539	0.956
	0.7	1180.5	0.504	0.963
	1	1594.4	0.459	0.976
	1.5	2563.4	0.388	0.975
60	0.5	680.7	0.568	0.958
	0.7	1060.7	0.507	0.959
	1	1329.9	0.468	0.981
	1.5	1952.1	0.432	0.978
100	0.5	291.1	0.669	0.987
	0.7	383.2	0.634	0.992
	1	516.4	0.590	0.991
	1.5	1408.7	0.460	0.997

As far as the effect of these concentrations on viscoelastic properties are concerned, **Figure 4.34**, **Figure 4.35** and **Figure 4.36** represent the results of measuring both elastic and viscous moduli as a function of frequency at 25, 60 and 100˚C, respectively. At the three temperatures, the elastic behavior of the emulsion is dominant, however, a crossover occurs at high frequency and this results in viscous behavior dominating on the emulsion. **Figure 4.34** indicates that at 25˚C increasing the emulsifier concatenation increases both moduli. Which is almost the case at 60˚C except for 0.5vol% as seen in **Figure 4.35**. At 100˚C, **Figure 4.36**, the emulsions with 0.7 and 1.0 vol% behave the same. Nonetheless, increasing the emulsifier concentration leads to increasing both moduli.

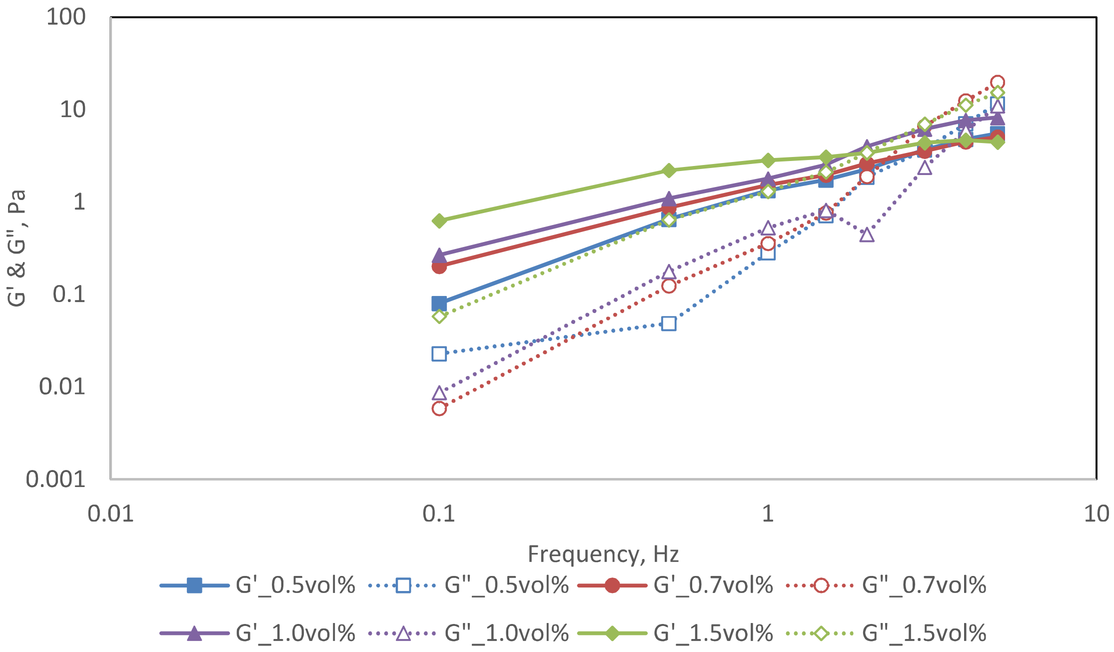


Figure 4.34: Effect of emulsifier concentration on G′ and G″ for diesel emulsion at 25˚C

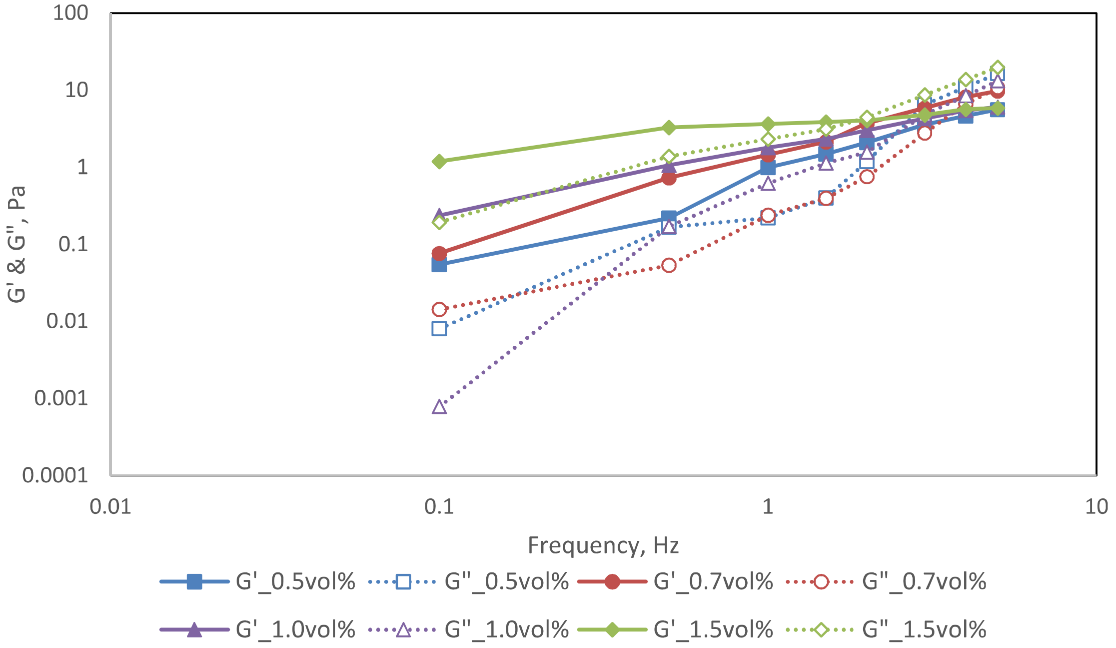


Figure 4.35: Effect of emulsifier concentration on G′ and G″ for diesel emulsion at 60˚C

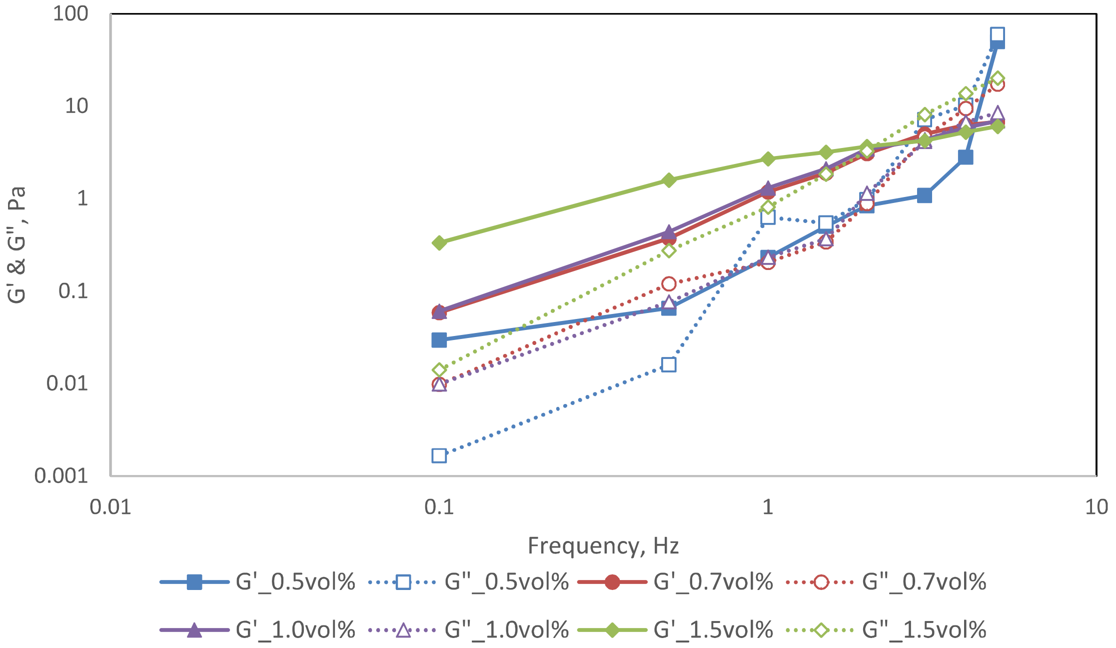


Figure 4.36: Effect of emulsifier concentration on G′ and G″ for diesel emulsion at 100˚C

4.4.2.2 Effect of mixing speed

As far as the effect of mixing speed on rheology of emulsion goes, four distinct speeds are used, namely 600, 800, 1000 and 1400 rpm. Apparent viscosity and oscillating tests are conducted at 25, 60 and 100˚C.

With regards to apparent viscosity tests, **Figure 4.37**, **Figure 4.38** and **Figure 4.39** represent the results of varying the mixing speed at 25, 60 and 100˚C, correspondingly. The general behavior is that emulsions prepared at 600 and 1400 rpm have the highest apparent viscosity. **Figure 4.37** indicates that at 25˚C, similar apparent viscosity data are obtained at high shear rates for all speeds. However, decreasing the shear rate results in increasing the apparent viscosity. Emulsions prepared at 1400 rpm have the highest apparent viscosity, followed by emulsions of 600 rpm then 1000 rpm and finally the 800 rpm. That is the same trend for the apparent viscosity at 60˚C (**Figure 4.38**), except for the emulsions of 1400 and 600 rpm which have almost same results. Moreover, at 100˚C (**Figure 4.39**), the 600 rpm emulsions has the highest apparent viscosity at high shear rates, but at low shear rates it has same apparent viscosity as the 1400 rpm emulsion. The power-law parameters for fitting the variation of mixing speed at different temperatures are summarized in **TABLE 4.4**, which shows that unlike emulsifier concertation, mixing speed does not have a clear trend with n and K of the power-law model.

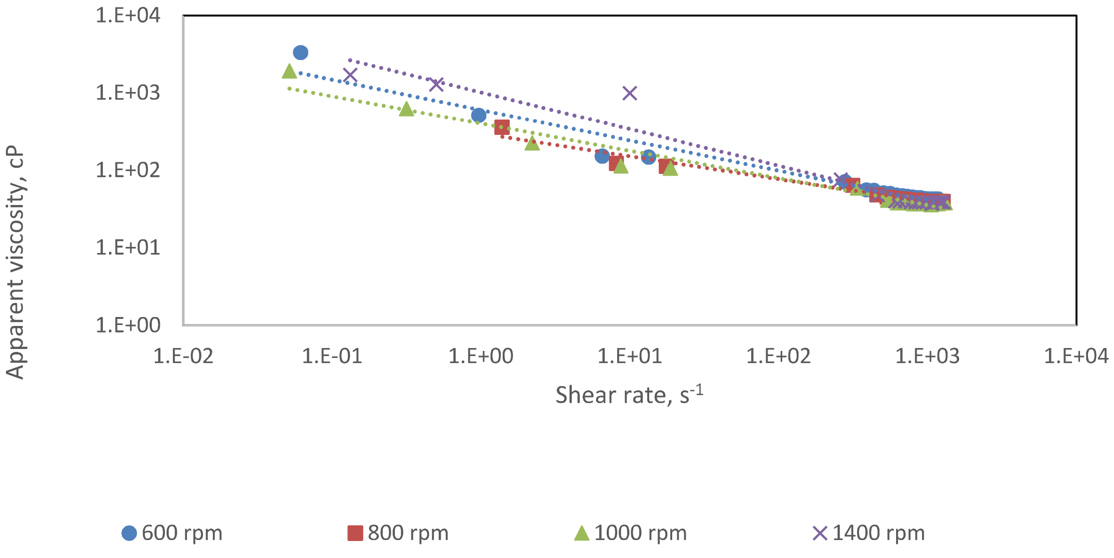


Figure 4.37: Effect of mixing speed on apparent viscosity for diesel emulsion at 25˚C

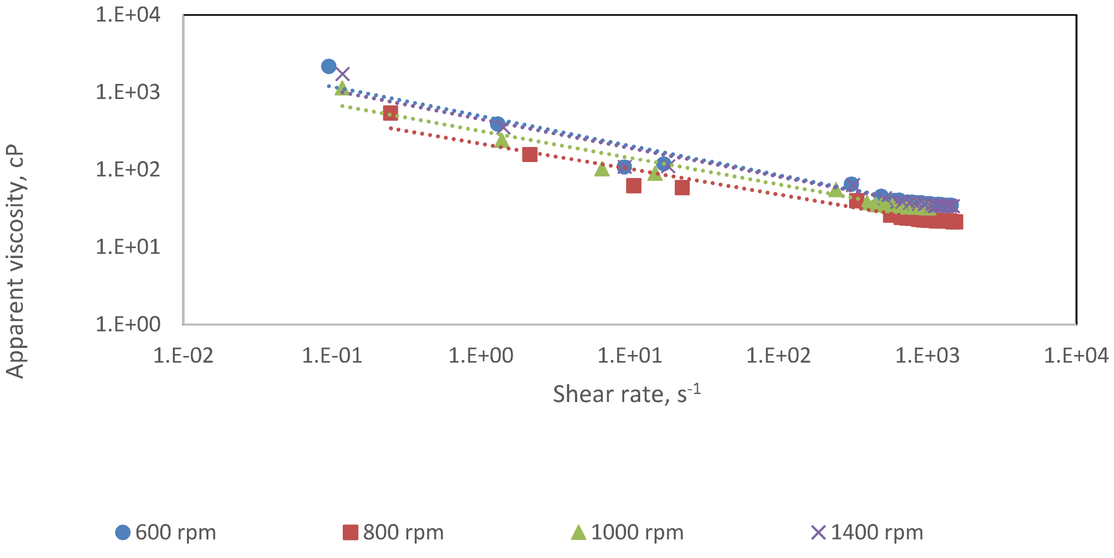


Figure 4.38: Effect of mixing speed on apparent viscosity for diesel emulsion at 60˚C

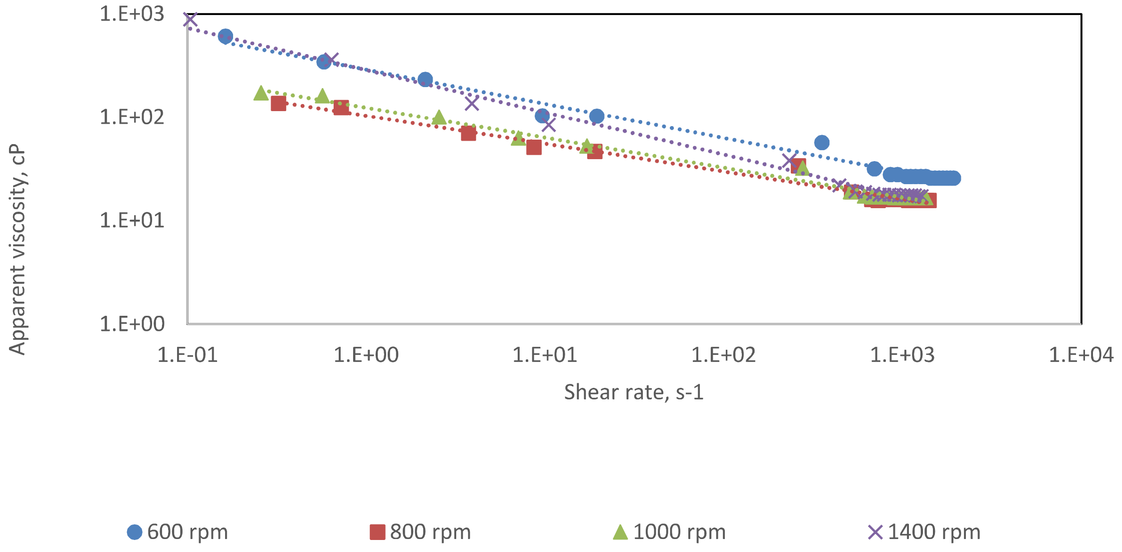


Figure 4.39: Effect of mixing speed on apparent viscosity for diesel emulsion at 100˚C

TABLE 4.4: Summary of power-law model for mixing speed for diesel emulsion

Temperature ˚C	**Mixing Speed rpm**	**Power Law Constant, K mPa.s^n**	**Power Law Index, n**	**Correlating Coefficient, R^2**
25	600	604.2	0.609	0.955
	800	300.4	0.706	0.965
	1000	404.3	0.649	0.965
	1400	1018.9	0.527	0.951
60	600	493.4	0.619	0.951
	800	218.0	0.672	0.955
	1000	317.8	0.655	0.952
	1400	452.0	0.629	0.954
100	600	291.1	0.669	0.987
	800	104.1	0.731	0.979
	1000	124.6	0.710	0.987
	1400	287.8	0.599	0.989

As for the oscillating tests, **Figure 4.40**, **Figure 4.41** and **Figure 4.42** show the effect of mixing speed on oscillatory tests at 25, 60 and 100˚C, respectively. The general trend is that the emulsion behaves as viscoelastic semi-solid at low frequency for all rpm speeds but then at high frequency a crossover occurs and the viscous modulus becomes dominant. Also, increasing the mixing speed from 800 to 1400 rpm results in increasing G′ at low frequencies with an exception to the 600 rpm emulsion. However, there is no clear trend on the viscous modulus, G″ as the data fluctuates as well as there is no major change in the data when rpm speed is changed.

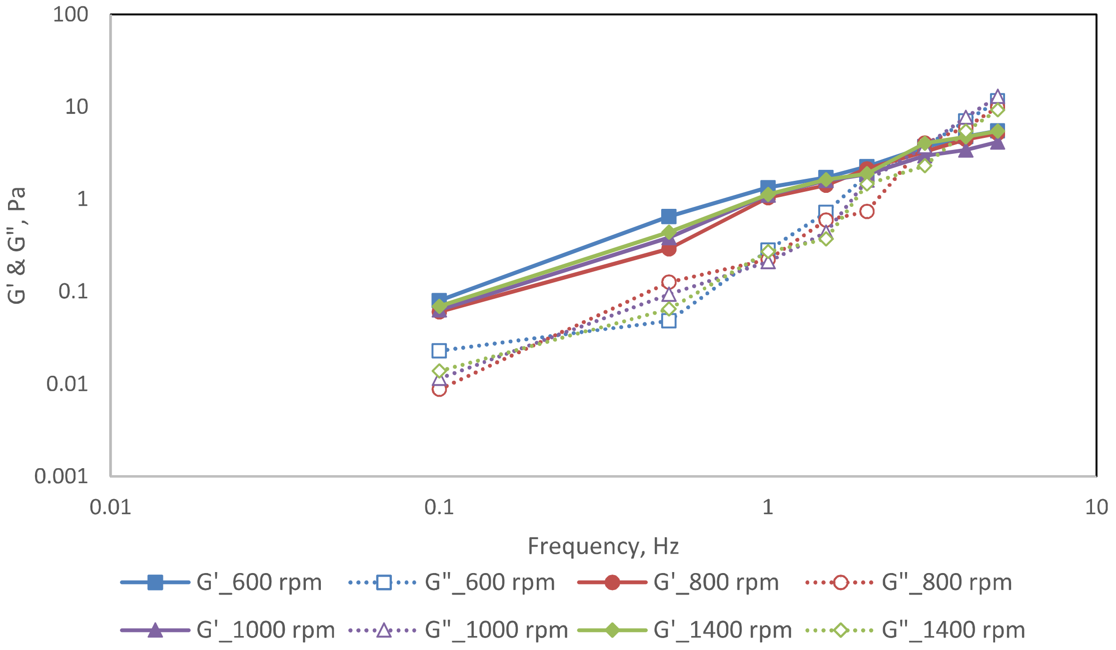


Figure 4.40: Effect of mixing speed on G′ and G″ for diesel emulsion at 25˚C

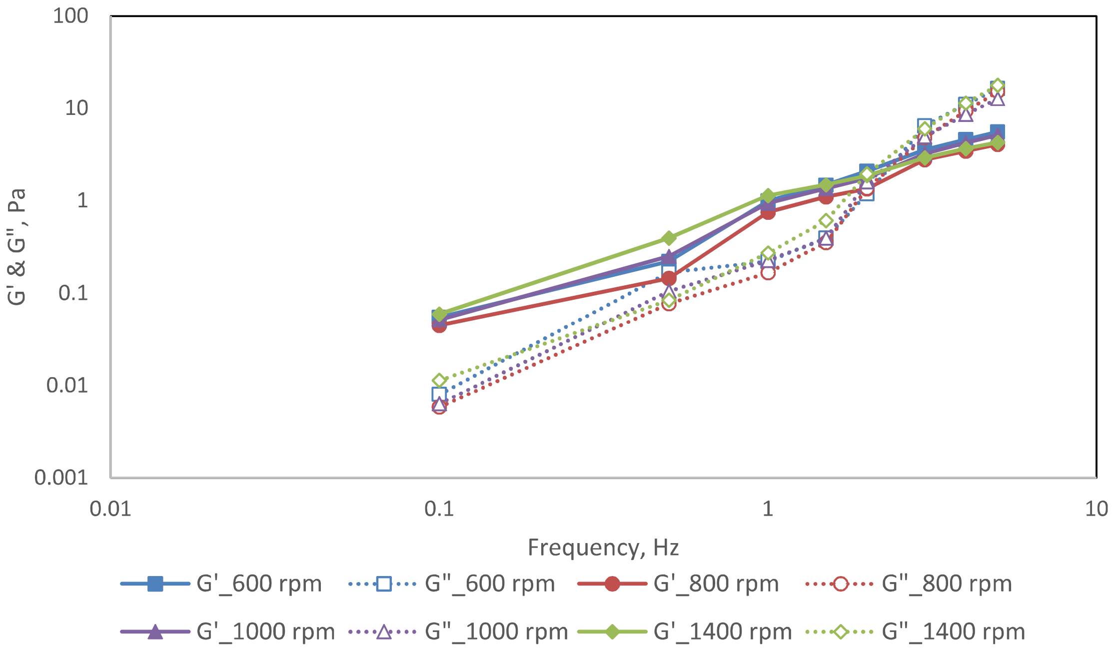


Figure 4.41: Effect of mixing speed on G′ and G″ for diesel emulsion at 60˚C

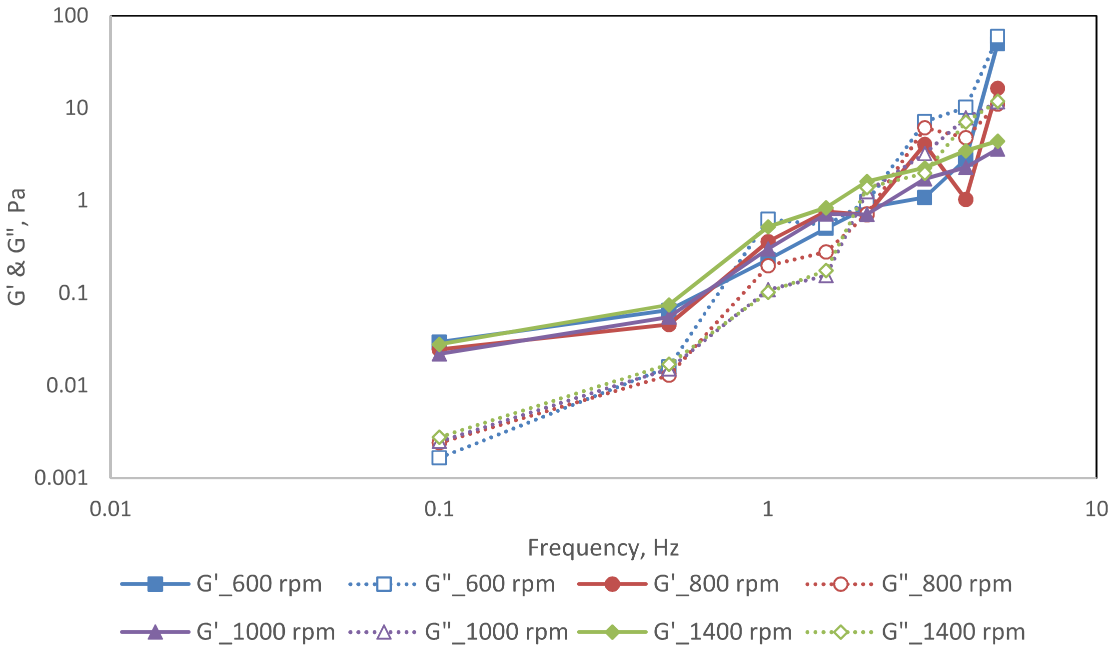


Figure 4.42: Effect of mixing speed on G′ and G″ for diesel emulsion at 100˚C

4.4.2.3 Effect of temperature

The temperature effect plays an important factor on rheology. **Figure 4.43** points out that increasing the temperature from 25˚C to 100˚C results in decreasing the apparent viscosity and this decrease is most substantial at low shear rates where the apparent viscosity could decrease by a 100-fold. In **TABLE 4.5**, the power-law model parameters for temperature effect are summarized, which shows that increasing the temperature results in decreasing K and in increasing n, hence decreasing the apparent viscosity.

Furthermore, **Figure 4.44** represents the effect of temperature on viscoelastic properties. With respect to G′, increasing the temperature from 25 to 60˚C has no significant effect; increasing it to 100˚C a significant decrease is the result. Whereas, there is no clear trend for G″ as the data fluctuates. In addition, **Figure 4.45** shows the apparent viscosity fitted in an exponential trend line plotted on semi-log graph as a function of temperature. The data are fitted perfectly in Arrhenius equation (Equation 1.5).

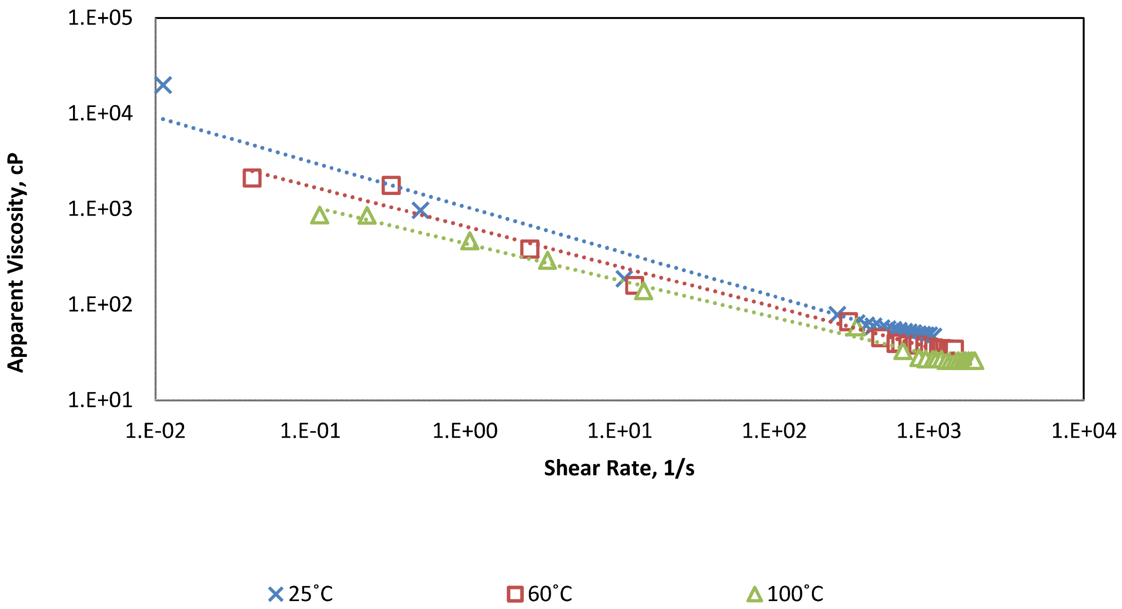


Figure 4.43: Effect of temperature on apparent viscosity for diesel emulsion

TABLE 4.5: Summary of power-law model for temperature effect for diesel emulsion

Temperature ˚C	**Power Law Constant, K mPa.s^n**	**Power Law Index, n**	**Correlating Coefficient, R^2**
25	1064.9	0.530	0.960
60	660.9	0.578	0.983
100	440.1	0.612	0.993

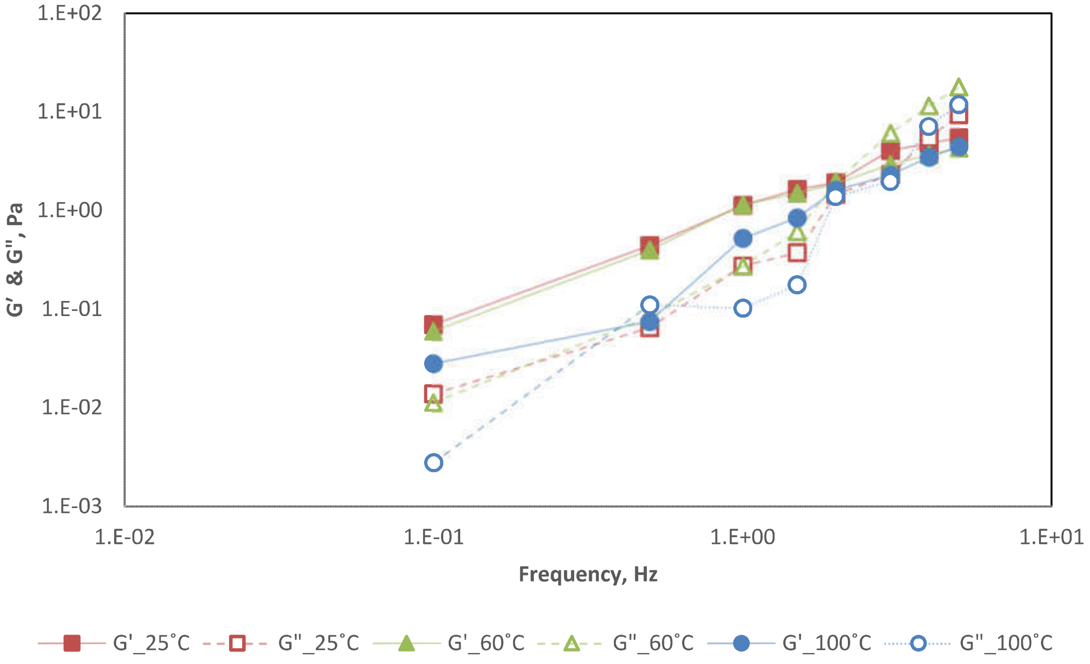


Figure 4.44: Effect of temperature on G′ and G″ for diesel emulsion

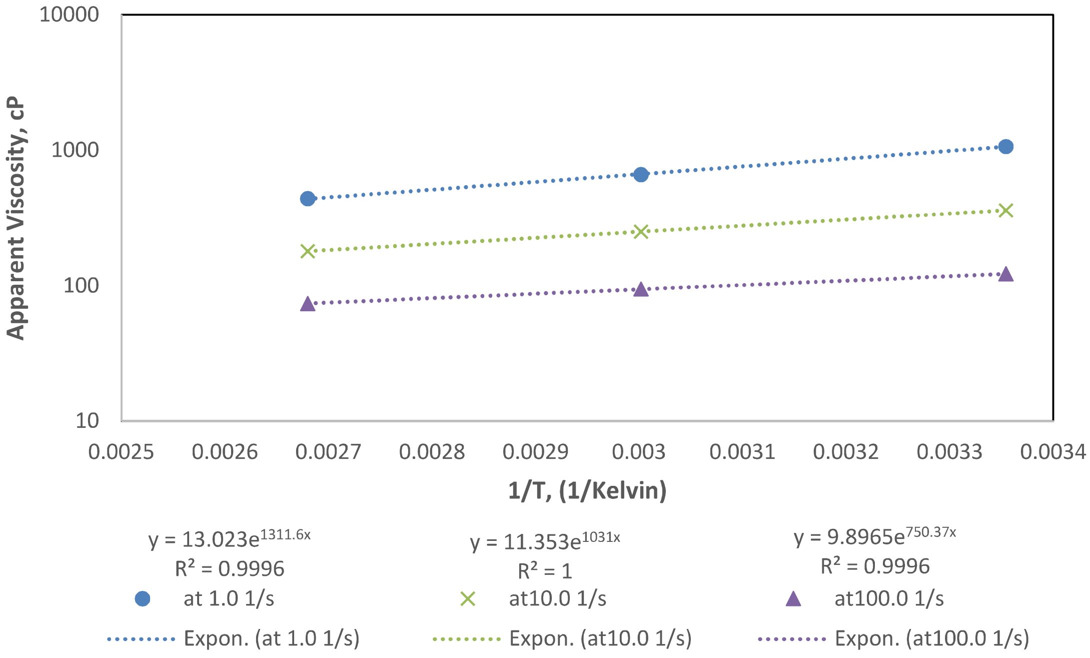


Figure 4.45: Apparent viscosity of diesel emulsion as a function of temperature

4.4.2.4 Effect of aging

One of the many positives of reproducible data is being able to conduct aging experiments with confidence. Hence, three samples of emulsions are prepared. Where, one sample is aged for 96 hours and the second is aged for 24 hours, all of the aging is done at room temperature. The third one is used as soon as the preparation is finished (fresh). Then, rheology tests are conducted on all of the three samples. These rheology tests are apparent viscosity and oscillatory measurements at 25, 60 and 100˚C. The reason for conducting the effect of aging at room temperature is that sometimes in the field after the emulsion is prepared with big quantities in the tank, some unforeseen conditions could occur resulting in a delay of pumping the emulsion and leaving it unused for a period of time.

Furthermore, **Figure 4.46** plots the apparent viscosity data at 25˚C of the three samples. It is inferred from the figure that the change in apparent viscosity at 25˚C due to aging is not significant. Also, the results of the apparent viscosity measurements at 60˚C are shown in **Figure 4.47**. It is clear that the fresh emulsion has a higher apparent viscosity compared to the aged ones, however, such difference is not major. Also, **Figure 4.48** shows the apparent viscosity at 100˚C, where the fresh and aged at 24 hours emulsions have the same data, and the 96 hour emulsion has lower apparent viscosity values. The power-law model parameters for effect of aging are tabulated in **TABLE 4.6**.

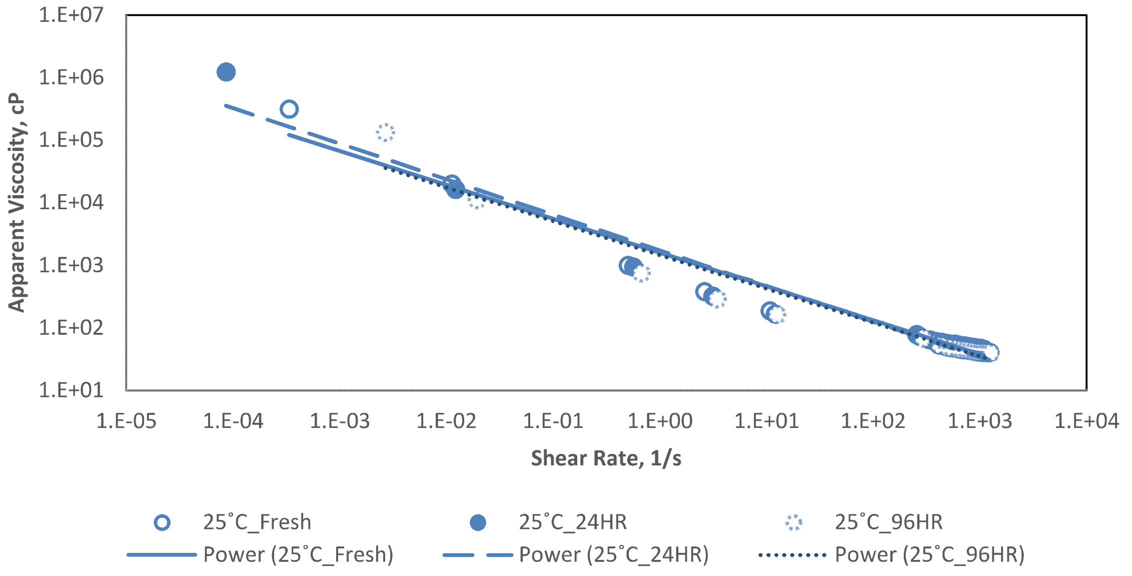


Figure 4.46: Effect of aging for 24 and 96 hours on apparent viscosity at 25˚C for diesel emulsion

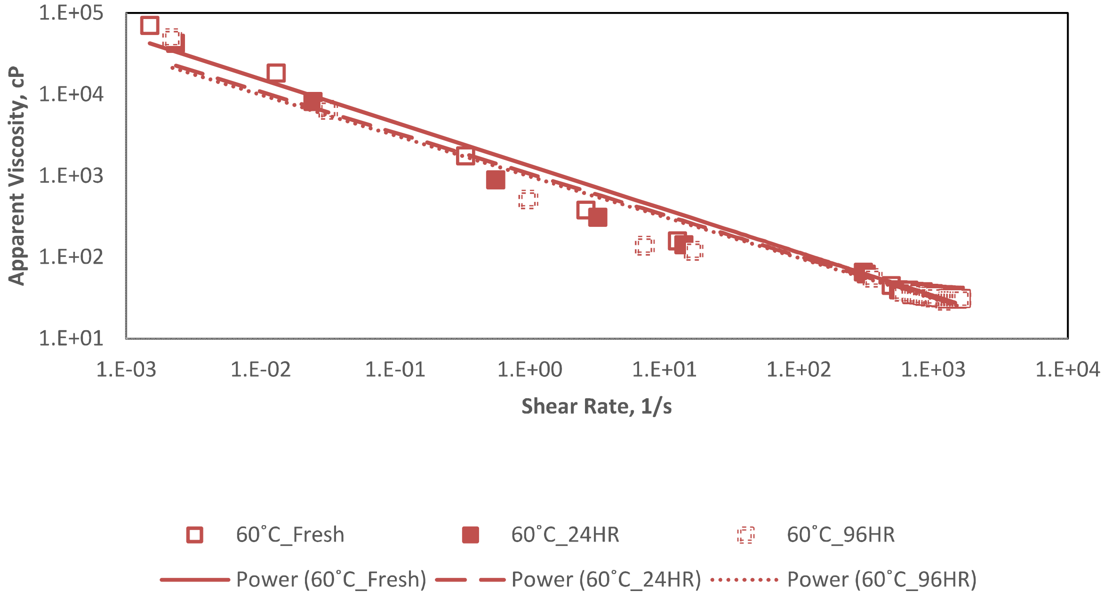


Figure 4.47: Effect of aging for 24 and 96 hours on apparent viscosity at 60˚C for diesel emulsion

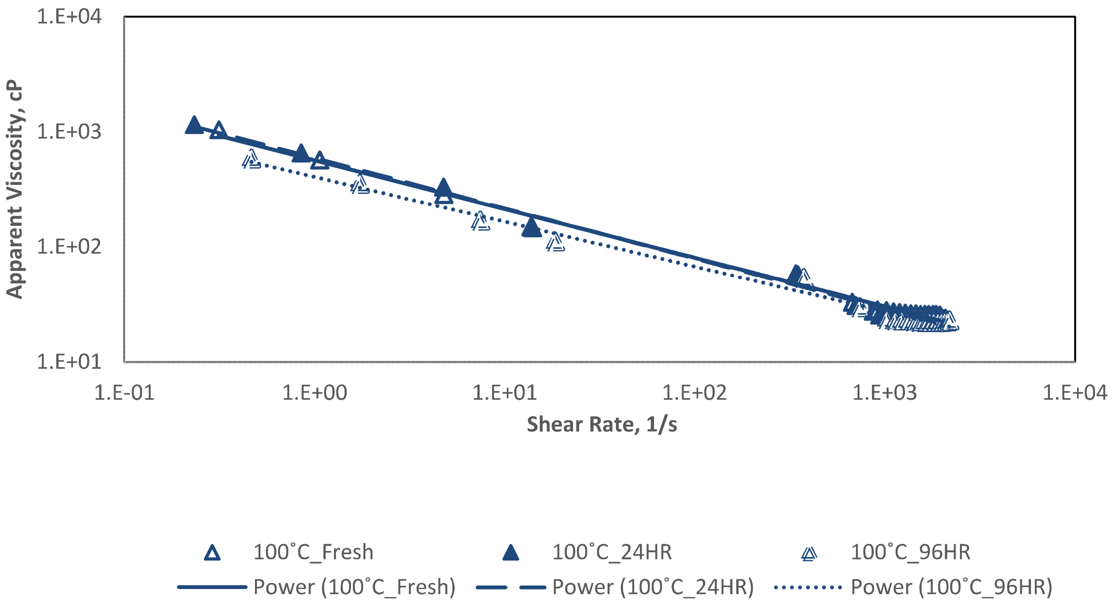


Figure 4.48: Effect of aging for 24 and 96 hours on apparent viscosity at 100˚C for diesel emulsion

TABLE 4.6: Summary of power-law model for effect of aging for diesel emulsion

Temperature ˚C	**Aged time at room temperature hour**	**Power Law Constant, K mPa.s^n**	**Power Law Index, n**	**Correlating Coefficient, R^2**
25	0	1594.4	0.459	0.966
	24	1736.2	0.431	0.963
	96	1465.2	0.459	0.951
60	0	1329.9	0.468	0.981
	24	1056.6	0.495	0.979
	96	986.6	0.499	0.963
100	0	565.6	0.577	0.992
	24	591.0	0.565	0.992
	96	906.3	0.610	0.989

Moreover, the elastic and viscous moduli of the three aged emulsions are represented in **Figure 4.49** and **Figure 4.50** respectively. As far as the elastic modulus (G′) is concerned, at 25˚C aging the emulsion causes a decrease in G′, but no noticeable difference between 24 and 96 hour emulsions. Further, at 60˚C, the fresh and 24 hour samples are the same at low frequency but at high frequency the 24 hour is higher than the fresh one. In addition, the 96 hour sample is the lowest at low frequency but the highest at high frequency. Also, at 100˚C there is a clear trend which is aging decreases the elastic modulus. As for the viscous modulus (G″), aging has no noteworthy effect on G″.

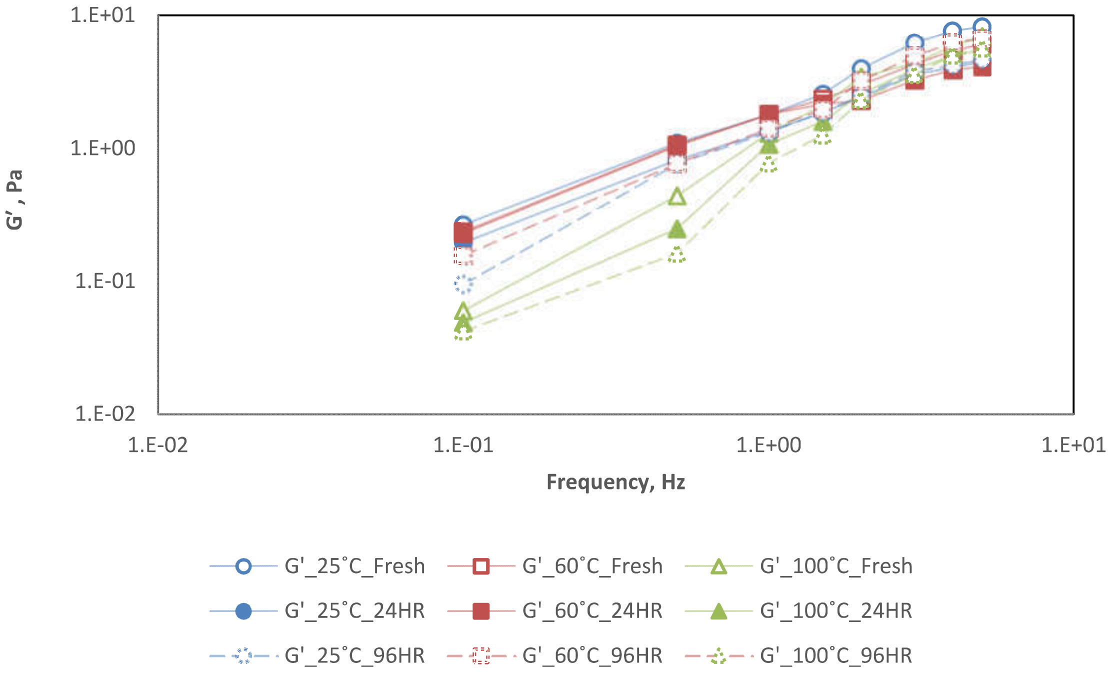


Figure 4.49: Effect of aging for 24 and 96 hours on elastic modulus for diesel emulsion

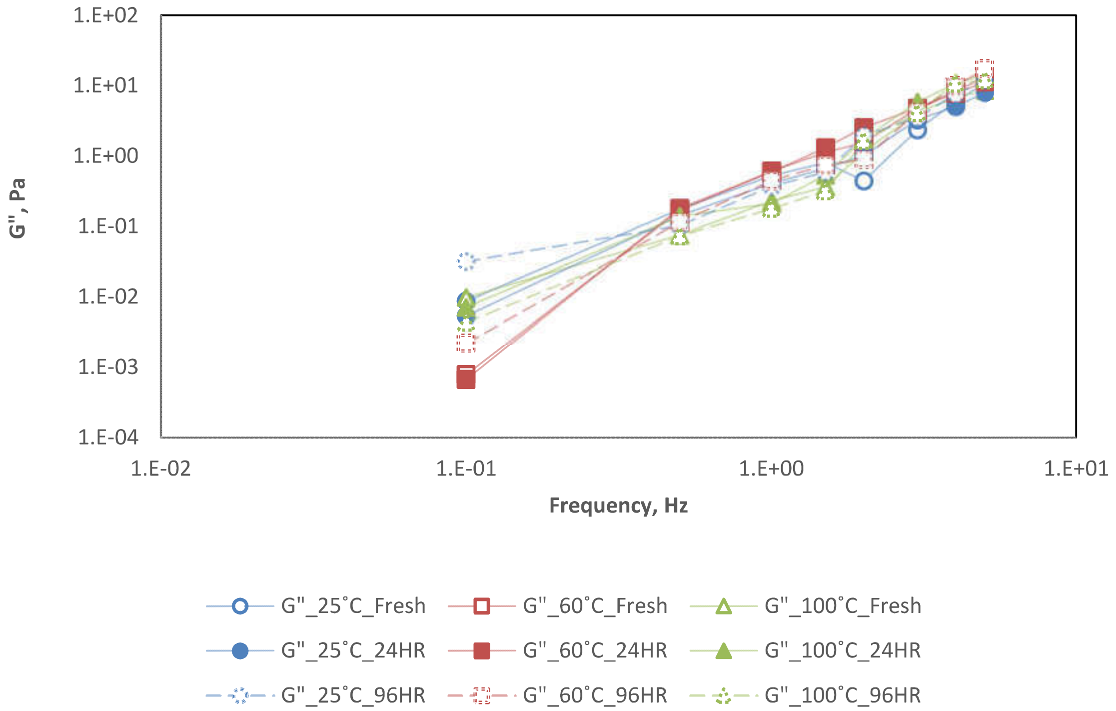


Figure 4.50: Effect of aging for 24 and 96 hours on viscous modulus for diesel emulsion

4.4.3 Droplet size distribution

To apprehend the effect of temperature as well as the effect of corrosion inhibitor on the emulsion, droplet size measurements are conducted. **Figure 4.51** and **Figure 4.52** depict the effect of heating on the droplets distribution of the emulsion without and with corrosion inhibitor, respectively. It is clearly seen that the addition of corrosion inhibitor causes to form polydispersed emulsions; whereas, emulsions without corrosion inhibitor are – to some extent- of monodispersed type. Moreover, in both cases, the 50 and 100˚C emulsions have –relatively- the same range of distribution of droplets. In addition, the 10th, 50th and 90th percentiles along with D[4,3] and D[3,2] means (Equations 1.7-1.8) of the emulsions are presented in **TABLE 4.7**.

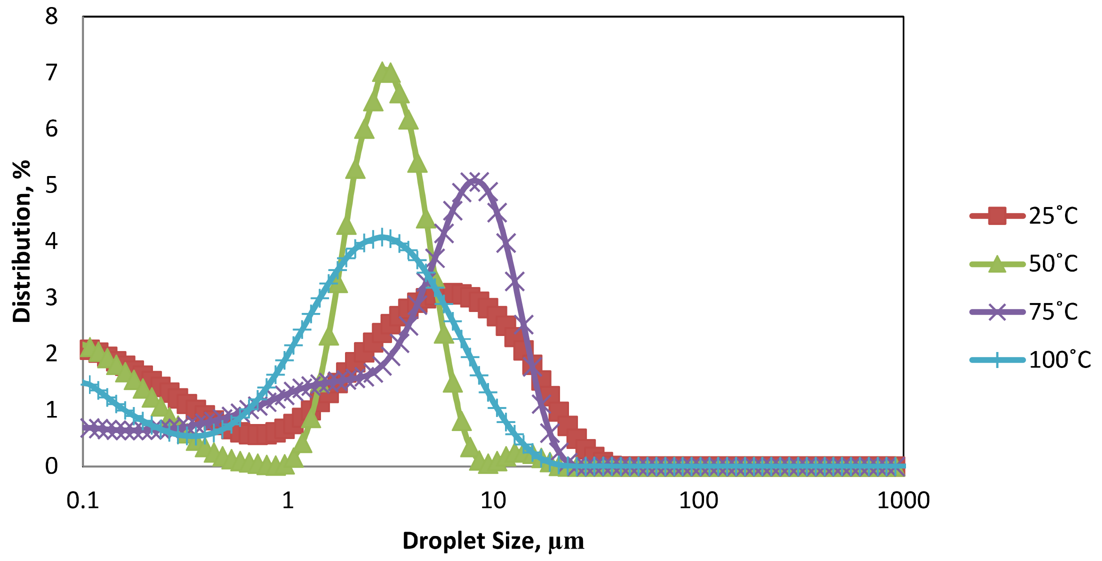


Figure 4.51: Effect of heating on droplet size distribution for diesel emulsion without corrosion inhibitor

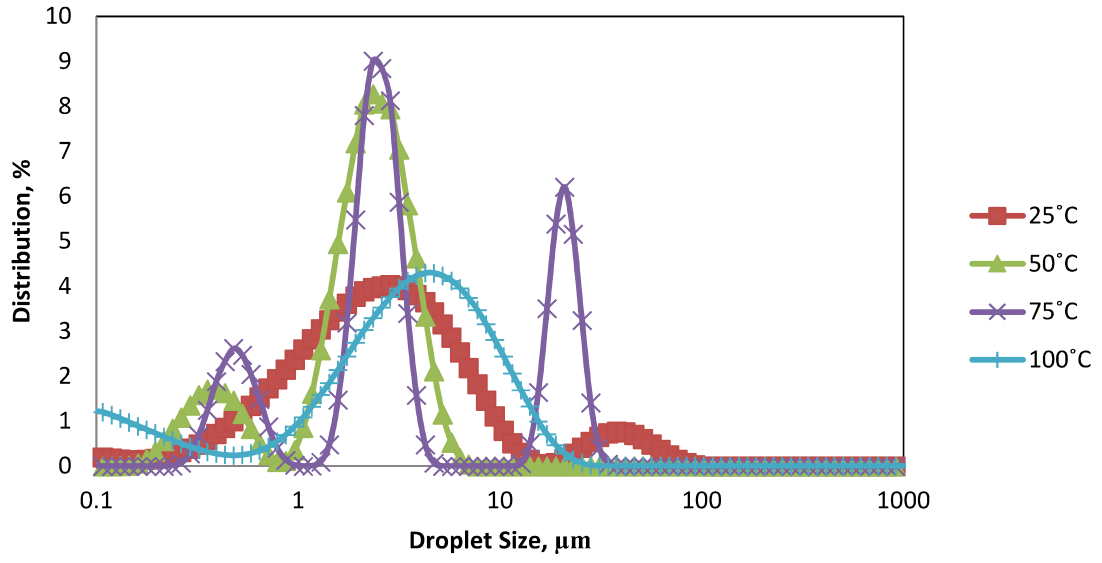


Figure 4.52: Effect of heating on droplet size distribution for diesel emulsion with corrosion inhibitor

TABLE 4.7: Summary of droplet size distribution for diesel emulsion with and without corrosion inhibitor

System	Temperature °C	10th percentile µm	50th percentile µm	90th percentile µm	D[4,3] µm	D[3,2] µm
Diesel emulsion without corrosion inhibitor	25	0.13	3.07	12.39	29.82	26.52
	50	0.13	2.46	4.68	16.42	14.61
	75	0.35	4.76	11.41	32.93	29.30
	100	0.17	2.13	6.47	18.14	16.14
Diesel emulsion with corrosion inhibitor	25	0.63	2.40	8.58	72.92	64.87
	50	0.41	2.10	3.65	6.08	5.41
	75	0.50	2.51	21.01	27.00	24.02
	100	0.21	3.38	9.55	59.78	53.18

4.5 Conclusions

The conclusions of this work can be summed up in the following points:

1. The effect of addition rate of acid phase to diesel was of major influence on reproducibility data. Therefore, it is advised to use a syringe pump with a specific rate in order to accomplish a consistent study.
2. In emulsion preparation, it is best to use a high-power mixer rather than a magnetic stirrer.
3. Diesel emulsified acid is a non-Newtonian shear-thinning fluid with a milky color.

4. There was no significant change of stability data when the emulsifier concentration was varied from 0.5 to 1.5 vol% while using the high-power mixer. In addition, the mixing speed (from 600 to 1400 rpm) did not constitute a major change on stability. Moreover, no water phase came out of the emulsion while being heated at 120˚C for 6 hours.
5. Increasing the emulsifier concentration only caused a noticeable difference on the apparent viscosity at 100˚C of 1.5 vol% and especially at low shear rates.
6. Increasing the emulsifier concentration resulted in increasing both elastic and viscous moduli. Further, the elastic behavior of the emulsion was dominant; however, a crossover occurred at high frequency and this resulted in viscous behavior dominating on the emulsion.
7. Emulsions prepared at 600 and 1400 rpm had the highest apparent viscosity.
8. For all rpm speeds, the emulsion behaved as viscoelastic liquid at low frequency but then at high frequency a crossover occurred and the viscous modulus became dominant.
9. Increasing the mixing speed from 800 to 1400 rpm resulted in increasing G' at low frequency. However, there was no clear trend on the viscous modulus, G''.
10. Increasing the temperature from 25˚C to 100˚C resulted in decreasing the apparent viscosity and this decrease was most substantial at low shear rates where the apparent viscosity decreased by a 100-fold.
11. Increasing the temperature from 25 to 60˚C had no significant effect on G'; however, increasing it further to 100˚C a significant decrease was the result. Whereas, there was no clear trend for G'' as the data fluctuated.

12. In general, aging the emulsion for 24 and 96 hours caused the emulsion to slightly decrease in its apparent viscosity values. Moreover, aging caused G′ to decrease, while it had no noteworthy effect on G″.
13. The addition of corrosion inhibitor had a negative effect on stability. Furthermore, emulsions prepared with corrosion inhibitor formed polydispersed droplets; whereas, emulsions without corrosion inhibitor were – to some extent- of monodispersed type.

CHAPTER 5

WASTE OIL EMULSIFIED ACID

5.1 Abstract

Acid in oil emulsion is used in the industry for stimulation purposes. In particular, HCl as the acid phase and diesel as the oil one. Emulsified HCl has numerous benefits over regular HCl. Perhaps the main benefit is to penetrate deeper. Apart from that, less corrosion damages are caused since the external phase is hydrocarbon. Several studies showed the success of replacing diesel as an external phase with other hydrocarbon oil, such as crude oil and xylene.

This work utilizes the extra hydrocarbon left unused –or sometimes dumped- from refineries to be used as the oil phase for emulsified HCl. This unused hydrocarbon is referred to as waste oil. First, the chemical composition of waste oil is studied using Gas Chromatography (GC). This helps in selecting the proper emulsifier agent for the waste oil. The HCl-waste-oil emulsion is prepared using 15 wt% HCl with a ratio of 70:30 of acid-to-oil. Extensive work is done to ensure reproducibility of data. This study is done to experimentally investigate the effects of distinct important variables on thermal stability and rheological properties of the HCl-waste-oil emulsion. These variables are: emulsifier concentration, mixing speed and the addition of corrosion inhibitor. All

experiments are conducted at high temperature, 120˚C. To assess the quality of the HCl-waste-oil emulsion, droplet size is measured as a function of temperature (up to 100˚C).

The results show that the HCl-waste-oil emulsion is a shear-thinning fluid. Power-law model is applicable seamlessly to all of the apparent viscosity data for all of measured temperatures. The viscous modulus (G'') is found to be the most dominant. The optimum conditions are found to be; 0.5 vol% and 600 rpm for emulsifier concentration and mixing speed, respectively. Apart from that, the emulsions which are prepared with corrosion inhibitor turn out to be less stable compared to the ones without it. However, the addition of corrosion inhibitor tend to generate polydispersed emulsions with a wider distribution of droplets, compared to the emulsions prepared without corrosion inhibitor. Droplet size measurements show a median size of 2.35 and 3.09 μm for emulsions without and with corrosion inhibitor, respectively. Overall, the lab results show a promising potential for the HCl-waste-oil emulsion to be used in the field.

This work takes into account; reducing the budget of acidizing job and environmental concerns. It makes use of the unwanted hydrocarbon from refiners. And, it saves the environment by using the waste oil instead of dumping it.

5.2 Introduction

The use of emulsified acid in the oil and gas industry was firstly introduced by De Groote (1933). Since then, emulsified acid has caught the eyes of many scholars. It has been used in the oil and gas industry for numerous purposes such as acidizing oil wells (Al-Anazi et al., 1998, Kasza et al., 2006), water disposal wells (Nasr-El-Din et al., 2000) and seawater injectors (Mohamed et al., 1999). As well as, acid fracturing (Bartko et al., 2003) especially for deep gas wells (Nasr-El-Din et al., 2001, Nasr-El-Din et al., 2008b).

Emulsified acid can be categorized into two types: micro-emulsion (Hoefner et al., 1985) & macro-emulsion (Al-Anazi et al., 1998, Mohamed et al., 1999, Nasr-El-Din et al., 2000, Kasza et al., 2006, Nasr-El-Din et al., 2008a). Mollet et al. (2008) specified that micro-emulsions are composed of droplet size of ($10^{-2} – 10^{-1}$) µm, and macro-emulsions are composed of any size bigger than that. It is common to represent the droplet size distribution of an emulsion by De Brouckere Mean Diameter D[4,3] which is shown in Equation 1.8 (Chapter 1).

When doing an acidizing job, it is essential for the emulsion to reach the formation with no separation of the acid phase. Otherwise, no retardation would occur. Hence, the stability of emulsions is very critical for field applications (Al-Anazi et al., 1998). For an emulsion to be stable, certain requirements should be met (Chen et al., 2005):

4- The two liquids must be mutually insoluble in each other
5- Addition of emulsifier agent to reduce the interfacial tension, and
6- A sufficient agitation in order to disperse one liquid into the other

Many researchers have addressed the effect of apparent viscosity on shear rate for emulsified acids. However, only a few studied the effect of viscoelastic properties (Sayed et al., 2011).

Sayed et al. (2011), investigated the effect of viscoelastic properties on emulsified acid and found out that generally the viscous modulus G″ was always greater than the elastic modulus G′. Also, they reported that the viscous behavior became more dominant as the emulsifier concentration increased above 2 vol%. However, an increase in emulsifier concentration up to 2 vol% would have no major effect on both G′ and G″.

Typically, it is the practice in the industry to emulsify HCl with diesel; diesel being the oil phase. Nonetheless, some researchers have tried different oil phase than diesel. Fattah et al. (2010) used xylene emulsified acid.

Fattah et al. (2010) developed an emulsified acid system with xylene instead of diesel to treat wells with asphaltene deposition. In their study, they reported that the apparent viscosity and the stability of emulsified acid are highly dependable on the hydrocarbon phase. Moreover, the apparent viscosity of xylene emulsified acid was lower than the conventional diesel emulsified acid and relatively less stable. In addition, Kasza et al. (2006) used crude oil emulsifieid acid to stimulate oil wells and it was successful.

Both xylene and crude oil are valuable and have other purposes to be used for. However, this work utilizes the extra hydrocarbon left unused –or sometimes dumped- from refineries. This unused hydrocarbon is referred to as waste oil.

5.3 Experimental Procedure

5.3.1 Materials

In this study both the cationic emulsifier (Armostim H-Mul) and the corrosion inhibitor (Sanjal AI-8) are supplied by AkzoNobel. The HCl used is of American Chemical Society (ACS) grade. Also, the HCl is titrated using sodium hydroxide solution to determine its concentration and is found to be of 36.9wt%. Distilled water is used to dilute the concentrated HCl to 15wt%. The waste oil is collected from a local refinery which has a composition illustrated in **Figure 5.1**. A more detailed analysis of waste oil is reported in **Appendix A**.

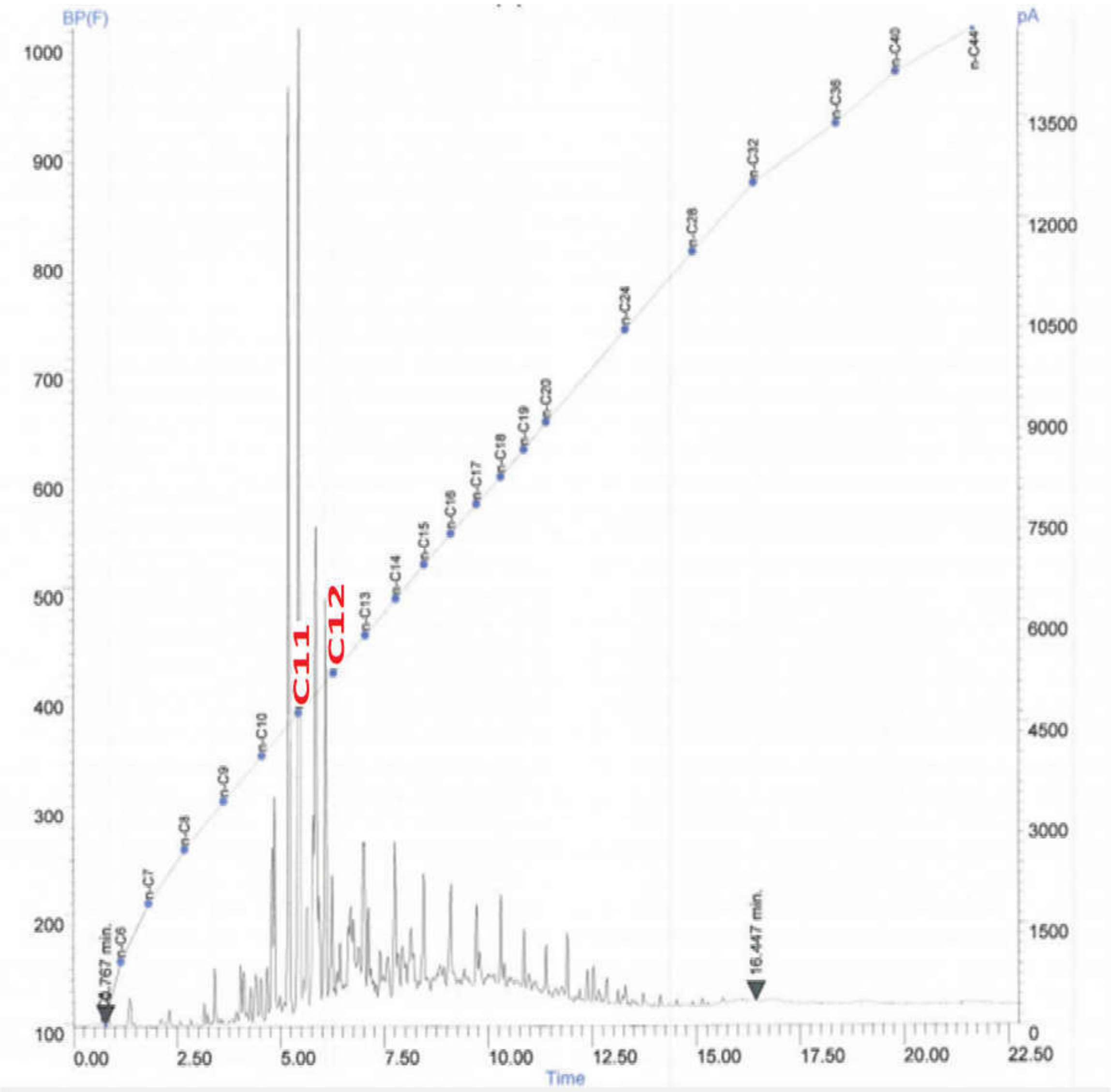


Figure 5.1: Waste oil composition

5.3.2 Preparation

In all of the experiments conducted in this study, the acid-to-oil ratio is 70:30 and the preparation is at room temperature. Since the emulsion is composed of two separate phases, two beakers are used to prepare each phase. The hydrocarbon phase (oil phase), in which waste oil is added to the emulsifier at a specific concentration. Then, the oil phase (waste oil + emulsifier) is mixed at a specific mixing speed for 5 minutes. In a separate beaker the water phase is prepared. Diluted HCl with distilled water (15 wt%) is poured in a separate beaker with the corrosion inhibitor of 0.3 vol% (if any) and then is let to be mixed for 5 minutes at the same speed used for the oil phase. While mixing the oil phase, using a syringe in a syringe pump the water phase is added to the oil phase, in a drop-wise manner at a specific rate. This rate should be known in order to assure reproducibility. A change of color should occur and the emulsion is in the generating form. After the last drop of the water phase is added, the two phases should be let to mix thoroughly for 5 minutes.

It should be noted that if the water phase is added to the oil phase at once coarse droplets would form; finer ones would form if the addition is of drop-wise kind (Al-Mutairi et al., 2008).

5.3.3 Apparatus

The mixer used in this study is of wide range of mixing speed (600 -10,000) rpm with 200 rpm increment and a speed deviation of 1%. Also, it is equipped with an acid-resistant dispersion element so it can be used to prepare emulsified acid. This mixer has

1100 W of power input which is provided by IKA®, model T 50 digital ULTRA-TURRAX®.

All rheological experiments are conducted with the use of an acid-resistant rheometer, manufactured by REOLOGICA®, model STRESSTECH. This rheometer has a range of 3.0×10^{-8} to 2.0×10^{-1} N.m of torque and a temperature range of -20 to 150˚C. In this study, the bob/cup set is used with a volume of 15.9 mL of the emulsion for testing.

When measuring the droplet size distribution, FRITSCH® ANALYSETTE 22 MicroTec plus of 0.1-600 μm of measuring range is used. This droplet analyzer works on diffraction of electromagnetic waves principle. The droplet size distribution is calculated using Lorenz-Mie or Fraunhofer theory.

5.3.4 Testing procedure

5.3.4.1 Emulsion type

The emulsion type is determined by dilution test. Dilution test is grounded on the principle of emulsions will be diluted by the liquid that constitutes its external phase. That being said, adding small amounts of the emulsion into two separate beakers, one containing pure water and the other pure oil, would result in dispersion in only one beaker. If the dispersion occurs in the pure water beaker the emulsion will be of oil-in-water type. In contrast, if the dispersion occurs in the pure oil beaker the emulsion will be of water-in-oil type (Pal, 1993). **Figure 5.2** shows that the emulsion disperses in pure oil but not in pure water indicating the water-in-oil emulsion type.

Also, to assess the quality of the emulsion, the electric conductivity is measured. If the conductivity reads a value near 0, then the emulsion is of good quality.

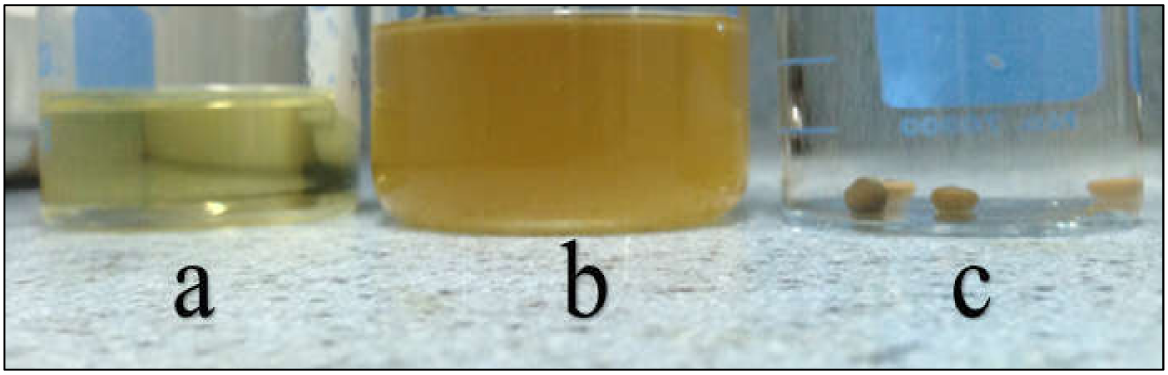


Figure 5.2: Dilution test: a) pure oil b) the emulsion is dispersed in pure oil c) the emulsion is not dispersed in pure water indicating a water-in-oil emulsion

5.3.4.2 Stability test

In order to investigate the thermal stability of the emulsion, graduated glass tubes are used to monitor the phase separation at a constant temperature. The thermal stability test is carried out at 120˚C and for 6 hour period. During that period, a multiple recording of the three phases (emulsion, water and oil) volume is done (Pei et al., 2015). **Figure 5.3** shows a waste oil emulsion while being heated at 120˚C.

5.3.4.3 Rheology test

In rheology tests, 15.9 mL of the emulsion is needed to measure the apparent viscosity and oscillating properties at temperatures of 25, 40 and 60˚C. Due to limitation from the rheometer, reaching 120˚C is challenging. As the set-up does not have proper ventilation.

5.3.4.4 Droplet size measurements

To get an indication of the emulsion quality, droplet measurements are done. The emulsion is heated for some time and then droplet size distribution is measured. For consistency, all sampling is done at the same time for all emulsions. For waste oil emulsion, the maximum temperature reached is 75˚C, due to equipment limitations and substance quality.

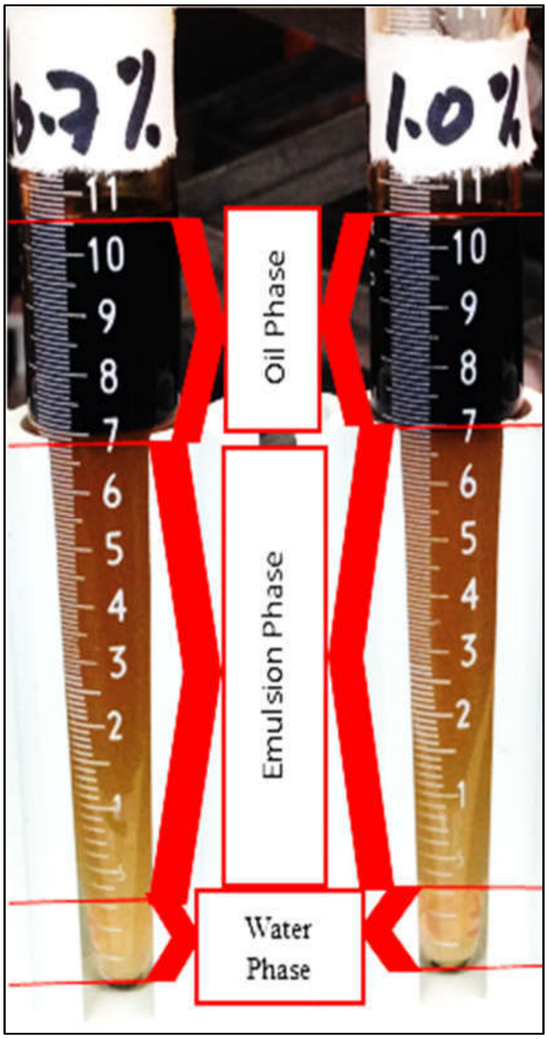


Figure 5.3: Waste oil emulsion while being heated at 120˚C

5.4 Results and Discussion

This section presents the results after conducting the aforementioned tests of waste oil emulsified acid. It categorizes them into three: thermal stability, viscosity and oscillating measurements and droplet size distribution measurements.

5.4.1 Thermal stability

The type and concentration of the emulsifier used are of the key parameters in formulating a stable emulsion (Nasr-El-Din et al., 2008a). At a temperature of 120˚C, both the effect of emulsifier concentration and the effect of mixing speed (rpm) are studied, consecutively. First the emulsifier concentration is optimized and later the optimum concentration is used to optimize the mixing speed.

5.4.1.1 Effect of emulsifier concentration

For emulsifier concentration effect on thermal stability, two sets of experiments are conducted; set one where the emulsion is prepared with corrosion inhibitor and set two where the emulsion is prepared without corrosion inhibitor. For both sets, four different emulsifier concentrations are used to study their effect on the thermal stability namely, 0.5, 0.7, 1.0 and 1.5 vol%. The emulsion is prepared with those concentrations separately at a mixing speed of 600 rpm. Then, in a high temperature graduated glass test tubes, the emulsions are poured and heated at 120˚C for 6 hours. The separation of the three phases are observed and recorded as a function of time.

Figure 5.4, **Figure 5.5** and **Figure 5.6** represent the results of emulsion, water and oil phases, respectively, for waste oil emulsion prepared with corrosion inhibitor. The overall trend is that the increase of emulsifier concentration results in forming more stable emulsions even at high temperature; 120˚C. This attribute is because more volume of emulsifier concentration means more molecules to reduce the interfacial tension between the two phases.

Initially, all of the emulsions are in emulsion phase. For concentration of 0.5 vol%, the emulsion- after just 21 minutes of heating- starts to break into water phase which happens very rapidly, and within 98 minutes the emulsion completely breaks into its original two phases. Increasing the emulsifier concentration to 0.7, 1.0 and 1.5 vol% results in a delay of the start time to breaking into water phase to 51, 90 and 130 minutes, respectively. Nevertheless, all of the emulsions break completely within 3 hours of heating at 120˚C.

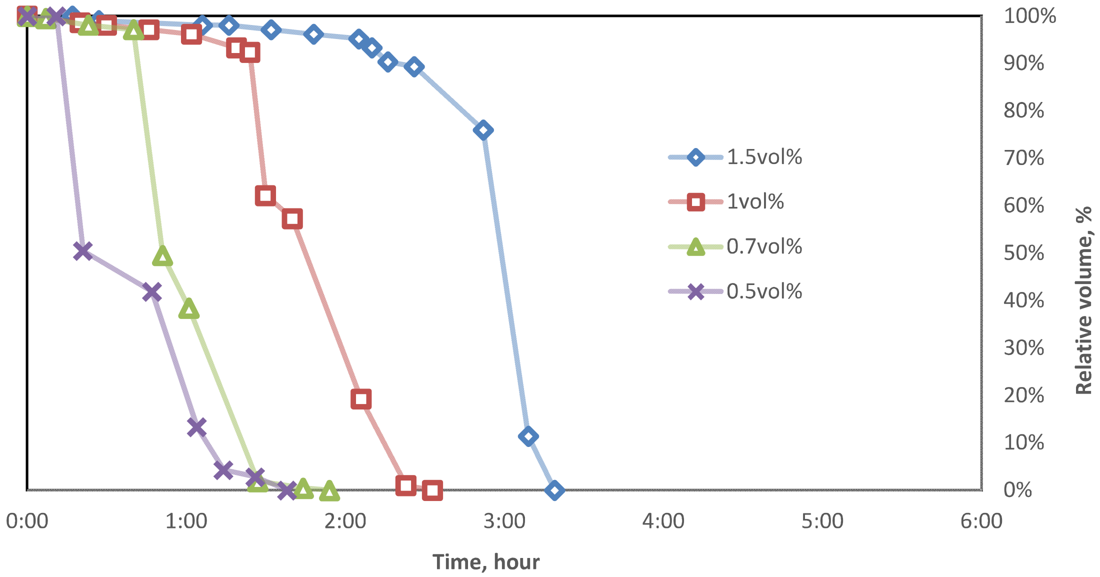


Figure 5.4: Emulsion phase of waste oil emulsion with corrosion inhibitor at different emulsifier concentration at 120˚C

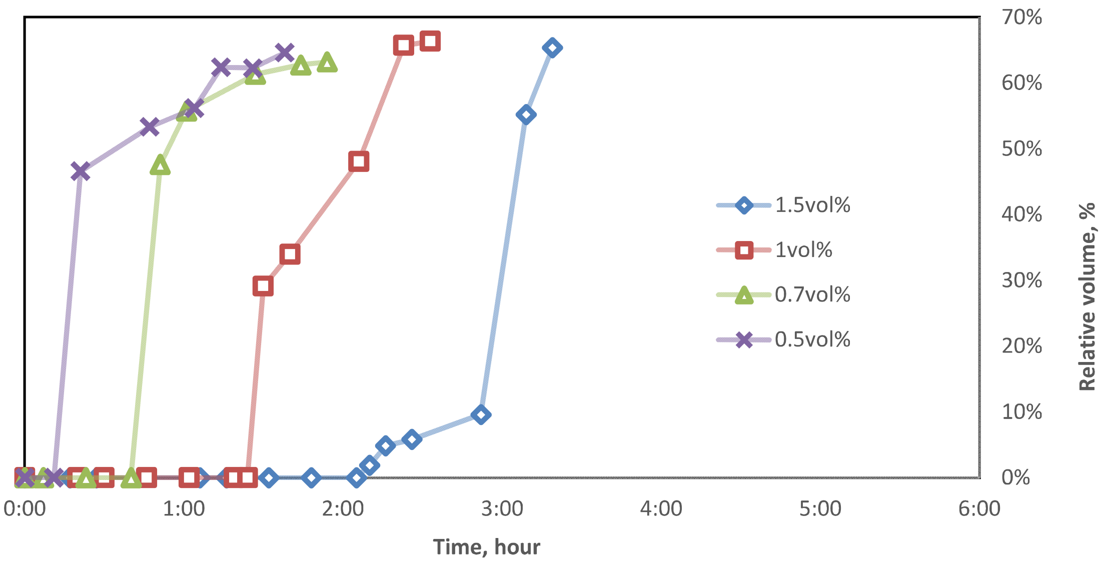


Figure 5.5: Water phase of waste oil emulsion with corrosion inhibitor at different emulsifier concentration at 120˚C

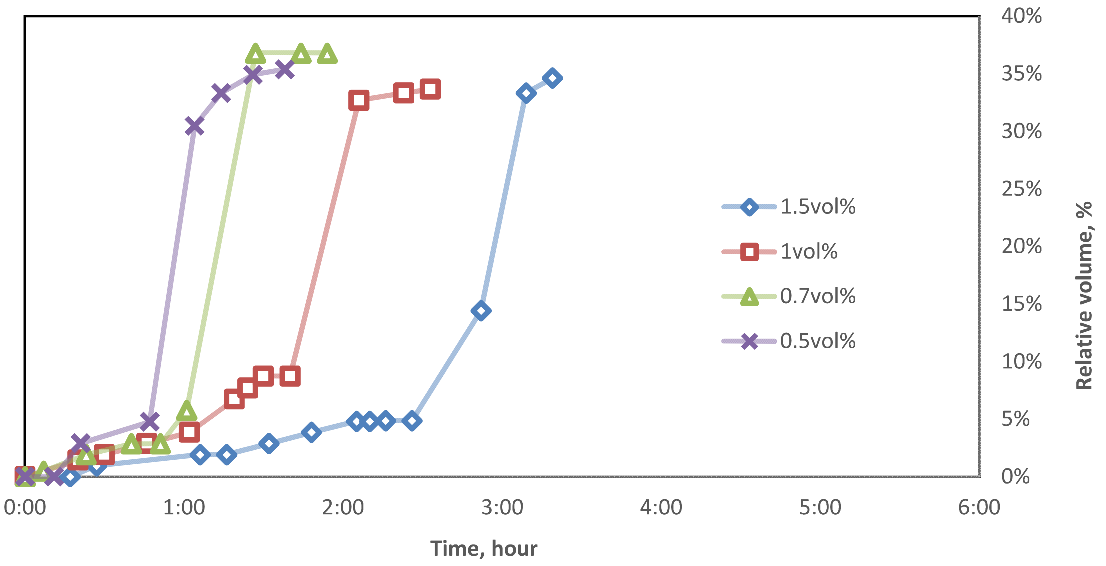


Figure 5.6: Oil phase of waste oil emulsion with corrosion inhibitor at different emulsifier concentration at 120˚C

On the other hand, the waste oil emulsions prepared without corrosion inhibitor are presented in **Figure 5.7**, **Figure 5.8** and **Figure 5.9**. Furthermore, these figures show a plot of the emulsion, water and oil phases, respectively, of the 4 concentrations as a function of time for 6 hour period at 120˚C. From those figures it clearly can be seen that the emulsifier concentration of 1.5 vol% is the most stable one. Also, after 120 minutes the emulsion phases of all concentrations start to break into water and oil phases. In terms of water phase, the 1 vol% emulsifier concentration starts to break early compared to others and it is considered as the least stable emulsion for the first 3 hours of heating. However, after the beginning of the second 3 hours, the emulsion becomes the second most stable after the 1.5% -as expected. During the stability test time (6 hours) all of the emulsions break down completely into oil and water phases. Overall, the difference between 0.5, 0.7 and 1.0 vol% is not that significant and a slight difference is observed with the 1.5 vol% emulsion. Hence, the optimum condition for emulsifier concentration is selected to be 0.5 vol%.

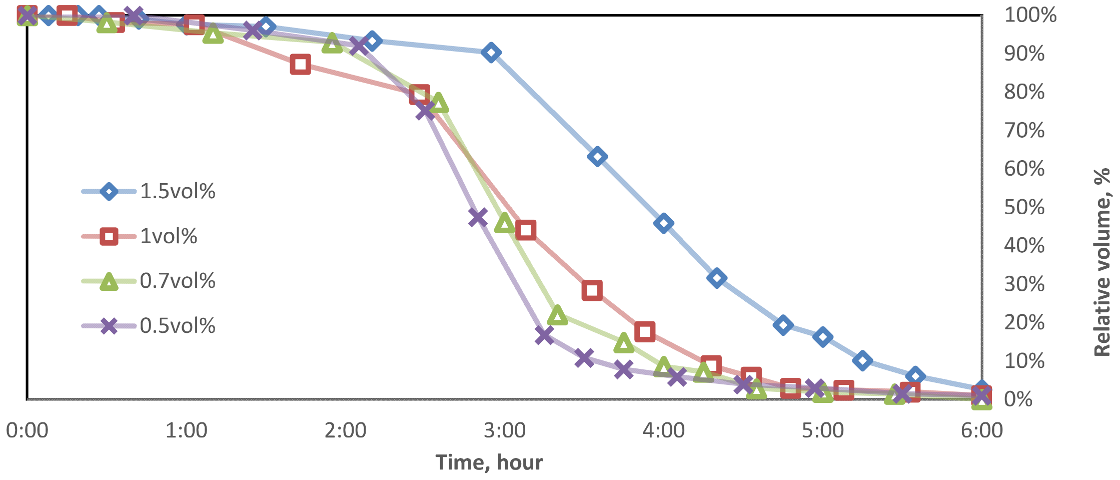


Figure 5.7: Emulsion phase of waste oil emulsion without corrosion inhibitor at different emulsifier concentration at 120˚C

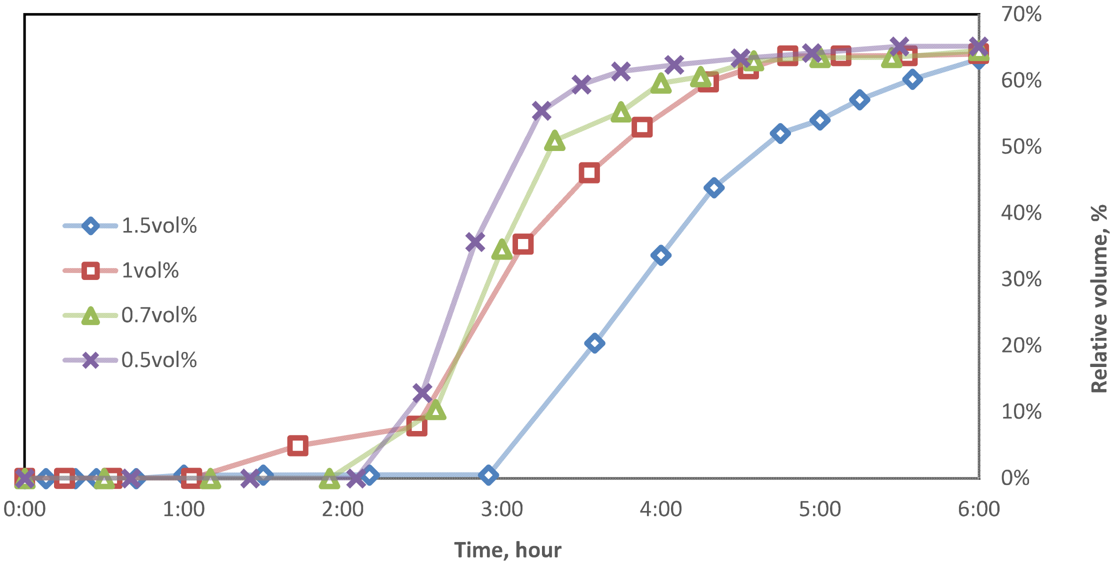


Figure 5.8: Water phase of waste oil emulsion without corrosion inhibitor at different emulsifier concentration at 120˚C

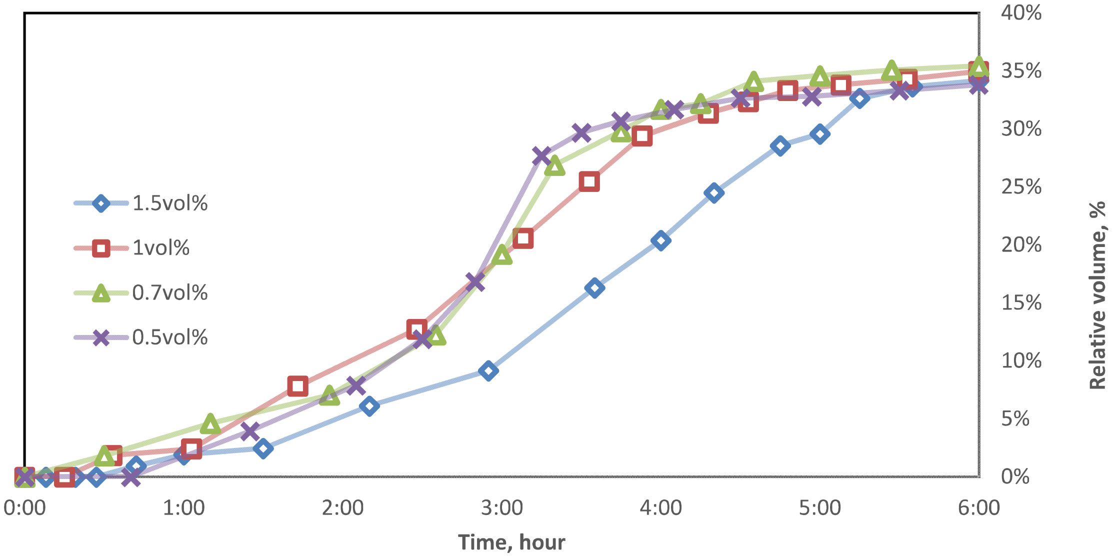


Figure 5.9: Oil phase of waste oil emulsion without corrosion inhibitor at different emulsifier concentration at 120˚C

5.4.1.2 Effect of addition rate

It was mentioned earlier – in the preparation section- the importance of addition rate of water phase to oil phase. This section re-emphasizes on the criticality of such factor. Two experiments are prepared at the same conditions but the difference is the addition rate. One has an addition rate of 0.92 mL/min and the second has an addition rate of 1.2 mL/min. **Figure 5.10** plots the two experiments. It clearly can be seen the significance of the addition rate, even if the difference is small as in this case ~ 0.3 mL/min. Such difference delays the break of the water phase by 20 minutes.

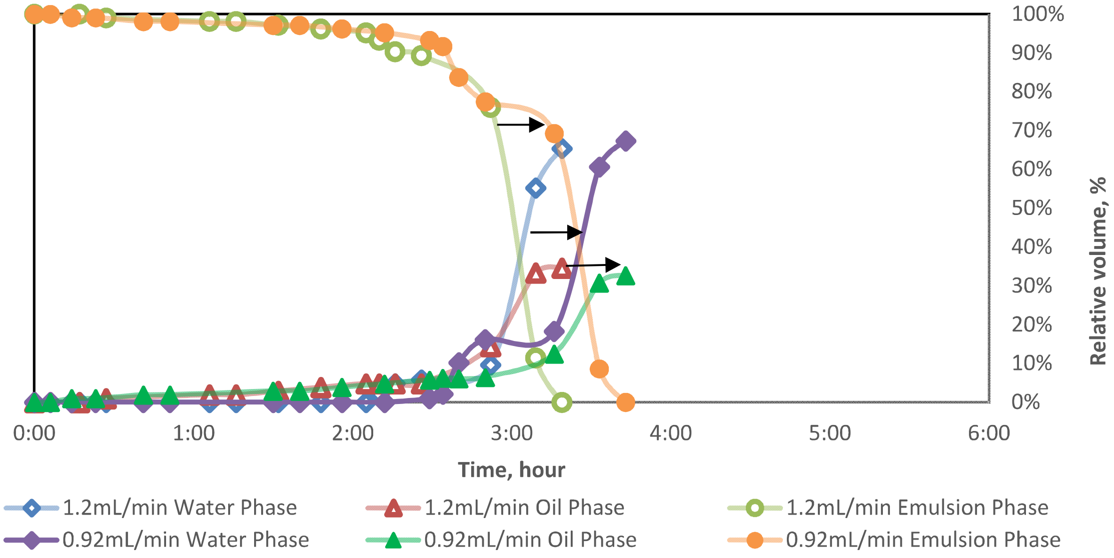


Figure 5.10: Effect of addition rate on thermal stability at 120˚C

5.4.1.3 Effect of mixing speed

Since the corrosion inhibitor has such a negative impact on the stability, all of the emulsions afterward are prepared without the addition of corrosion inhibitor.

After the emulsifier concentration is optimized (0.5 vol %), four distinct mixing speeds (rpm) are used to be optimized. The mixing speeds used are 600, 800, 1000 and 1400 rpm. The emulsions are prepared at the optimum emulsifier concentration (0.5 vol %) and at the four mixing speeds, successively. Then, the thermal stability is studied to address the effect of mixing speed on it. The same procedure in studying the effect of emulsifier concentration on thermal stability is followed in here. **Figure 5.11**, **Figure 5.12** and **Figure 5.13** show the effect of the mixing speed on emulsion, water and oil phases for waste oil emulsions, respectively. Generally, all of the mixing speeds have similar trends except for the 1000 rpm which is the least stable. It is very difficult to pinpoint one speed and say it is the optimum since the other three rpm speeds are very close to each other. However, for the sake of saving energy and since the rpm speed for the other three are similar, 600 rpm should be chosen.

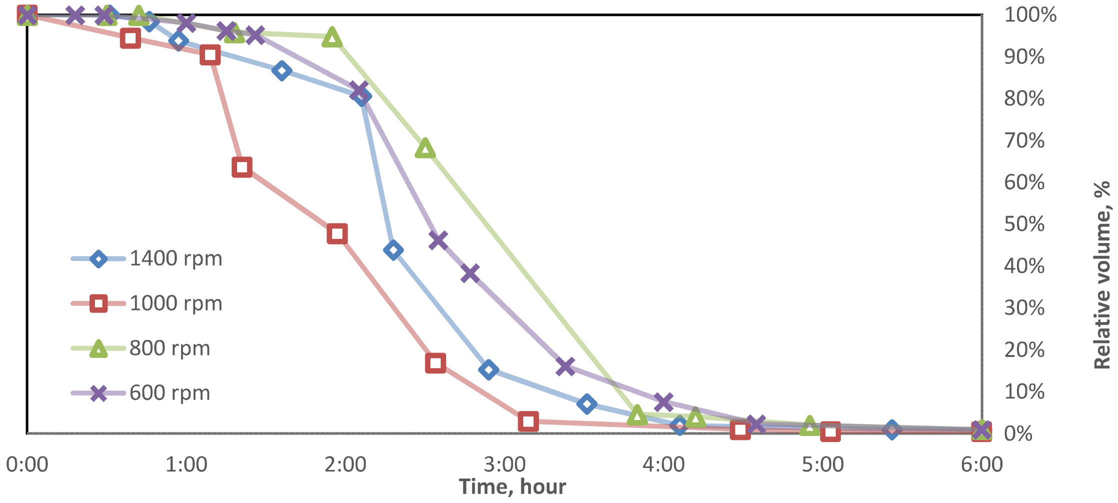


Figure 5.11: Emulsion phase of waste oil emulsion at different mixing speed at 120˚C

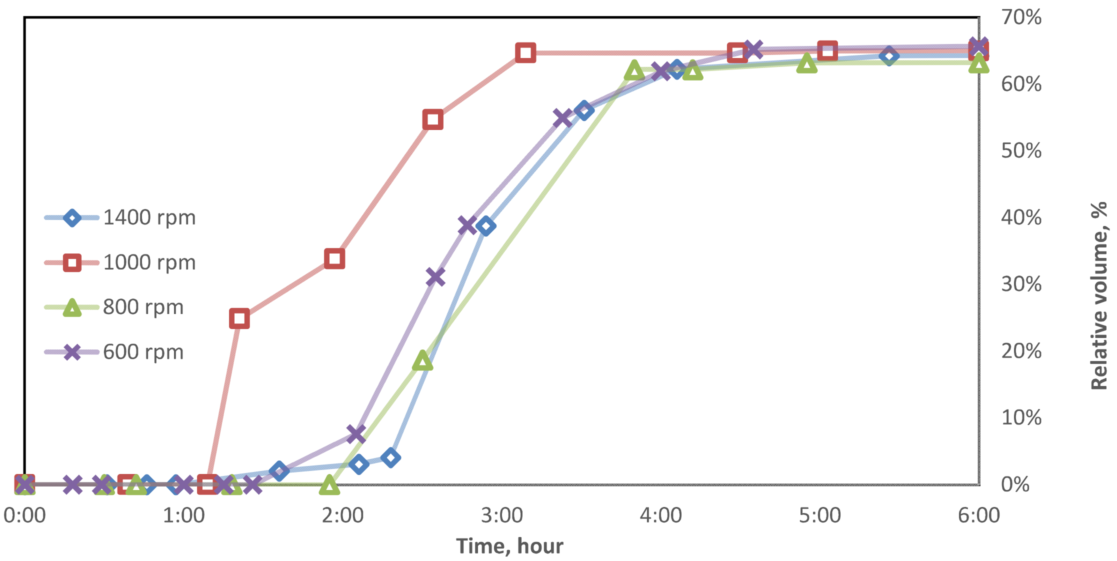


Figure 5.12: Water phase of waste oil emulsion at different mixing speed at 120˚C

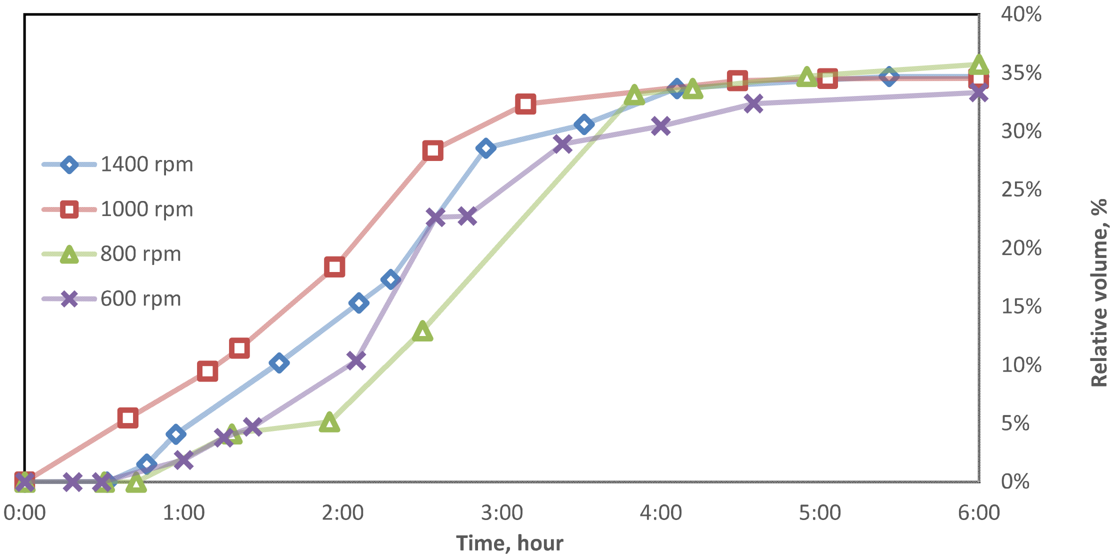


Figure 5.13: Oil phase of waste oil emulsion at different mixing speed at 120˚C

After stability tests, rheology tests are next where apparent viscosity at different shear rates and oscillating properties at different frequencies are measured. In order to conduct the rheological measurements, fresh samples yet the same of the ones used in stability tests are needed to be formed for the sake of consistency of the study. Therefore, a reproducibility experiment is conducted to make sure the emulsion is of the same behavior. And, at this point preparing the emulsion methodically becomes very crucial. **Figure 5.14** shows the results of two emulsions prepared at different times but with the same conditions (0.5 vol%, 600 rpm and 120˚C) to assure reproducibility of the data. Clearly, **Figure 5.14** confirms that the data are reproducible.

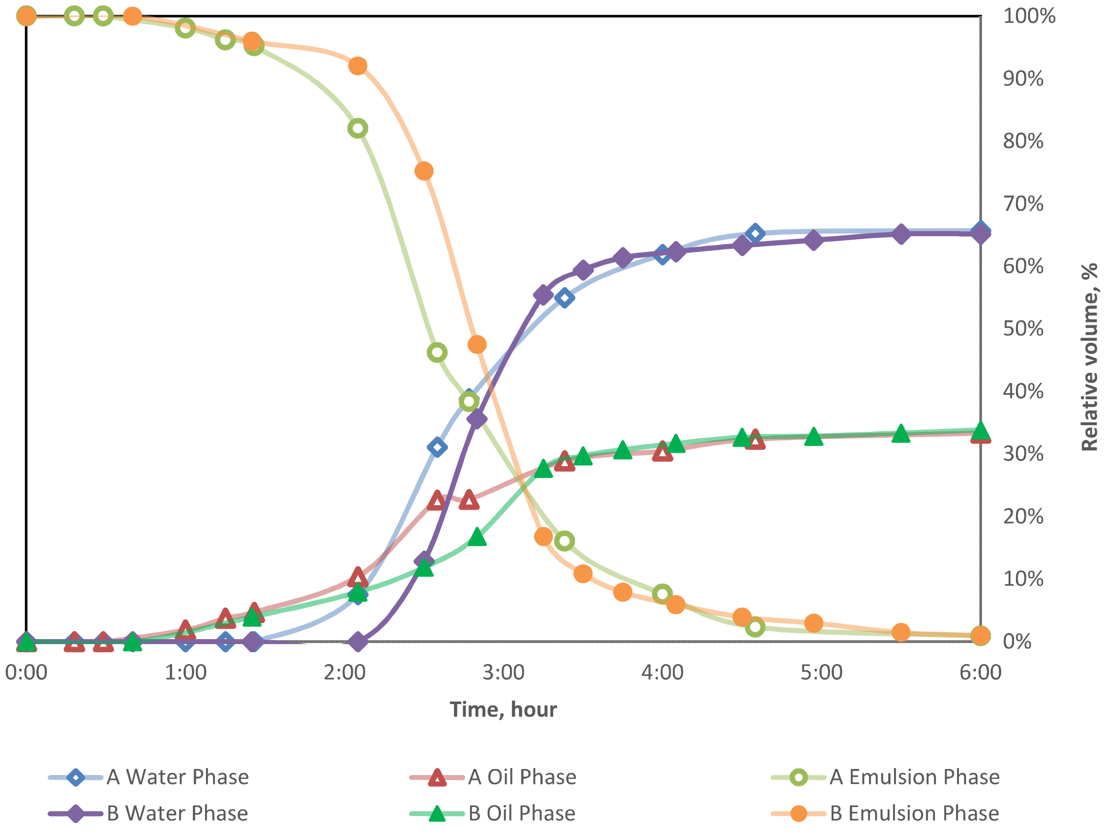


Figure 5.14: Reproducibility data for waste oil emulsion at 120˚C

5.4.2 Viscosity and oscillating measurements

After assuring reproducibility of the data, rheological measurements are carried out. A fresh sample of emulsion is prepared at a specific concentration and at a specific mixing speed to investigate the effect of several factors on rheological behavior. The factors studied are: the effect of emulsifier concentration, mixing speed, temperature and aging, separately.

5.4.2.1 Effect of emulsifier concentration

The same emulsifier concentrations used in thermal stability tests are used in here. They are: 0.5, 0.7, 1.0 and 1.5 vol%. The effect of changing the emulsifier concentration on apparent viscosity as well as viscoelastic properties is studied.

Figure 5.15, **Figure 5.16** and **Figure 5.17** show the effect of the four concentrations on apparent viscosity at 25, 40 and 60˚C, respectively. The results indicate that the change of emulsifier concentration has no significant effect on the apparent viscosity whatsoever. Nonetheless, all of the apparent viscosity data are perfectly fitted in power-law model and the parameter of the model are presented in **TABLE 5.1**. This table shows that the emulsifier concertation is –to some extent- directly related to power law constant, K and inversely related to power law index, n.

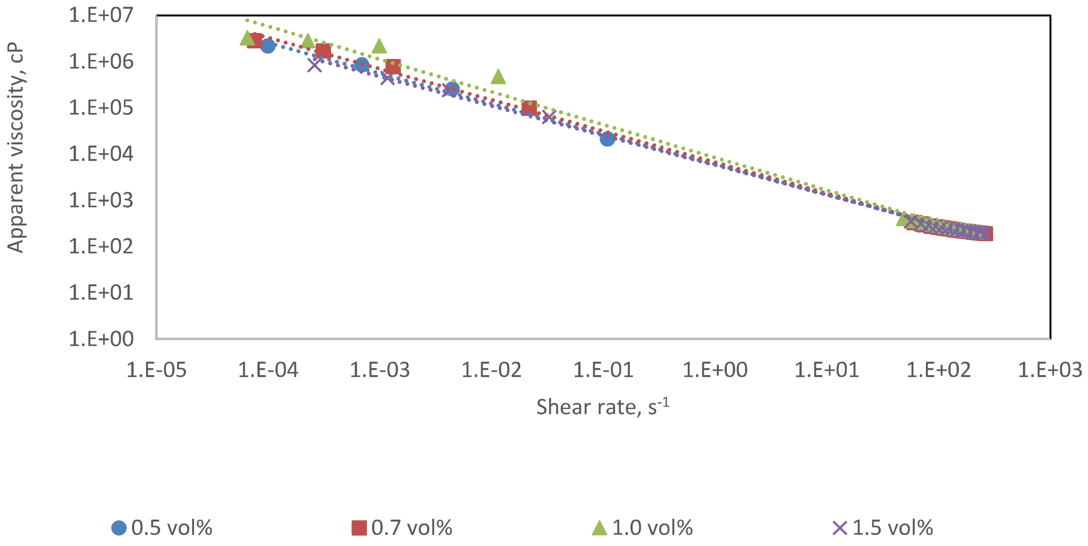


Figure 5.15: Effect of emulsifier concentration on apparent viscosity for waste oil emulsion at 25˚C

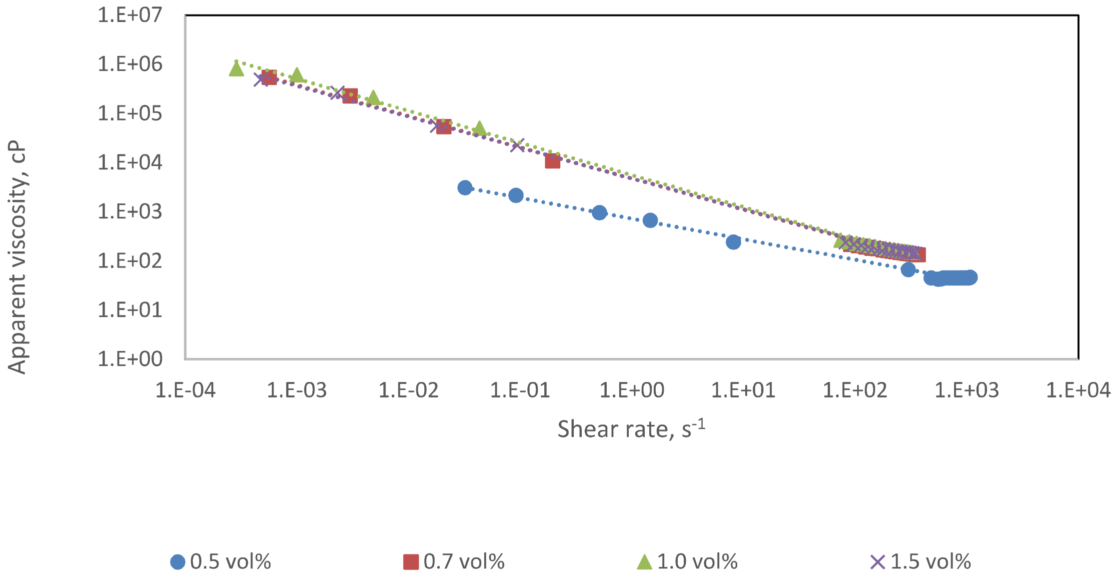


Figure 5.16: Effect of emulsifier concentration on apparent viscosity for waste oil emulsion at 40˚C

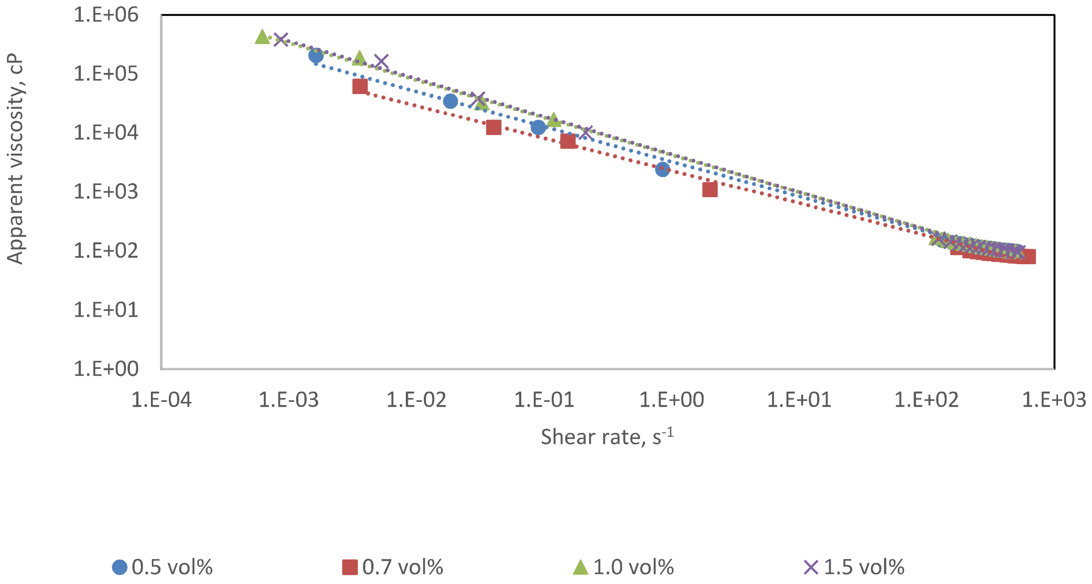


Figure 5.17: Effect of emulsifier concentration on apparent viscosity for waste oil emulsion at 60˚C

TABLE 5.1: Summary of power-law model for emulsifier concentration for waste oil emulsion

Temperature ˚C	**Emulsifier Concentration vol%**	**Power Law Constant, K mPa.s^n**	**Power Law Index, n**	**Correlating Coefficient, R^2**
25	0.5	6029.3	0.344	0.998
	0.7	6699.1	0.327	0.998
	1	8476.0	0.291	0.991
	1.5	5757.9	0.360	0.998
40	0.5	736.4	0.581	0.994
	0.7	4747.7	0.366	0.998
	1	5632.4	0.347	0.998
	1.5	4795.6	0.372	0.998
60	0.5	3287.7	0.408	0.995
	0.7	2304.7	0.451	0.995
	1	4241.8	0.368	0.998
	1.5	4351.5	0.360	0.998

Furthermore, the effect of these concentrations on viscoelastic properties is studied. **Figure 5.18**, **Figure 5.19** and **Figure 5.20** depict the results of measuring storage modulus G′, and loss modulus G″ as a function of frequency for different emulsifier concentrations. At 25˚C (**Figure 5.18**), the emulsifier concentration of 0.5 vol% behaves elastically at low frequency, but at a frequency of 0.25 Hz, the viscous modulus G″ crosses over the elastic modulus G′ indicating the viscous behavior. In contrast, 0.7, 1 and 1.5 vol% of emulsifier concentration result in no crossover point and G″ is always dominant.

At 40˚C (**Figure 5.19**), for 0.7, 1 and 1.5 vol%, G′ is higher for only low frequency, however a rise in G″ occurs. This rise results from a very relaxed structural rearrangement of the droplets.

Further, at 60˚C (**Figure 5.20**), 0.5 vol% behaves as a solid-like material at all frequency range. Also, 0.7 vol% behaves as a solid material for most of the range but at high frequency, a sudden rise in G″ takes place reflecting the dominance of the viscous-like material. However, 1 and 1.5 vol% behave similarly as if the temperature were 40˚C.

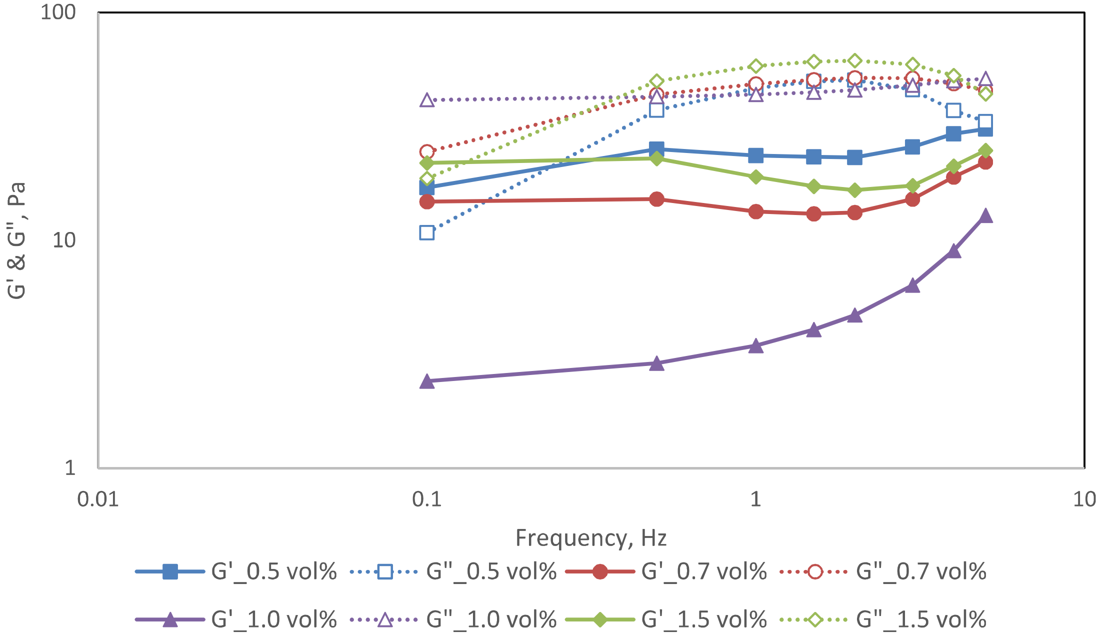


Figure 5.18: Effect of emulsifier concentration on G′ and G″ for waste oil emulsion at 25˚C

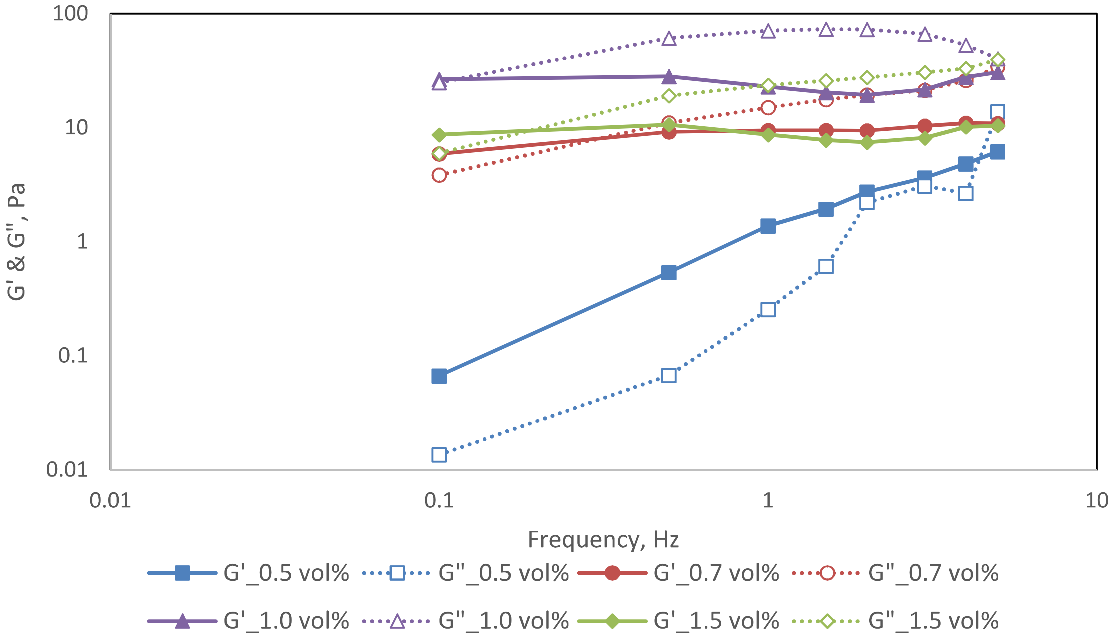


Figure 5.19: Effect of emulsifier concentration on G′ and G″ for waste oil emulsion at 40˚C

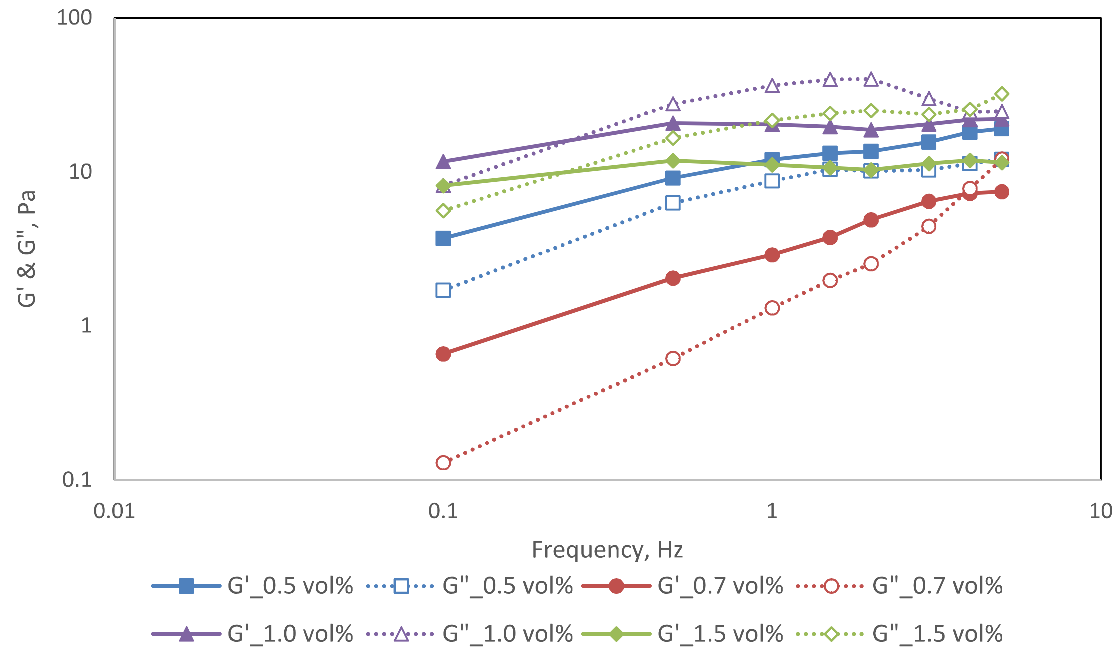


Figure 5.20: Effect of emulsifier concentration on G′ and G″ for waste oil emulsion at 60˚C

5.4.2.2 Effect of mixing speed

Moreover, the effect of varying the mixing speed on rheological behavior is addressed. Also, the mixing speeds used are the same as in stability tests, namely 600, 800, 1000 and 1400 rpm.

The effect of mixing speed on the apparent viscosity is shown in **Figure 5.21**, **Figure 5.22** and **Figure 5.23**. Clearly from these figures, the mixing speed has no significant effect on the apparent viscosity for all temperature rang used in this study. Hence, the speed of 600 rpm is the optimum one. The power-law model data are shown in **TABLE 5.2**, which indicates that there is no clear trend for mixing speed with power-law model parameters; in agreement with diesel emulsion results.

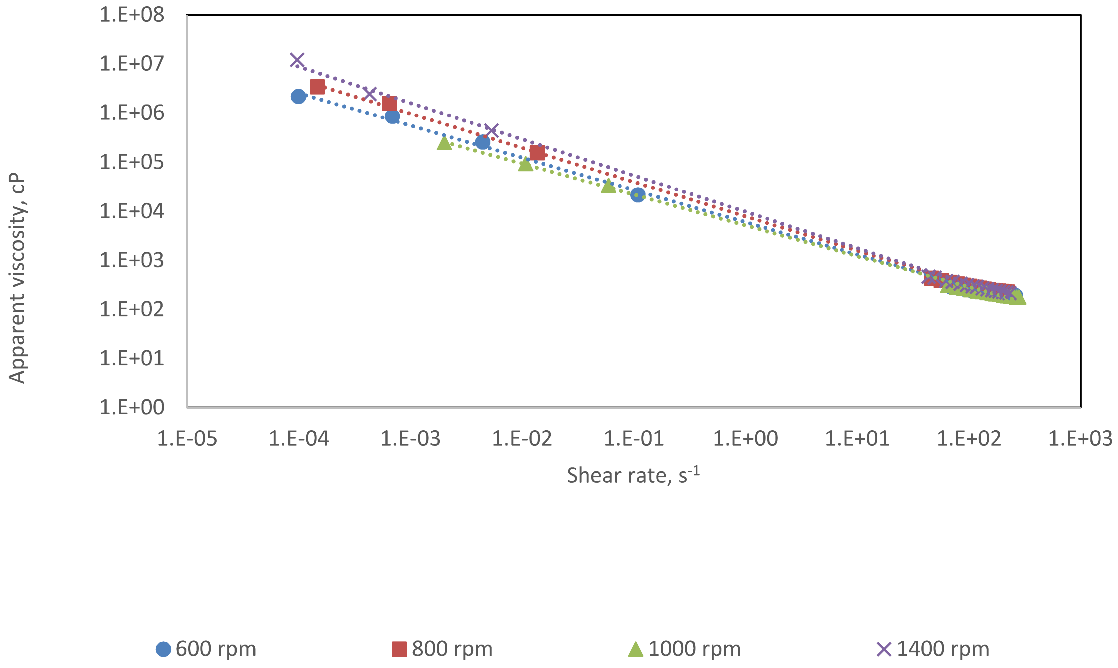


Figure 5.21: Effect of mixing speed on apparent viscosity for waste oil emulsion at 25˚C

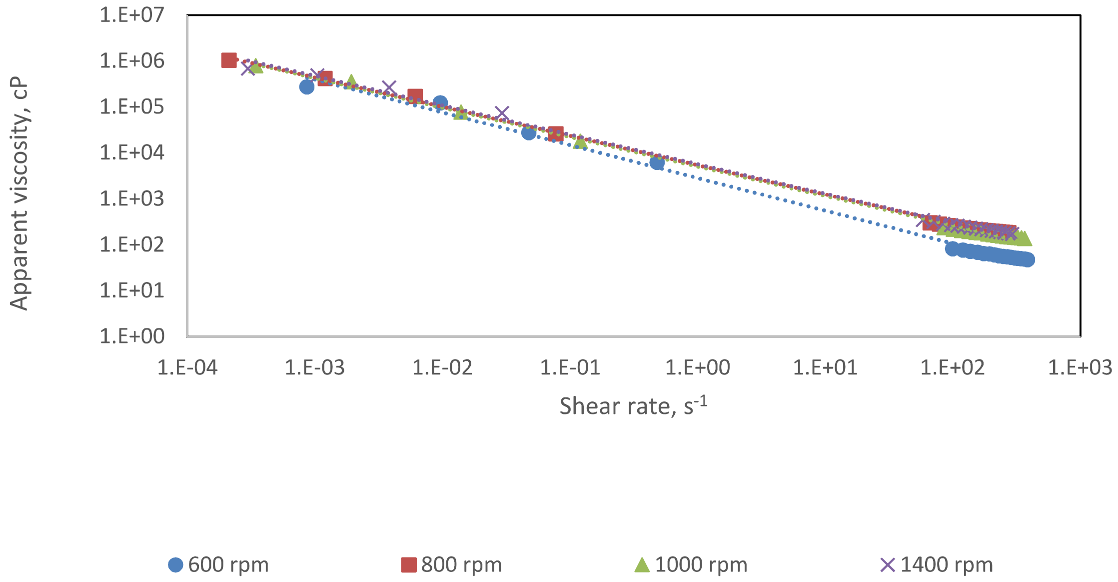


Figure 5.22: Effect of mixing speed on apparent viscosity for waste oil emulsion at 40˚C

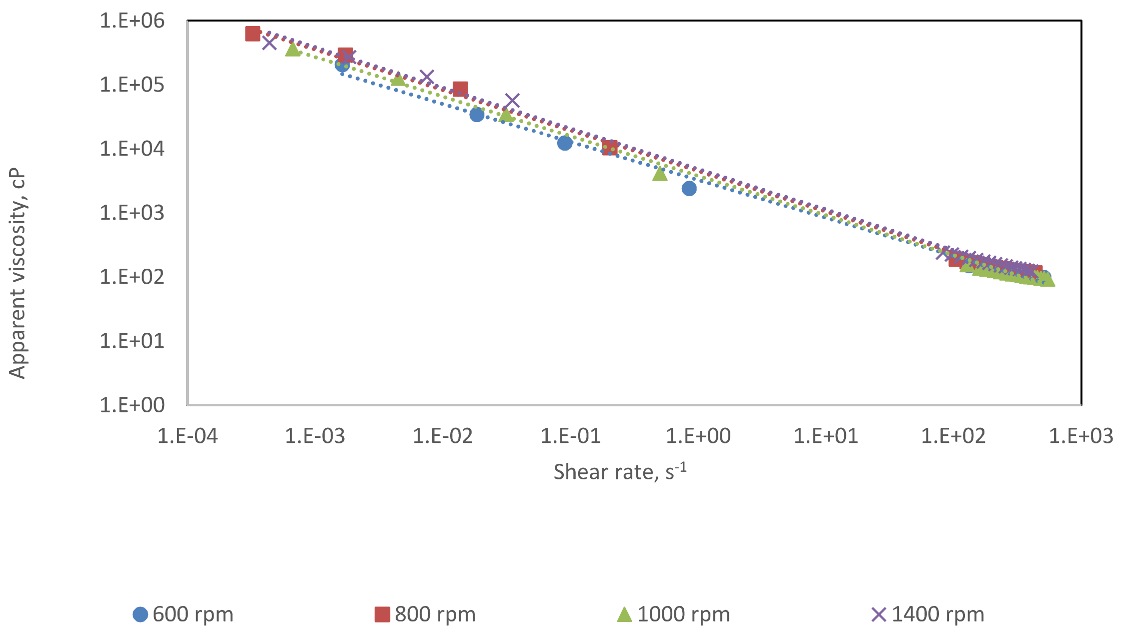


Figure 5.23: Effect of mixing speed on apparent viscosity for waste oil emulsion at 60˚C

TABLE 5.2: Summary of power-law model for mixing speed for waste oil emulsion

Temperature ˚C	Mixing Speed rpm	Power Law Constant, K mPa.s^n	Power Law Index, n	Correlating Coefficient, R^2
25	600	6029.3	0.344	0.998
	800	7930.9	0.304	0.998
	1000	5201.8	0.372	0.998
	1400	9765.9	0.262	0.998
40	600	2864.0	0.286	0.995
	800	5402.7	0.364	0.998
	1000	5071.9	0.358	0.998
	1400	5675.2	0.359	0.997
60	600	3287.7	0.408	0.995
	800	4502.4	0.367	0.998
	1000	3801.8	0.381	0.998
	1400	4858.5	0.366	0.997

Moreover, the effect of mixing speed on the viscoelastic properties is shown in **Figure 5.24**, **Figure 5.25** and **Figure 5.26** at temperatures of 25, 40 and 60˚C, respectively. At 25˚C (**Figure 5.24**), and generally speaking, the viscous modulus is always higher for all speeds. Although, at low frequency the elastic modulus is higher and then a crossover occurs for 600 and 1000 rpm. The same scenario holds for the 1000 rpm when the temperature is raised to 40˚C (**Figure 5.25**). Furthermore, **Figure 5.25** indicates that the 800 and 1400 speeds continues to show the same behavior regardless of the temperature. However, when the emulsions are heated to 60˚C (**Figure 5.26**) no crossover occurs for all speeds except for 800 rpm. The viscous modulus is dominant for all except at low rpm; 600.

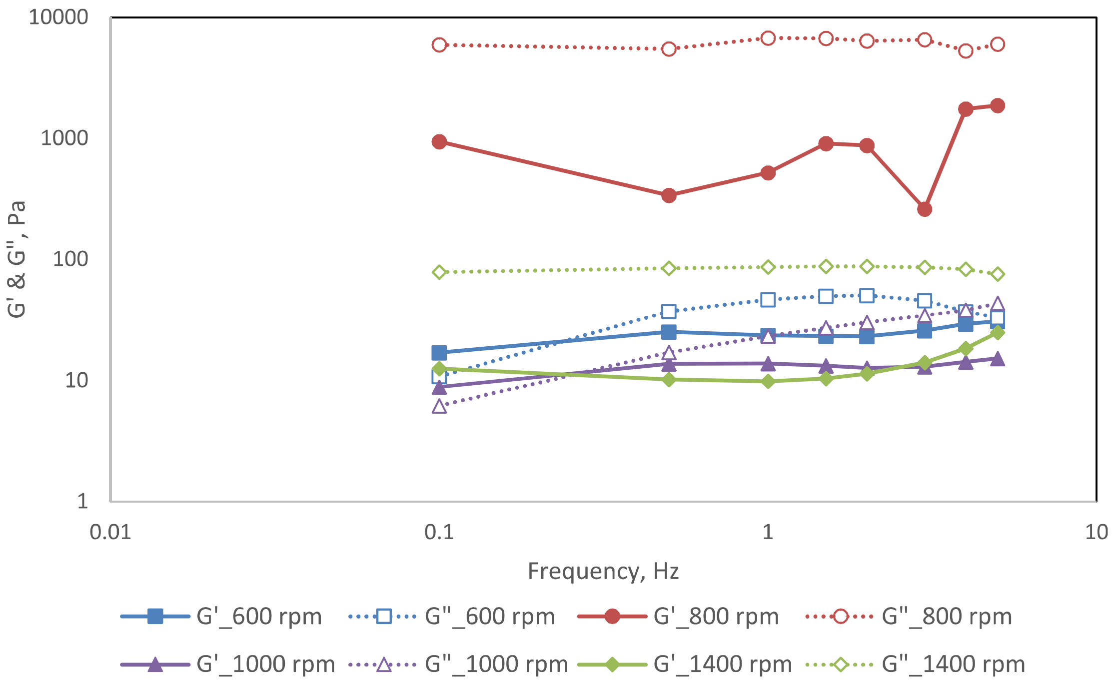


Figure 5.24: Effect of mixing speed on G′ and G″ for waste oil emulsion at 25˚C

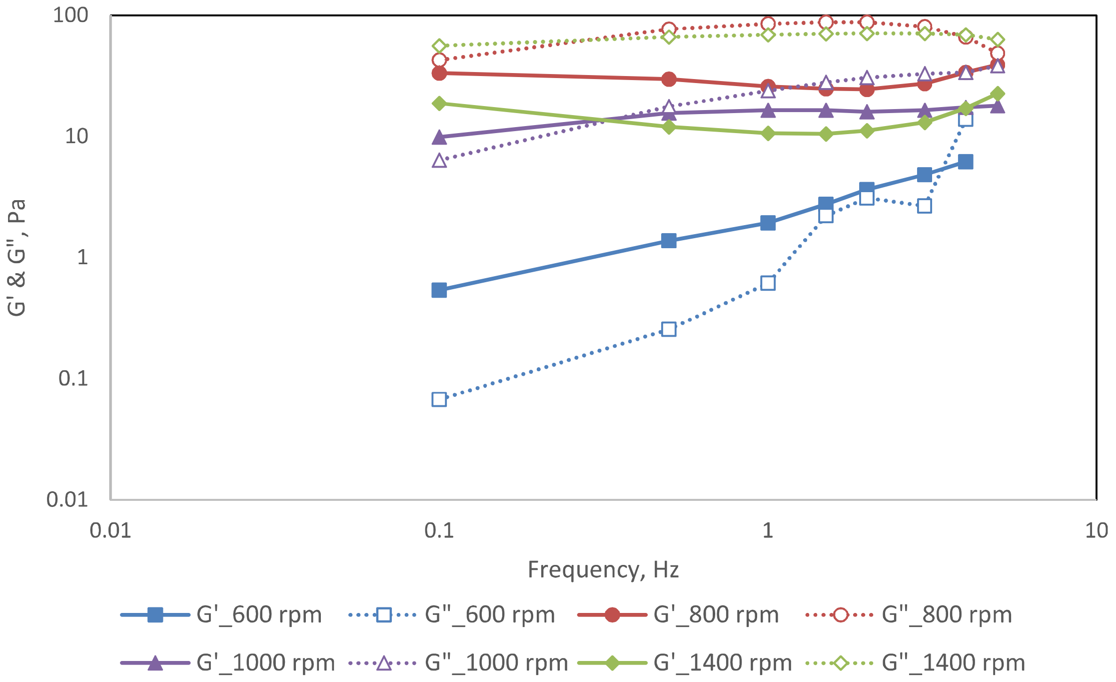


Figure 5.25: Effect of mixing speed on G′ and G″ for waste oil emulsion at 40˚C

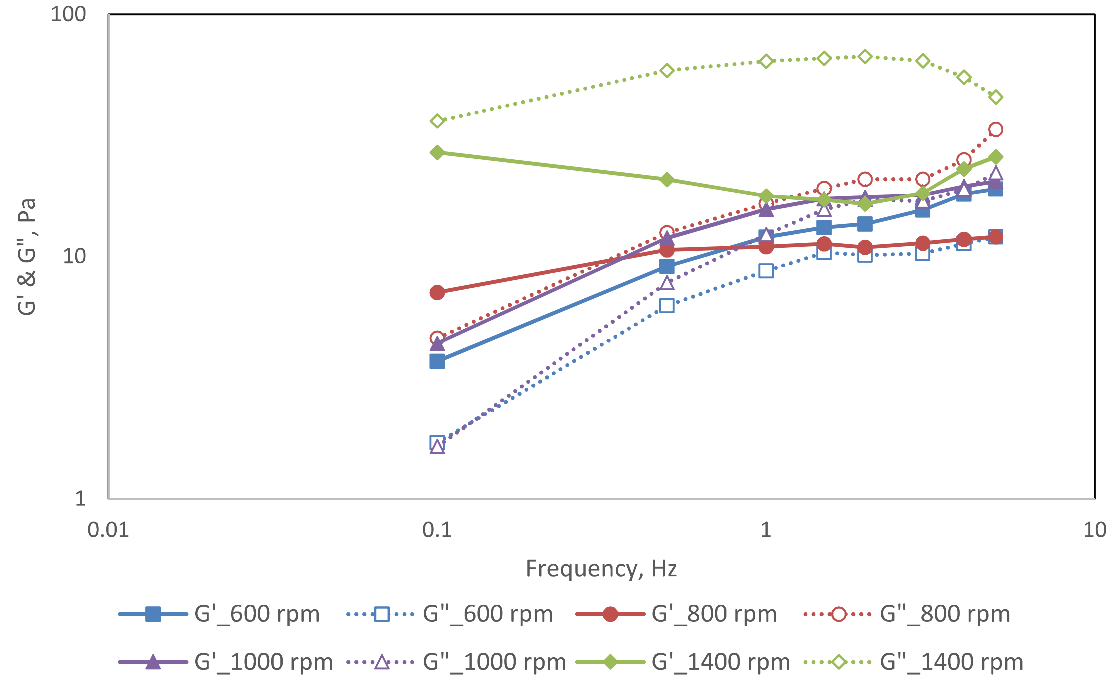


Figure 5.26: Effect of mixing speed on G′ and G″ for waste oil emulsion at 60˚C

5.4.2.3 Effect of temperature

The effect of temperature is studied, where temperature is increased from 25˚C to 100˚C and the rheological behavior is measured. **Figure 5.27** and **Figure 5.28** show the rheological properties at different temperatures. **Figure 5.27** indicates that an increase in temperature results in a decrease in the apparent viscosity. **Figure 5.28** shows that at low temperature, G″ is dominant but increasing the temperature makes G′ dominant. **TABLE 5.3** shows the parameters of the power-law model indicating that increasing the temperature results in decreasing K and in increasing n, hence decreasing the apparent viscosity. In addition, **Figure 5.29** shows the apparent viscosity plotted on semi-log graph as a function of temperature and the data are seamlessly fitted in Arrhenius equation (Equation 1.5).

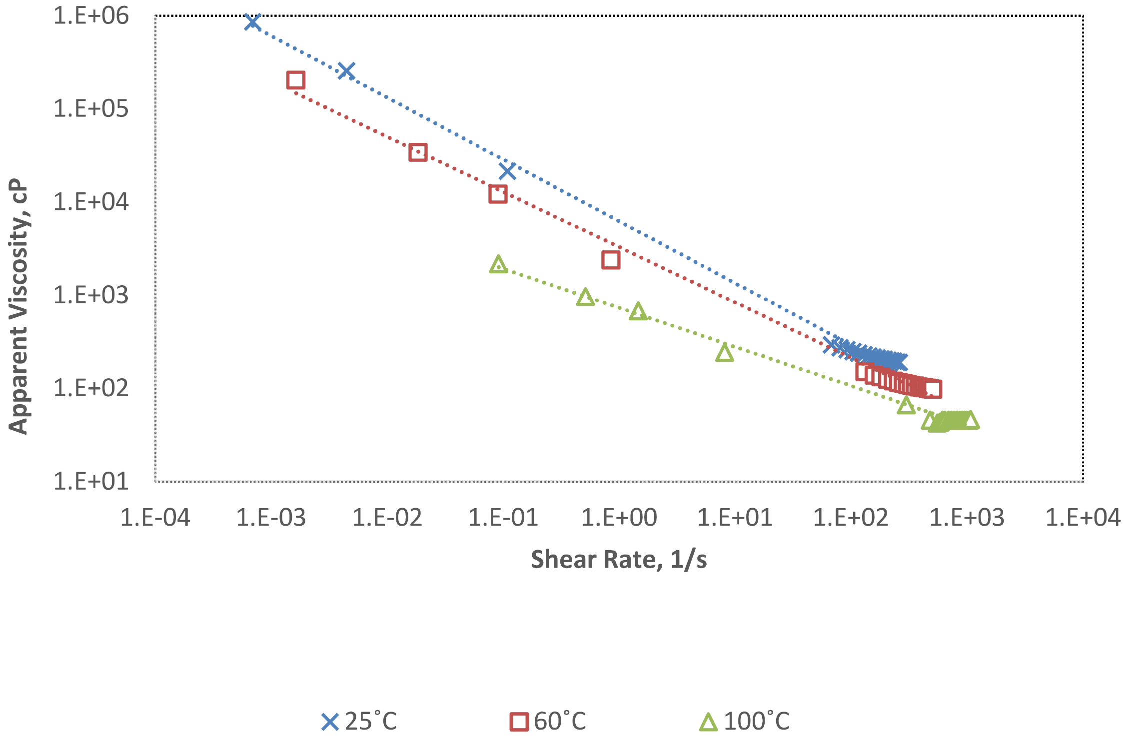


Figure 5.27: Effect of temperature on apparent viscosity for waste oil emulsion

TABLE 5.3: Summary of power-law model for temperature effect for waste oil emulsion

Temperature **˚C**	**Power Law Constant, K mPa.s^n**	**Power Law Index, n**	**Correlating Coefficient, R^2**
25	6233.6	0.337	0.997
60	3287.7	0.408	0.995
100	735.6	0.581	0.991

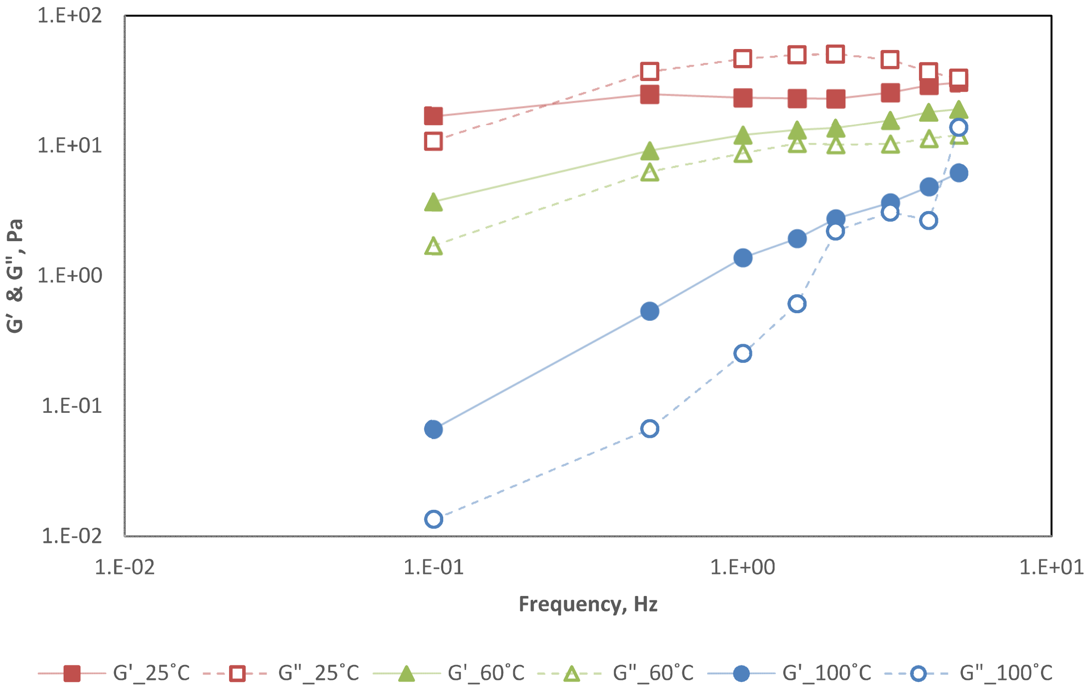


Figure 5.28: Effect of temperature on G′ and G″ for waste oil emulsion

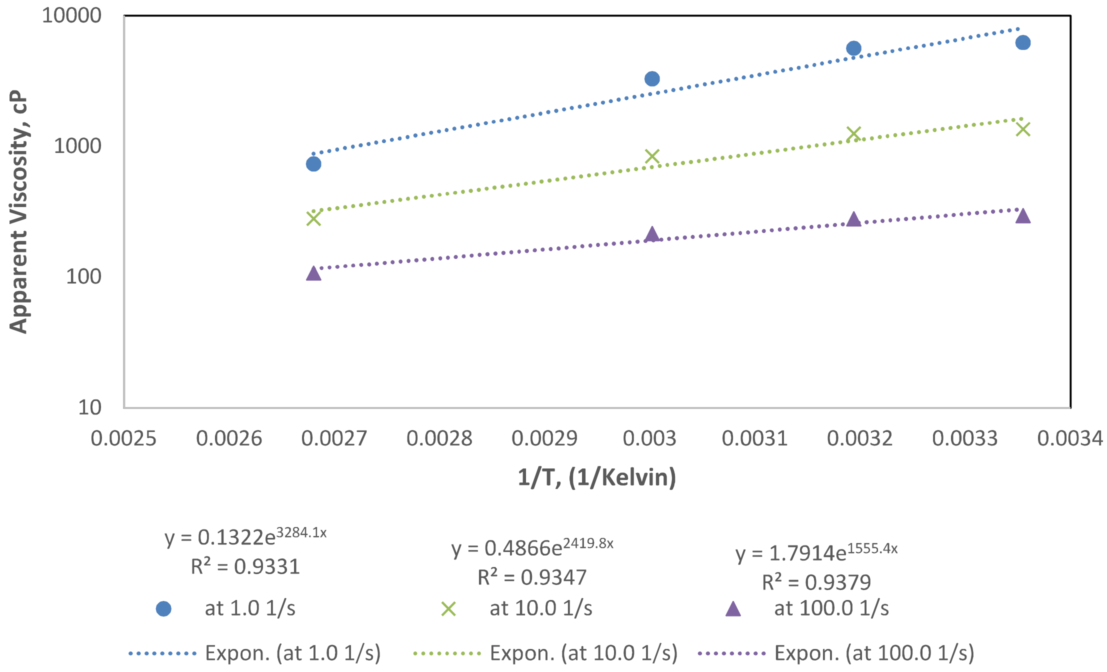


Figure 5.29: Apparent viscosity of waste oil emulsion as a function of temperature

5.4.2.4 Effect of aging

Two different samples are prepared freshly and then are aged for different time periods. The rheological behavior is studied for the two samples when they are fresh and when they are aged. All samples are aged at room temperature. Then, rheological tests are conducted at 25, 40 and 60˚C. Later, they are plotted with the data obtained from the fresh sample in order to observe the rheological behavior of the emulsion when prepared and left unused for whatever reason.

The first sample is aged for 24 and 96 hours. **Figure 5.30**, **Figure 5.31** and **Figure 5.32** indicate that aging decreases the apparent viscosity. As far as viscoelastic properties go,

Figure 5.33 and **Figure 5.34** indicate that G′ tends to increase with aging for tests done at 25˚C. On the other hand, for tests done at 40˚C and 60˚C, G′ tends to decrease. Which is, also, the case for G″ at all temperatures used in this study. That said, G″ decreases with aging. In **TABLE 5.4**, the parameters of power-law model are shown.

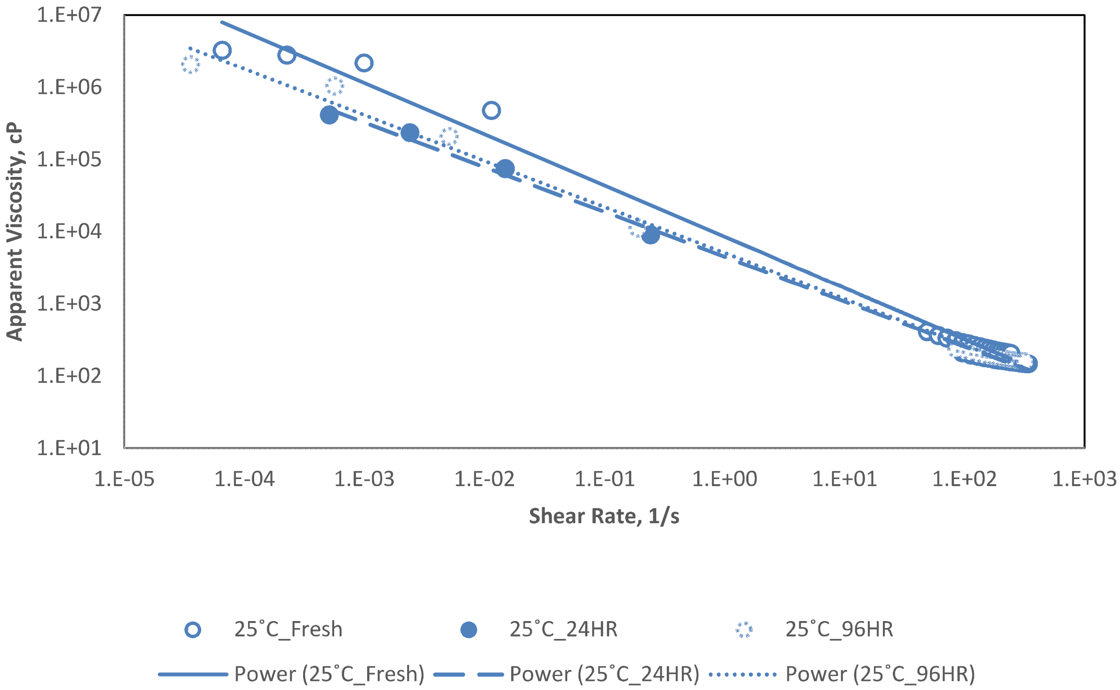


Figure 5.30: Effect of aging for 24 and 96 hours on apparent viscosity at 25˚C for waste oil emulsion

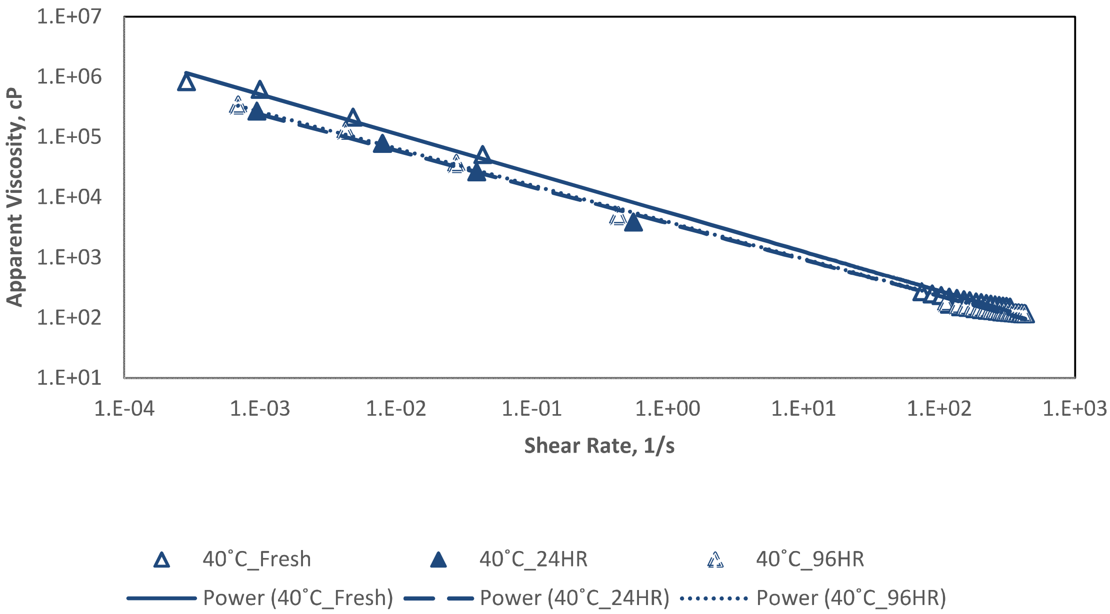


Figure 5.31: Effect of aging for 24 and 96 hours on apparent viscosity at 40˚C for waste oil emulsion

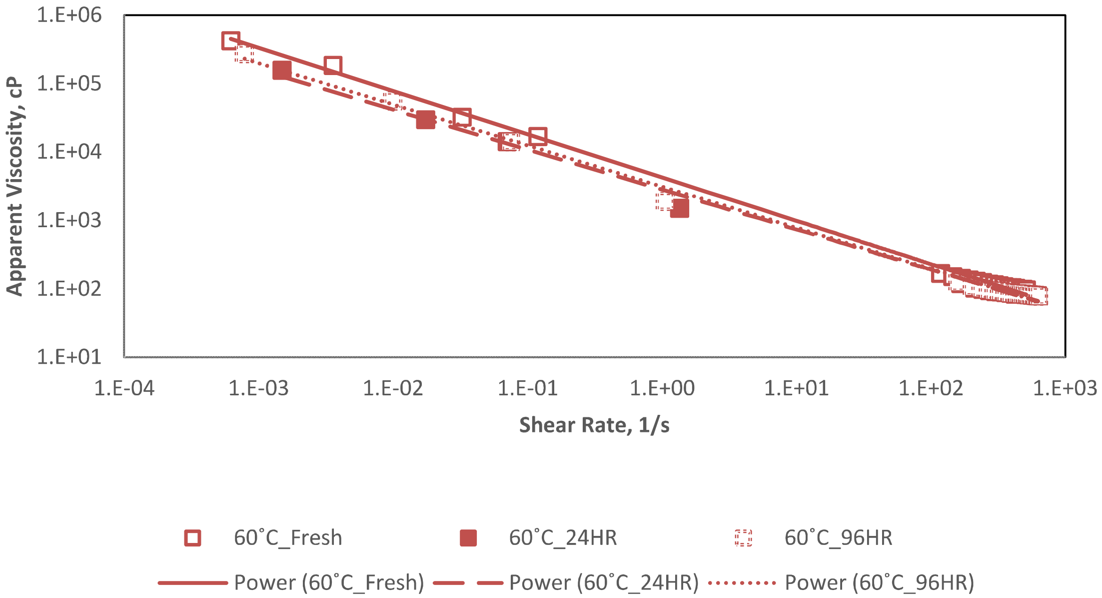


Figure 5.32: Effect of aging for 24 and 96 hours on apparent viscosity at 60˚C for waste oil emulsion

TABLE 5.4: Summary of power-law model for effect of aging for waste oil emulsion

Temperature ˚C	**Aged time at room temperature hour**	**Power Law Constant, K mPa.s^n**	**Power Law Index, n**	**Correlating Coefficient, R^2**
25	0	8476.0	0.291	0.991
	24	4500.0	0.380	0.997
	96	5082.5	0.363	0.994
40	0	5632.4	0.347	0.998
	24	3718.1	0.397	0.997
	96	3917.1	0.390	0.997
60	0	4241.8	0.368	0.998
	24	2837.5	0.416	0.995
	96	3137.7	0.400	0.996

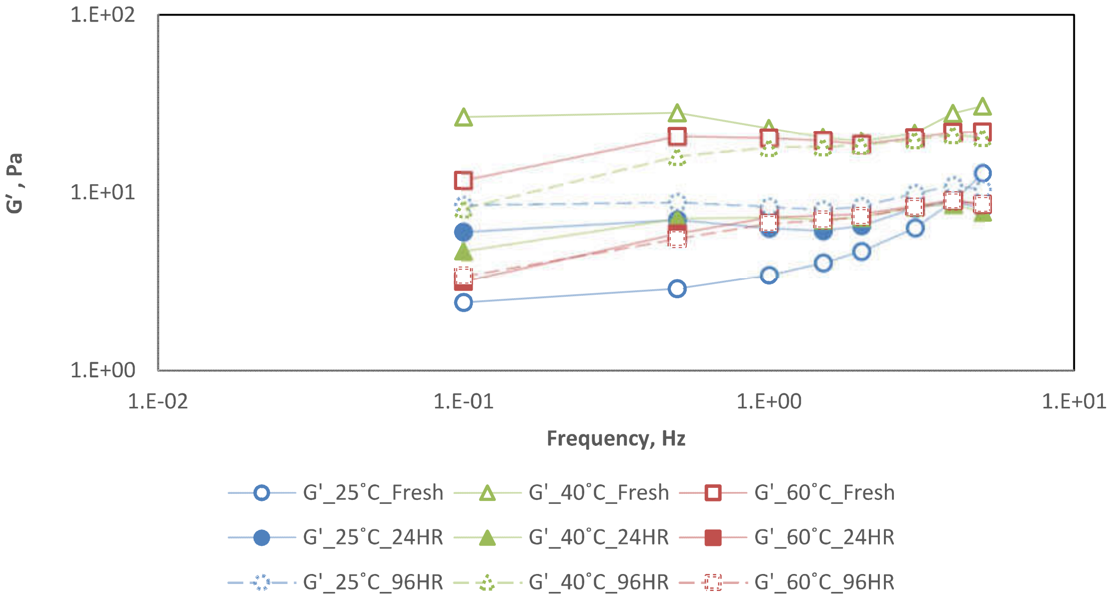


Figure 5.33: Effect of aging for 24 and 96 hours on elastic modulus for waste oil emulsion

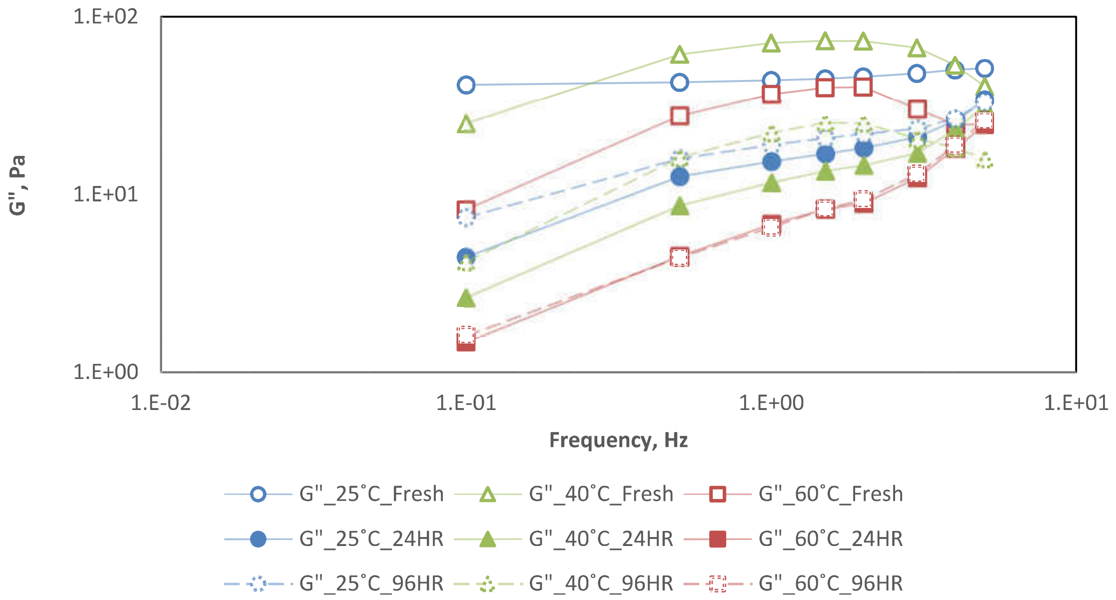


Figure 5.34: Effect of aging for 24 and 96 hours on viscous modulus for waste oil emulsion

As for the second sample, it is left to be aged for longer time, 14 days. **Figure 5.35** shows that when the test is done at higher temperature such as 40˚C and 60˚C, a decrease in apparent viscosity is spotted, which is the logical behavior. Interestingly, the 14-day-aged emulsion at 40˚C behaves similarly to the fresh 60˚C emulsion. Also, **Figure 5.36** and **Figure 5.37** show a decrease in both G′ and G″ when the emulsion is aged. Moreover, **TABLE 5.5** shows the power-law model parameters for aging for 14 days indicting that aging is related directly to n and inversely to K.

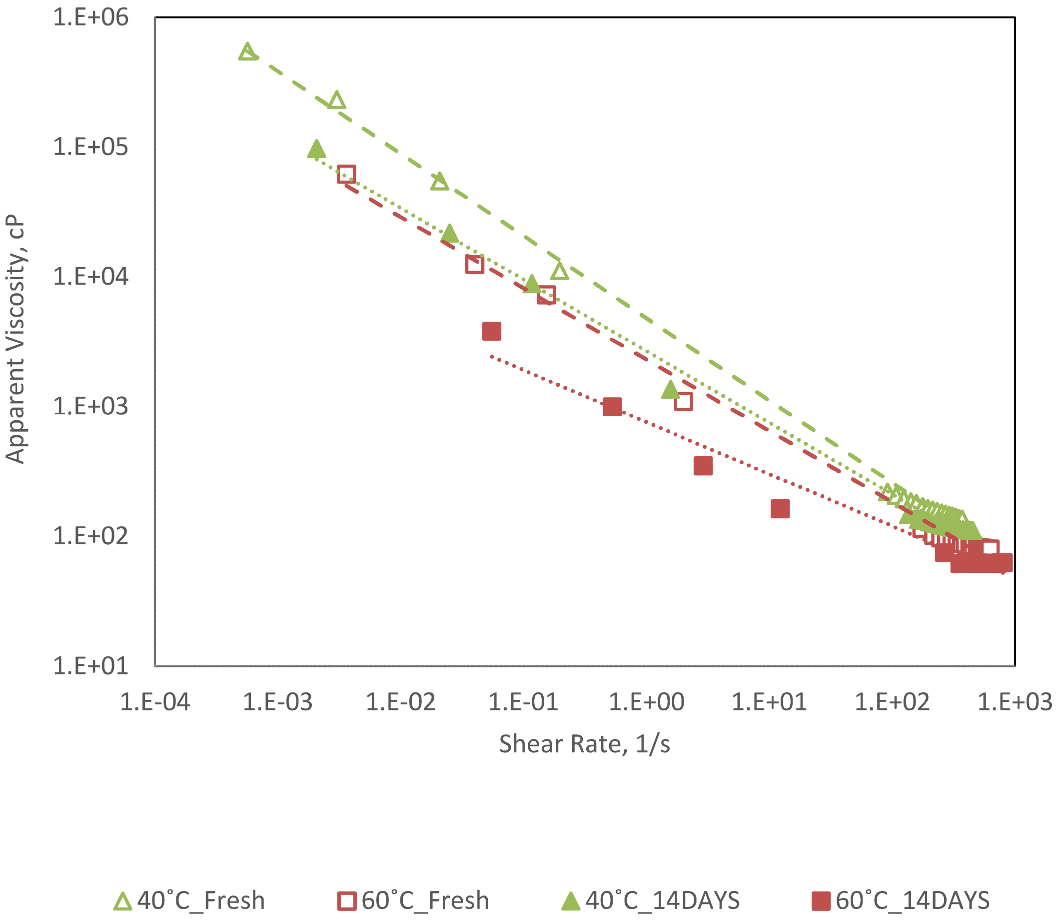


Figure 5.35: Effect of aging for 14 days on apparent viscosity for waste oil emulsion

TABLE 5.5: Summary of power-law model for effect of aging (14 days) for waste oil emulsion

Temperature **˚C**	**Aged time at room temperature** **day**	**Power Law Constant, K** **mPa.s^n**	**Power Law Index, n**	**Correlating Coefficient, R^2**
40	0	4797.7	0.366	0.998
	14	2673.7	0.454	0.994
60	0	2304.7	0.449	0.995
	14	760.4	0.600	0.967

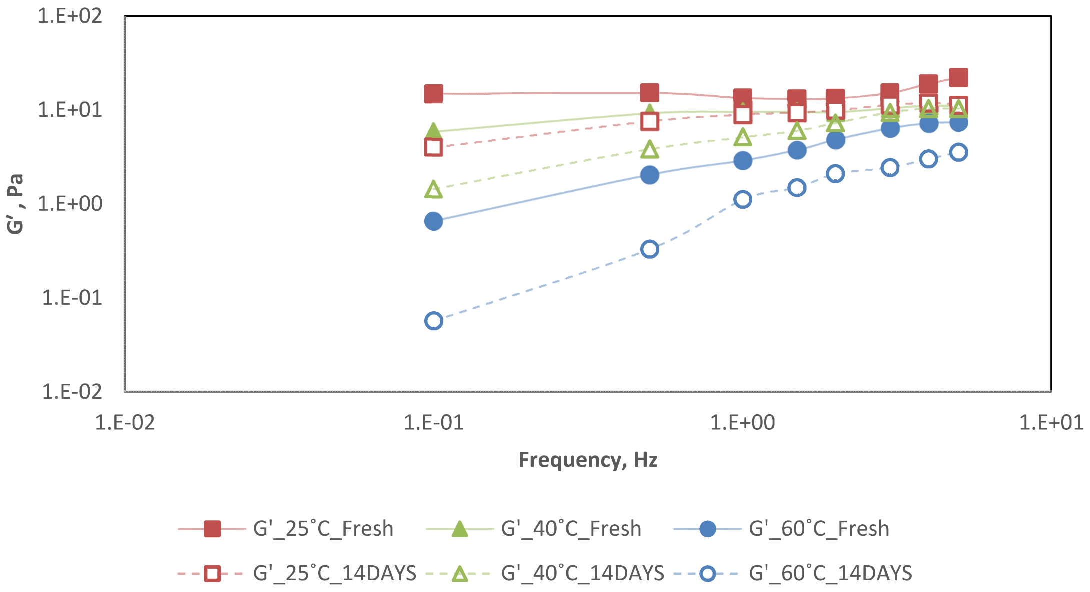


Figure 5.36: Effect of aging for 14 days on elastic modulus for waste oil emulsion

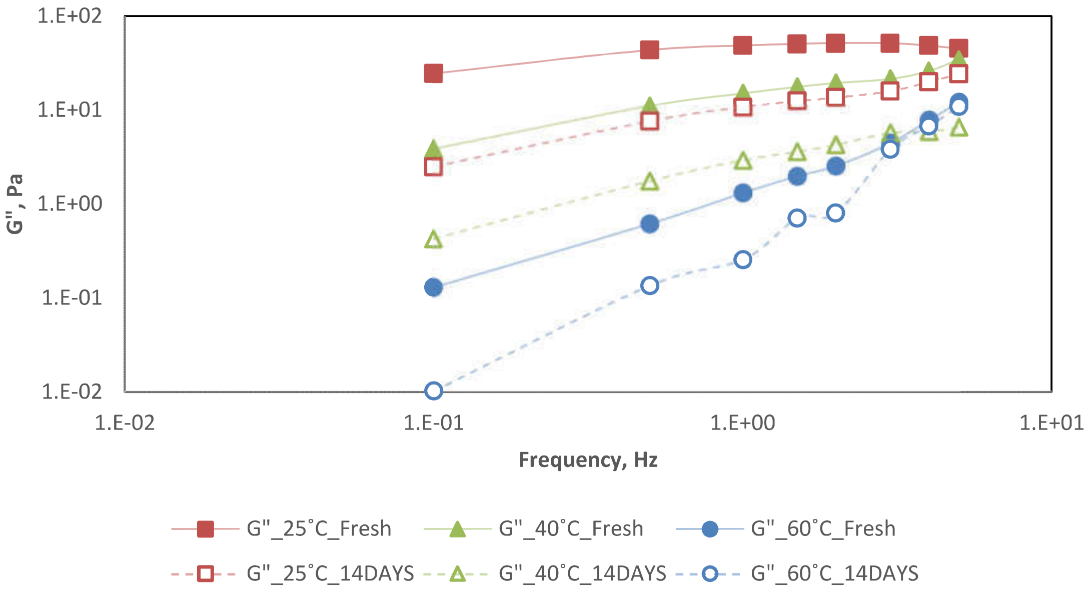


Figure 5.37: Effect of aging for 14 days on viscous modulus for waste oil emulsion

5.4.3 Droplet size distribution

Droplet size distribution is studied for both sets of the emulsions; with corrosion inhibitor and without. **Figure 5.38** and **Figure 5.39** show the effect of heating on the droplet size distribution of waste oil emulsion without and with corrosion inhibitor, respectively. It can be concluded from these graphs that emulsions of higher temperatures tend to have smaller droplet size compared to those of lower temperatures. Moreover, the addition of corrosion inhibitor tends to distribute the emulsion droplets over a wider range. It is noted that emulsions prepared without corrosion inhibitor have narrow size distribution, which is considered favorable for emulsion stability (Ganguli et al., 2003). In addition, the 10th, 50th and 90th percentiles along with D[4,3] and D[3,2] means (Equations 1.7-1.8) of the emulsions are presented in **TABLE 5.6**.

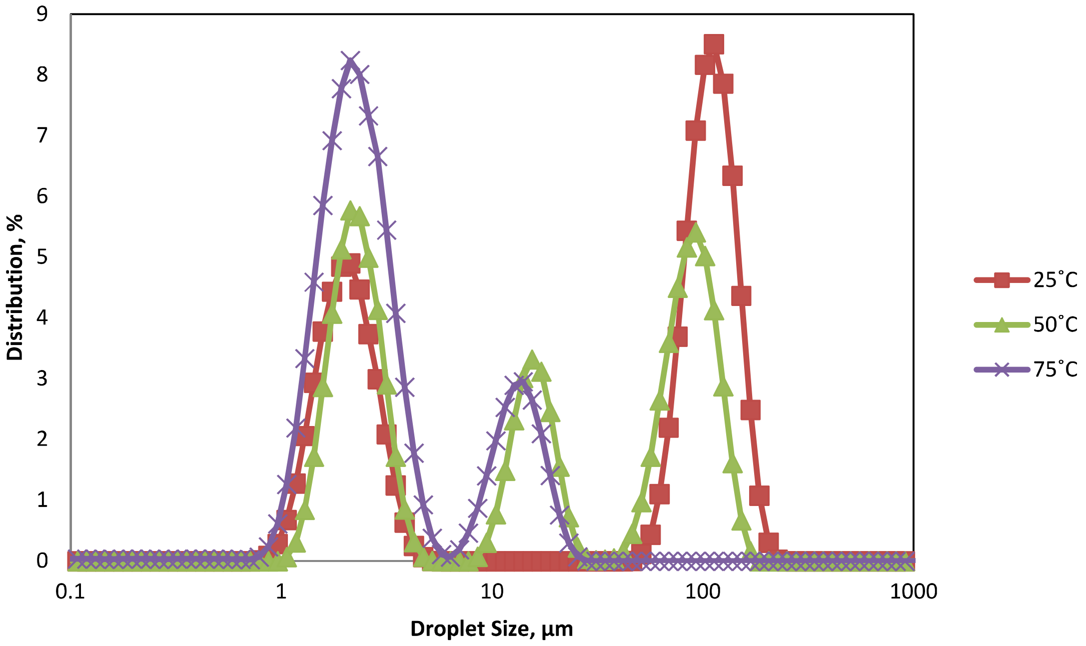


Figure 5.38: Effect of heating on droplet size distribution for waste oil emulsion without corrosion inhibitor

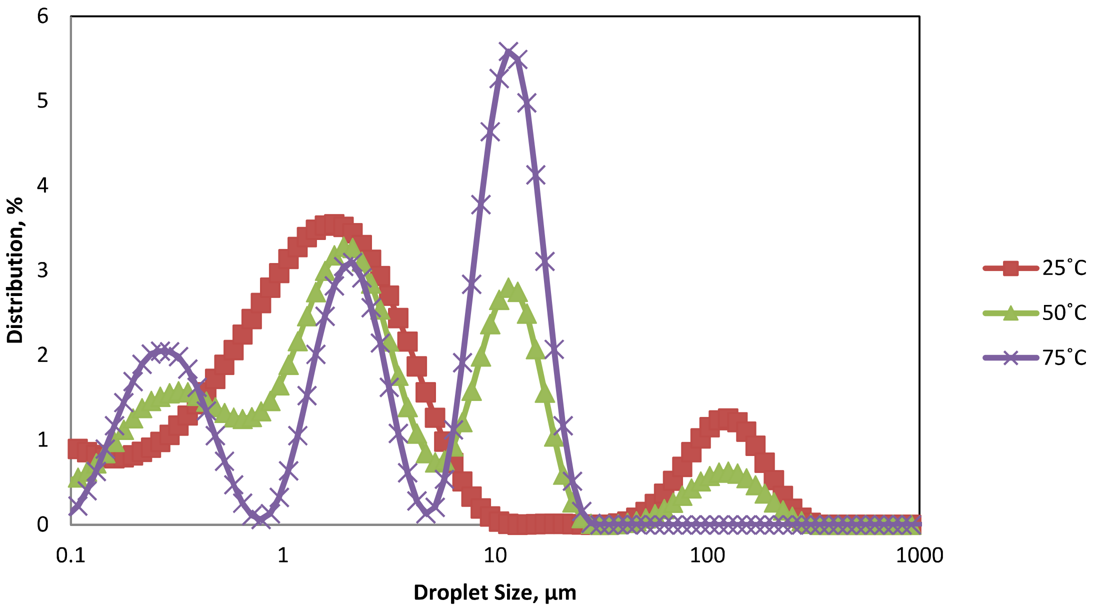


Figure 5.39: Effect of heating on droplet size distribution for waste oil emulsion with corrosion inhibitor

TABLE 5.6: Summary of droplet size distribution for waste oil emulsion with and without corrosion inhibitor

System	Temperature ˚C	10th percentile µm	50th percentile µm	90th percentile µm	D[4,3] µm	D[3,2] µm
Waste oil emulsion without corrosion inhibitor	25	1.53	78.5	134.49	178.35	158.67
	50	1.75	14.3	101.42	132.38	117.76
	75	1.34	2.35	12.83	24.44	21.74
Waste oil emulsion with corrosion inhibitor	25	0.25	1.47	81.87	240.30	213.77
	50	0.24	2.75	30.1	142.93	127.17
	75	0.23	3.09	14.46	22.13	19.69

5.5 Conclusions

This chapter clearly investigated the potential of using waste oil as the oil phase in emulsified acid by addressing its stability and rheological behavior. The following conclusions can be drawn:

1. Waste oil emulsion was found to be a shear-thinning fluid with brownish color.
2. Increasing the emulsifier concentration resulted in a slightly more stable emulsion, but no significant effect on apparent viscosity. Nonetheless, it had a different impact on viscoelastic properties. As for G′, it flocculated between increasing and decreasing at different temperatures. That was the same scenario for G″. However, G″ of emulsifier concentration of 1 vol% was always the highest.
3. As far as mixing speed is concerned, increasing the rpm speed form 600 to 1400 did not show any major effect on both stability and apparent viscosity. Moreover, no clear trend was found on viscoelastic properties.
4. Addition rate of acid phase to oil phase showed a significant effect on stability results. For reproducible emulsion and consistency of the results, it must be fixed at a specific rate.
5. For the temperature, an increase in the temperature was accompanied by a decrease in the apparent viscosity. Moreover, at low temperatures, G″ was dominant but increasing the temperature made G′ the dominant one.
6. Generally, aging caused the emulsion to degrade.

7. Moreover, adding corrosion inhibitor to the emulsion caused a negative effect on the stability. Further, emulsions without corrosion inhibitor were found to form polydispersed droplets of narrow range. Unlike when corrosion inhibitor was added, wider ranges of droplets were formed.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

This work clearly addressed emulsified HCl. First, it conducted experiments on diesel emulsion to use the results as a base line. Then, it investigated the potential of using waste oil emulsion. Overall, the following can be concluded:

1. Both diesel and waste oil emulsions were shear-thinning fluids.
2. The addition rate of acid (water) phase to oil phase played a significant role on thermal stability.
3. Increasing the emulsifier concentration from 0.5 to 1.5 vol%:
    a. Resulted in a slightly more stable emulsion for both diesel and waste oil emulsion, hence 0.5 vol% was chosen as the optimum concentration.
    b. For waste oil emulsion, it did not constitute a major difference in the apparent viscosity. Whereas, for diesel emulsion, a difference was only observed for 1.5 vol% emulsion at 100˚C.
    c. Had no clear effect on viscoelastic properties for waste oil emulsion. Nevertheless, for diesel emulsion, it resulted in an increase of G′ and G″.
4. Increasing the mixing speed from 600 to 1400rpm:
    a. Did not show any major effect on thermal stability for both emulsions.

    b. Resulted in obtaining the highest apparent viscosity for emulsions of 600 and 1400 rpm of diesel emulsion. On the contrary, no effect was observed for waste oil emulsion.
    c. Showed an increase in G′ at low frequency, but no clear effect on G″; for diesel emulsion. As for waste oil emulsion, no clear trend was spotted.
5. Increasing the temperature:
    a. Resulted in decreasing the apparent viscosity for both emulsions.
    b. For diesel emulsion, from 25 to 60˚C, it had no significant effect on G′, however, increasing it further to 100˚C a significant decrease was the result. Whereas, there was no clear trend for G″ as the data fluctuated.
    c. For waste oil emulsion, it resulted in a decrease in the apparent viscosity. Moreover, at low temperatures, G″ was dominant but increasing the temperature made G′ the dominant one.
6. Generally, aging caused both of the emulsions to degrade.
7. Addition of corrosion inhibitor caused a negative effect on the thermal stability of both emulsions.

6.2 Recommendations

Definitely, the ultimate goal is to try the waste oil emulsion (novel emulsion) in the field, in order to confirm the laboratory results. However, before doing so, the following is recommended to be done in the laboratory:

1. To conduct reaction rate experiments in order to apprehend how the novel emulsion will react with the rock formation.
2. To conduct core-flooding experiments in order to study the wormholes and to know the optimum injection rate.

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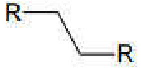
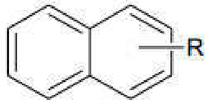
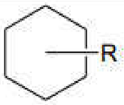
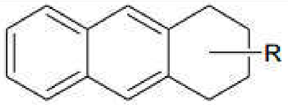
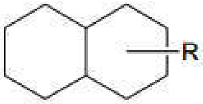
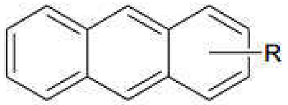
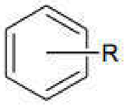
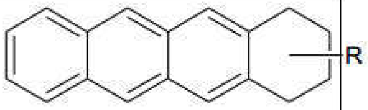
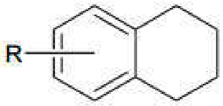
Appendix A

In this Appendix, the hydrocarbon specifications of both diesel and waste oil which are used in this work are presented. A method involving two-dimensional Gas Chromatography (GCxGC) hyphenated to a universal Flame Ionization Detector (FID) is applied to obtain group type analysis of the two samples. Both samples are found to contain paraffins, mono-naphtenes, dinaphtenes, monoaromatics, naphteno monoaromatcis, diaromatics, naphteno-diaromatics, triaromatics, naphteno-triaromatics, tetraaromatics and pentaaromatics, albeit at different concentrations.

FID is used to determine the relative abundances of the hydrocarbons in the samples. The first non-polar and the second polar chromatographic columns allow the separation of the hydrocarbons according to their boiling points and their polarity, respectively. The GCxGC oven is operated from 50ºC to 320ºC at a temperature gradient of 2 ºC/min. The modulation is set at 10 seconds. The relative abundance of the different hydrocarbon species is achieved by normalizing the total area of the chromatogram. The structures of the molecules reported in this Appendix are presented in **TABLE A.1**.

Figure A.1 presents the GCxGC-FID chromatogram obtained for the diesel sample. It can be seen that the diesel sample contains paraffins, mono-naphtenes, dinaphtenes, monoaromatics, naphteno-monoaromatcis, diaromatics, naphteno-diaromatics, triaromatics, naphteno-triaromatics, tetraaromatics and naphteno-tetraaromatics. Moreover, the hydrocarbon families are further separated into groups of isomers along the x-axis which allows for their quantification. A similar chromatogram is obtained for the waste oil sample, indicating that the two samples contain the same groups of compounds, albeit at different concentrations (**Figure A.2**). Furthermore, The carbon breakdown is available in **TABLE A.2 and TABLE A.3**.

TABLE A.1: Molecular structures of identified species, R represents one or more alkyl groups that can be either linear or branched

Name	Structure	Name	Structure
Paraffins (P)		Diaromatics (DA)	
Naphtenes (MN)		Naphtenodiaromatics (NDA)	
Polynaphtenes (DN)		Triaromatics (TA)	
Monoaromatics (MA)		Naphtenotriaromatics (NTA)	
Naphtenomonoaromatics (NMA)			

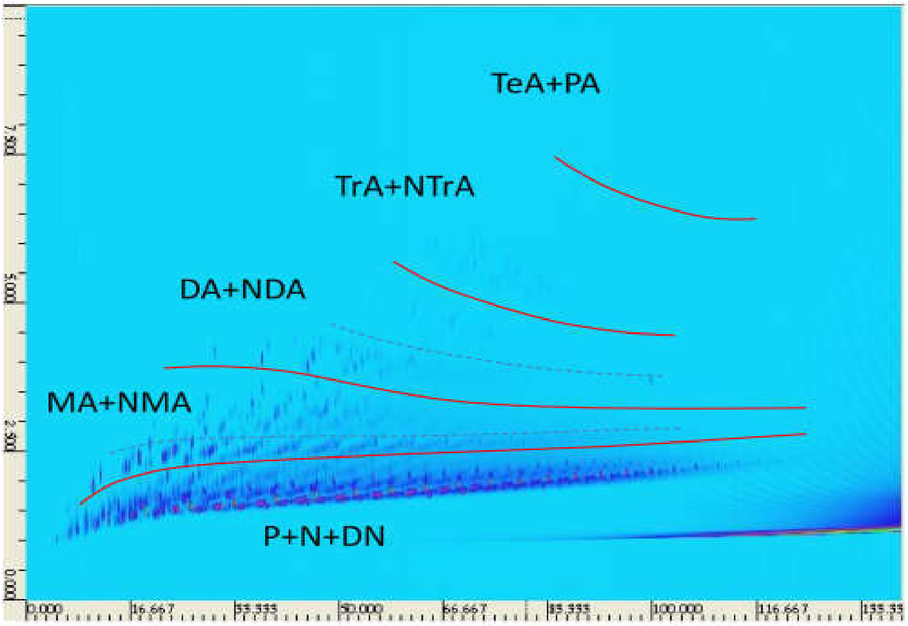


Figure A.1: GCxGC chromatography of diesel sample

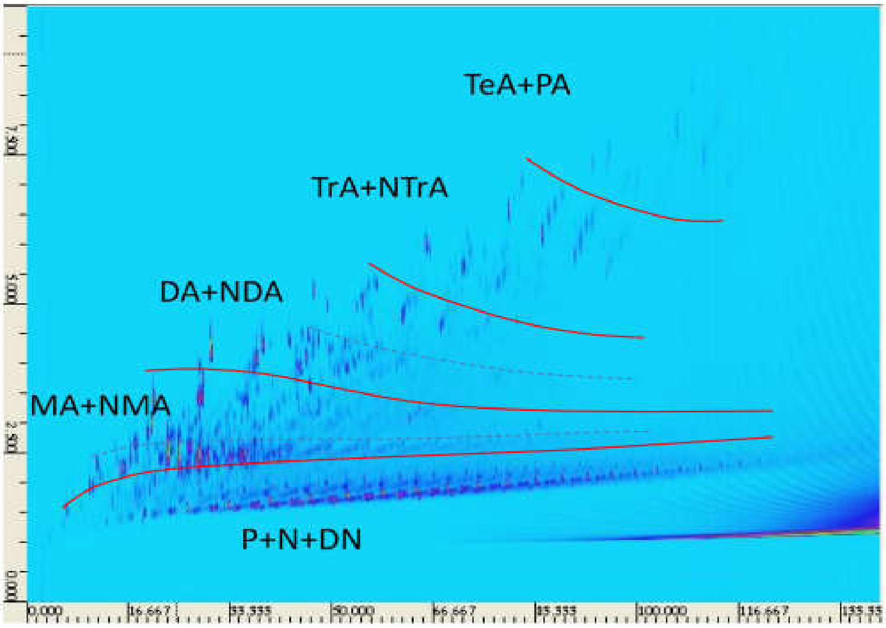
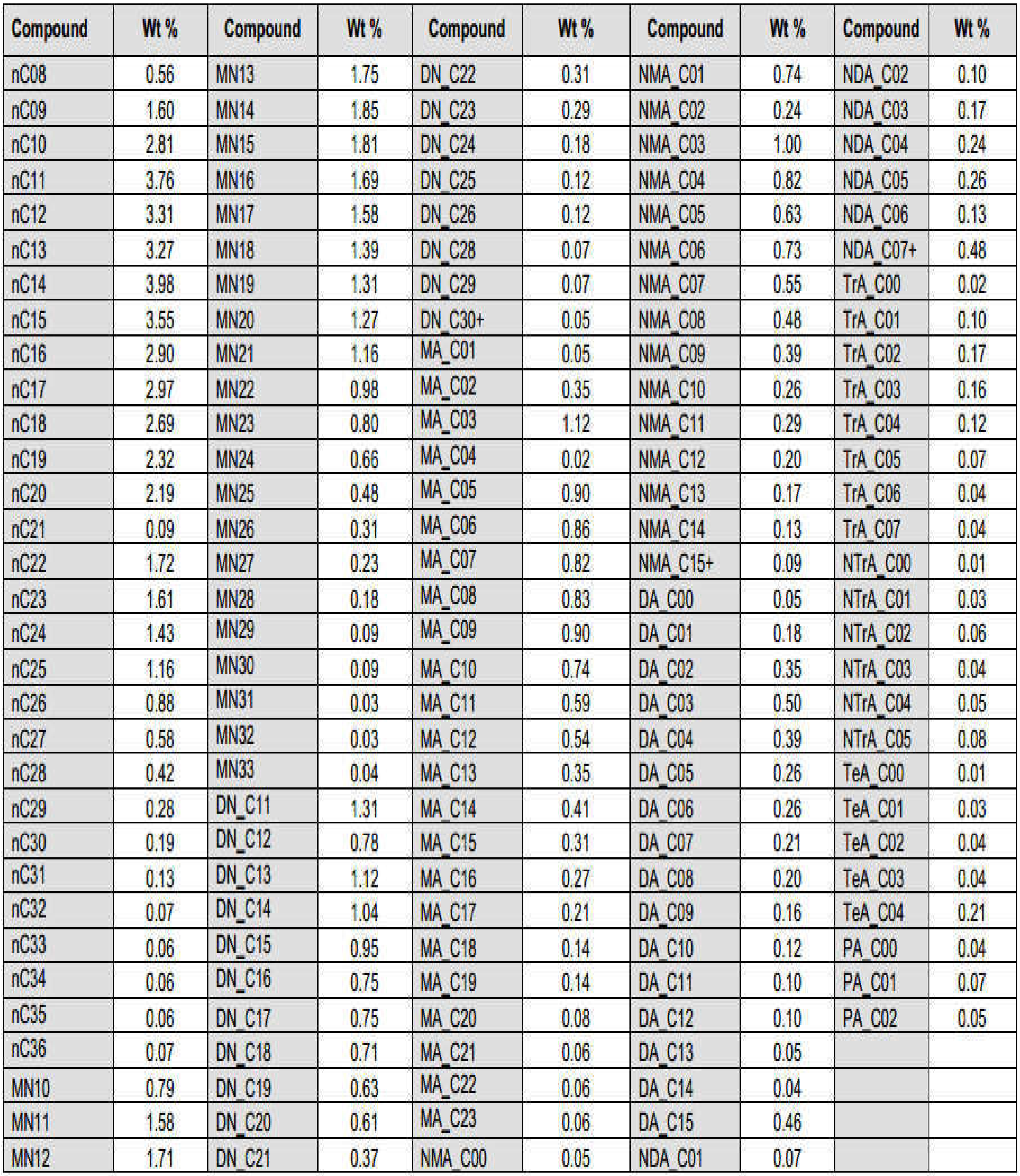


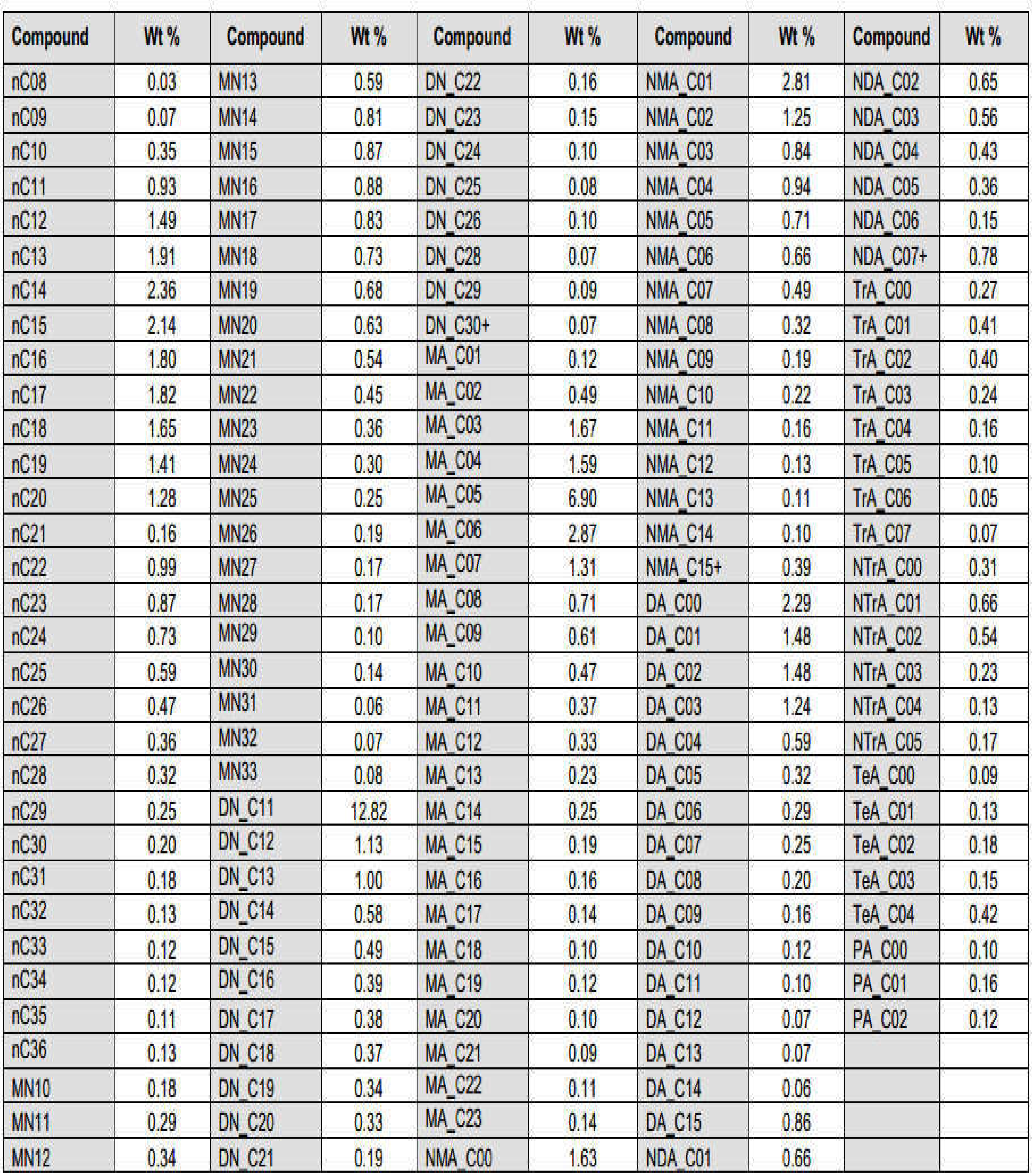
Figure A.2: GCxGC chromatography of waste oil sample

TABLE A.2: Distribution of the hydrocarbon families in diesel sample



Compound	Wt %	Compound	Wt %	Compound	Wt %	Compound	Wt %	Compound	Wt %
nC08	0.56	MN13	1.75	DN_C22	0.31	NMA_C01	0.74	NDA_C02	0.10
nC09	1.60	MN14	1.85	DN_C23	0.29	NMA_C02	0.24	NDA_C03	0.17
nC10	2.81	MN15	1.81	DN_C24	0.18	NMA_C03	1.00	NDA_C04	0.24
nC11	3.76	MN16	1.69	DN_C25	0.12	NMA_C04	0.82	NDA_C05	0.26
nC12	3.31	MN17	1.58	DN_C26	0.12	NMA_C05	0.63	NDA_C06	0.13
nC13	3.27	MN18	1.39	DN_C28	0.07	NMA_C06	0.73	NDA_C07+	0.48
nC14	3.98	MN19	1.31	DN_C29	0.07	NMA_C07	0.55	TrA_C00	0.02
nC15	3.55	MN20	1.27	DN_C30+	0.05	NMA_C08	0.48	TrA_C01	0.10
nC16	2.90	MN21	1.16	MA_C01	0.05	NMA_C09	0.39	TrA_C02	0.17
nC17	2.97	MN22	0.98	MA_C02	0.35	NMA_C10	0.26	TrA_C03	0.16
nC18	2.69	MN23	0.80	MA_C03	1.12	NMA_C11	0.29	TrA_C04	0.12
nC19	2.32	MN24	0.66	MA_C04	0.02	NMA_C12	0.20	TrA_C05	0.07
nC20	2.19	MN25	0.48	MA_C05	0.90	NMA_C13	0.17	TrA_C06	0.04
nC21	0.09	MN26	0.31	MA_C06	0.86	NMA_C14	0.13	TrA_C07	0.04
nC22	1.72	MN27	0.23	MA_C07	0.82	NMA_C15+	0.09	NTrA_C00	0.01
nC23	1.61	MN28	0.18	MA_C08	0.83	DA_C00	0.05	NTrA_C01	0.03
nC24	1.43	MN29	0.09	MA_C09	0.90	DA_C01	0.18	NTrA_C02	0.06
nC25	1.16	MN30	0.09	MA_C10	0.74	DA_C02	0.35	NTrA_C03	0.04
nC26	0.88	MN31	0.03	MA_C11	0.59	DA_C03	0.50	NTrA_C04	0.05
nC27	0.58	MN32	0.03	MA_C12	0.54	DA_C04	0.39	NTrA_C05	0.08
nC28	0.42	MN33	0.04	MA_C13	0.35	DA_C05	0.26	TeA_C00	0.01
nC29	0.28	DN_C11	1.31	MA_C14	0.41	DA_C06	0.26	TeA_C01	0.03
nC30	0.19	DN_C12	0.78	MA_C15	0.31	DA_C07	0.21	TeA_C02	0.04
nC31	0.13	DN_C13	1.12	MA_C16	0.27	DA_C08	0.20	TeA_C03	0.04
nC32	0.07	DN_C14	1.04	MA_C17	0.21	DA_C09	0.16	TeA_C04	0.21
nC33	0.06	DN_C15	0.95	MA_C18	0.14	DA_C10	0.12	PA_C00	0.04
nC34	0.06	DN_C16	0.75	MA_C19	0.14	DA_C11	0.10	PA_C01	0.07
nC35	0.06	DN_C17	0.75	MA_C20	0.08	DA_C12	0.10	PA_C02	0.05
nC36	0.07	DN_C18	0.71	MA_C21	0.06	DA_C13	0.05		
MN10	0.79	DN_C19	0.63	MA_C22	0.06	DA_C14	0.04		
MN11	1.58	DN_C20	0.61	MA_C23	0.06	DA_C15	0.46		
MN12	1.71	DN_C21	0.37	NMA_C00	0.05	NDA_C01	0.07		

TABLE A.3: Distribution of the hydrocarbon families in waste oil sample



Compound	Wt %	Compound	Wt %	Compound	Wt %	Compound	Wt %	Compound	Wt %
nC08	0.03	MN13	0.59	DN_C22	0.16	NMA_C01	2.81	NDA_C02	0.65
nC09	0.07	MN14	0.81	DN_C23	0.15	NMA_C02	1.25	NDA_C03	0.56
nC10	0.35	MN15	0.87	DN_C24	0.10	NMA_C03	0.84	NDA_C04	0.43
nC11	0.93	MN16	0.88	DN_C25	0.08	NMA_C04	0.94	NDA_C05	0.36
nC12	1.49	MN17	0.83	DN_C26	0.10	NMA_C05	0.71	NDA_C06	0.15
nC13	1.91	MN18	0.73	DN_C28	0.07	NMA_C06	0.66	NDA_C07+	0.78
nC14	2.36	MN19	0.68	DN_C29	0.09	NMA_C07	0.49	TrA_C00	0.27
nC15	2.14	MN20	0.63	DN_C30+	0.07	NMA_C08	0.32	TrA_C01	0.41
nC16	1.80	MN21	0.54	MA_C01	0.12	NMA_C09	0.19	TrA_C02	0.40
nC17	1.82	MN22	0.45	MA_C02	0.49	NMA_C10	0.22	TrA_C03	0.24
nC18	1.65	MN23	0.36	MA_C03	1.67	NMA_C11	0.16	TrA_C04	0.16
nC19	1.41	MN24	0.30	MA_C04	1.59	NMA_C12	0.13	TrA_C05	0.10
nC20	1.28	MN25	0.25	MA_C05	6.90	NMA_C13	0.11	TrA_C06	0.05
nC21	0.16	MN26	0.19	MA_C06	2.87	NMA_C14	0.10	TrA_C07	0.07
nC22	0.99	MN27	0.17	MA_C07	1.31	NMA_C15+	0.39	NTrA_C00	0.31
nC23	0.87	MN28	0.17	MA_C08	0.71	DA_C00	2.29	NTrA_C01	0.66
nC24	0.73	MN29	0.10	MA_C09	0.61	DA_C01	1.48	NTrA_C02	0.54
nC25	0.59	MN30	0.14	MA_C10	0.47	DA_C02	1.48	NTrA_C03	0.23
nC26	0.47	MN31	0.06	MA_C11	0.37	DA_C03	1.24	NTrA_C04	0.13
nC27	0.36	MN32	0.07	MA_C12	0.33	DA_C04	0.59	NTrA_C05	0.17
nC28	0.32	MN33	0.08	MA_C13	0.23	DA_C05	0.32	TeA_C00	0.09
nC29	0.25	DN_C11	12.82	MA_C14	0.25	DA_C06	0.29	TeA_C01	0.13
nC30	0.20	DN_C12	1.13	MA_C15	0.19	DA_C07	0.25	TeA_C02	0.18
nC31	0.18	DN_C13	1.00	MA_C16	0.16	DA_C08	0.20	TeA_C03	0.15
nC32	0.13	DN_C14	0.58	MA_C17	0.14	DA_C09	0.16	TeA_C04	0.42
nC33	0.12	DN_C15	0.49	MA_C18	0.10	DA_C10	0.12	PA_C00	0.10
nC34	0.12	DN_C16	0.39	MA_C19	0.12	DA_C11	0.10	PA_C01	0.16
nC35	0.11	DN_C17	0.38	MA_C20	0.10	DA_C12	0.07	PA_C02	0.12
nC36	0.13	DN_C18	0.37	MA_C21	0.09	DA_C13	0.07		
MN10	0.18	DN_C19	0.34	MA_C22	0.11	DA_C14	0.06		
MN11	0.29	DN_C20	0.33	MA_C23	0.14	DA_C15	0.86		
MN12	0.34	DN_C21	0.19	NMA_C00	1.63	NDA_C01	0.66		

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Professional Experience

Nov 2016 – Present
Research Engineer, SCHLUMBERGER
- Reaction kinetics and modeling
- Poly-axial stress frame analysis
- Core-flooding for carbonate cores (dolomite and calcite)

May 2015 – Oct 2016
Research Engineer Trainee, SCHLUMBERGER: **Rheological Properties of Waste Oil Emulsion**
- Apparent viscosity and viscoelastic properties of waste oil emulsion
- Stability of waste oil emulsion
- Core-flooding for carbonate cores (dolomite and calcite)

June - Sep 2014
Petroleum Engineer Trainee, HALLIBURTON: **HCl Emulsion for Stimulation**
- Emulsified HCl testing for stimulation purposes
- Study of factors affecting the stability of HCl emulsion

June - Aug 2012
Application Engineer Trainee, BAKER HUGHES: **Drilling Optimization**
- Risk assessment and management for Manifa Field drilling operations
- Finding and highlighting the major causes of Non-Productive Time during drilling for Manifa field
- Suggesting risk-reduced plan for future drilling in Manifa Field

Academic Background

I received a scholarship to do my bachelor's degree at KFUPM after graduating high school. I completed my bachelor's degree in petroleum engineering in May 2013. Immediately after graduation, I received another scholarship to pursue my master's degree in petroleum engineering at KFUPM which I completed in May 2016.

Patent

Development of Novel Emulsified Acid Using Waste Oil. Submitted to office of Innovation Center, KFUPM. November 2016.

Publications

Sidaoui, Z., Sultan, A. 2016. **Formulating a Stable Emulsified Acid at High Temperatures: Stability and Rheology Study**, IPTC-19012-MS presented at IPTC, Bangkok, Thailand, November 14 – November 16

Sidaoui, Z., Sultan, A., Qiu, X. 2016. **Viscoelastic Properties of Novel Emulsified Acid Using Waste Oil: Effect of Emulsifier Concentration, Mixing Speed and Temperature**, SPE-182845-MS presented at SPE Annual Technical Symposium and Exhibition, Khobar, Saudi Arabia, April 25-28

Sidaoui, Z., Sultan, A. 2016. **A Combined Rheology and Stability Study on Emulsified Acid for High Temperature Applications**, 2016 AIChE Spring Meeting and 12th Global Congress on Process Safety, Houston, Texas, USA, April 10 – April 14

Sidaoui, Z., Siddiqui, M. A.Q., Al-Dawood, J. 2014. **A Productive Technique to Do Drilling Analysis and Risk Assessment**, SPE-172168-MS presented at SPE Annual Technical Symposium and Exhibition, Khobar, Saudi Arabia, April 21-24