COMPARISON OF MICROWAVE-ASSISTED CHEMICALS IN DEMULSIFICATION OF WATER-IN-CRUDE OIL EMULSIONS

CHEW JUN JIAN

Report submitted in partial fulfillment of the requirements for the award of the

Degree of Bachelor of Chemical Engineering (Chemical)

Faculty of Chemical and Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

JANUARY 2012

UNIVERSITI MALAYSIA PAHANG

BORANG PENGESAHAN STATUS TESIS

F

JUDUI		COMPARISO	ON OF MICROW	AVE-ASSISTED CHEMICALS IN
	-	DEMULSIFIC	CATION OF WA	TER-IN-CRUDE OIL EMULSIONS
		SI	ESI PENGAJIAN	: <u>2011/2012</u>
Saya		CHEW JUN (HURUF BESA	JIAN R)	
mengaku Malaysia	membe Pahang	markan tesis (PS dengan syarat-sy	M/ Sarjana / Doktor I arat kegunaan seper	Calsafah)* ini disimpan di Perpustakaan Universiti ti berikut :
1. 2.	Tesis ad Perpusta	alah hakmilik Un Ikaan Universiti 1	iversiti Malaysia Pa Malaysia Pahang di	hang benarkan membuat salinan untuk tujuan pengajian
3.	Perpusta pengajia **Sila ta	ıkaan dibenarkan n tinggi. undakan (√)	membuat salinan	tesis ini sebagai bahan pertukaran antara institusi
1.		SULIT	(Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia seperti yang termaktub di dalam AKTA RAHSIA RASMI 1972)	
		TERHAD	(Mengandungi ma oleh organisasi/ba	klumat TERHAD yang telah ditentukan dan di mana penyelidikan dijalankan)
		TIDAK TERHA	D	Disahkan oleh
	(TAND	ATANGAN PEN	ULIS)	(TANDATANGAN PENYELIA)
Alamat T	etap:	C/O, 79 Jalan M	uar,	ASSOCIATE PROF.
	··· I , ,	83500 Parit Sulc	ong,	DR. ABDURAHMAN H. NOUR
		Batu Pahat , Johor Darul Tak	zim.	Nama Penyelia
Tarikh: .	January	2012		Tarikh: January 2012
CATATA	AN:	* Potong ya ** Jika te berkuasa/ dikelaska	ang tidak berkenaan. sis ini SULIT ata ⁄organisasiberkenaan de n sebagai SULIT atau T	u TERHAD , sila lampirkan surat daripada pihak ngan menyatakan sekali sebab dan tempoh tesis ini perlu ERHAD .
		 Tesis di penyelici Lapuran 	imaksudkan sebagai likan, atau disertasi ba Projek Sarjana Muda	tesis bagi Ijazah Doktor Falsafah dan Sarjana secara agi pengajian secara kerja kursus dan penyelidikan, atau (PSM).

SUPERVISOR'S DECLARATION

I hereby declare that I have checked this project and in my opinion, this project is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering (Chemical).

Signature	:	
Name of Supervisor	:	ASSOC. PROF. DR. ABDURAHMAN H. NOUR
Position	:	SENIOR LECTURER
Date	:	JANUARY 2012

STUDENT'S DECLARATION

I hereby declare that the work in this project is my own except for quotations and summaries which have been duly acknowledged. The project has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature:Name:CHEW JUN JIANID Number:KA 08099Date:JANUARY 2012

Special Dedication to my supervisor, my family members, my friends, my fellow colleague and all faculty members for all your care, support and believe in me.

ACKNOWLEDGEMENTS

I am grateful and would like to express my sincere gratitude to my supervisor Assoc. Prof. Dr. Abdurahman H. Nour for his germinal ideas, invaluable guidance, continuous encouragement and constant support in making this research possible. He has always impressed me with his outstanding professional conduct, his strong conviction for science, and his belief that a degree program is only a start of a life-long learning experience. I appreciate his consistent support from the first day I applied to Undergraduate Research Program (URP) to these concluding moments. I am truly grateful for his progressive vision about my training in science, his tolerance of my naïve mistakes, and his commitment to my future career.

My sincere thanks go to all my labmates and members of staff of the Faculty of Chemical and Natural Resources Engineering, who helped me in many ways and made my stay at UMP pleasant and unforgetables. I am very thankful for the facilities provided in the lab from University Malaysia Pahang (UMP) and to all the stuffs that ever helped me during my experimental works.

I acknowledge my sincere indebtedness and gratitude to my parents for their love, dream and sacrifice throughout my life. I acknowledge the sincerity of my parents, who consistently encouraged me to carry on my higher studies in Malaysia. I cannot find the appropriate words that could properly describe my appreciation for their devotion, support and faith in my ability to attain my goals. Special thanks should be given to my beloved fellow friends and course mates. I would like to acknowledge their comments and suggestions, which was crucial for the successful completion of this research of study. The completion of this writing shows how presence and patient my friends in making an effort to help me in succeeding this writing.

ABSTRACT

Demulsification (emulsion breaking or emulsions destabilizing) is important in many industry applications such as the petroleum industry, painting and waste-water treatment in environmental technology. Chemical and microwave heating demulsification is the most widely used method of demulsifying the water-in-crude oil emulsions and both methods accelerate the emulsion destabilizing process. This research combined the chemical with microwave-assisted to increase the efficiency of demulsification and reduce the chemical usage to prevent any environmental issues. The effect of chemical demulsification with microwave-assisted operations on the stability and properties of water-in-crude oil emulsions was assessed experimentally by using different types of demulsifiers which are Amine and Polymeric demulsifiers with microwave heating. By using the sample of water-in-crude oil emulsions which prepared by adding artificial emulsifiers (Span 83) which had formed the most stable emulsion after the complete screening of stability part was conducted, the chemical demulsifiers were added in the emulsions to break the emulsion with the assistant of microwave heating to increase the performance. The research found that Hexylamine and Cocoamine had the high efficiency of the demulsification with the assistant of microwave heating which was different from the conventional method but the latter was better as it was more environmental friendly. Overall results show that demulsification by microwave heating was faster as compared to the gravity sedimentation and it does not require much chemical additions to boost the breaking of the emulsion.

ABSTRAK

Demulsifikasi (pemecahan emulsi atau pentidakstabilan emulsi) adalah penting dalam banyak aplikasi industri, misalnya industri petroleum, lukisan dan rawatan air sisa dalam teknologi alam sekitar. Demulsifikasi dengan menggunakan kimia dan pemanasan dengan gelombang mikro adalah kaedah yang digunakan secara meluas dalam memecahkan emulsi air dalam minyak mentah dan kedua-dua kaedah ini dapat mempercepatkan proses pentidakstabilan emulsi. Kajian ini menggabungkan bahan kimia dengan pembantuan pemanasan gelombang mikro untuk meningkatkan kecekapan demulsifikasi dan mengurangkan penggunaan bahan kimia untuk mengurangkan mana-mana isu alam sekitar. Kesan operasi demulsifikasi kimia dengan bantuan gelombang mikro terhadap kestabilan dan sifat-sifat emulsi air dalam minyak mentah telah dinilai melalui uji kaji dengan menggunakan pelbagai jenis pendemulsi seperti pendemulsi Amine dan polimer dengan bantuan pemanasan gelombang mikro. Dengan menggunakan sampel emulsi air dalam minyak mentah yang disediakan dengan menambahkan pengemulsi tiruan atau buatan (SPAN 83) dimana ia membentuk emulsi yang paling stabil selepas proses pemerhatian lengkap dijalankan terhadap kestabilan emulsi. Selepas itu, pendemulsi kimia ditambah dalam emulsi untuk memecahkan emulsi dengan pembantuan pemanasan gelombang mikro untuk meningkatkan prestasi. Penyelidikan mendapati bahawa demulsifikasi kimia dengan pembantuan pemanasan gelombang mikro dengan mengunakan pendemulsifi Hexylamine dan Cocoamine mempunyai kecekapan yang paling tinggi dimana ia berbeza dari kaedah konvensional tetapi Cocoamine adalah lebih baik kerana ia adalah lebih mesra alam sekitar. Keputusan secara keseluruhan menunjukkan bahawa demulsifikasi kimia dengan bantuan pemanasan gelombang mikro adalah lebih cepat berbanding dengan pemendapan graviti dan tambahan lagi ia tidak memerlukan penambahan bahan kimia vang banyak untuk meningkatkan prestasi pemecahan emulsi.

TABLE OF CONTENTS

PAGE

7

SUP	PERVISOR'S DECLARATION	iv
STU	UDENT'S DECLARATION	V
ACH	KNOWLEDGEMENT	vii
ABS	STRACT	viii
ABS	STRAK	ix
TAE	BLE OF CONTENTS	X
LIS	T OF TABLES	XV
LIS	T OF FIGURES	xviii
LIS	T OF SYMBOLS	xxvi
LIS	T OF ABBREVIATIONS	xxix
CHA	APTER 1 INTRODUCTION	1
1.1	Background of Study	1
1.2	Significance of the Study	2
1.3	Problem Statement	3
1.4	Research Objectives	4

1.5	Scope of Research	4
1.6	Research Questions	6
1.7	Summary	6

CHAPTER 2 LITERATURE REVIEW

2.1	Introduction	7
2.2	Crude Oil Emulsion Composition	9
	2.2.1 Natural Emulsifiers (SARA)	9
	2.2.2 Asphaltenes	13
	2.2.3 Resins	19

	2.2.4 2.2.5	Waxes Solids	21 21
2.3	Crude	Oil Emulsion Formations and Stability	23
	2.3.1 2.3.2 2.3.3	Classification of Emulsions Emulsion Stability Colloid Rheology 2.3.3.1 Non-Newtonian Flow Properties 2.3.3.2 Pseudoplastic 2.3.3.3 Dilatancy 2.3.3.4 Plasticity/Pseudoplasticity with Yield Stress 2.3.5 Thixotropy 2.3.3.6 Rheopexy	23 26 27 27 29 30 30 30 30
2.4	Demu	lsification of Crude Oil Emulsion	32
	2.4.1 2.4.2 2.4.3	Demulsification (Destabilizing Or Breaking of Emulsion) Destabilizing Emulsions Demulsification Mechanisms	32 33 36
2.5	Chem	ical Demulsification of Crude Oil Emulsion	39
	2.5.1 2.5.2	Factors that affect Chemical Demulsification Types of Demulsifiers for Demulsification 2.5.2.1 Physical and Chemical Properties Of Demulsifiers 2.5.2.2 Hydrophilic Lipophilic Balance	39 40 41 43
2.6	Micro	wave Demulsification of Crude Oil Emulsion	45
	2.6.1 2.6.2	Theory of Microwave Heating 2.6.1.1 Dielectric Properties 2.6.1.2 Attenuation Factor 2.6.1.3 Volume Rate of Heat Generation 2.6.1.4 Temperature Increase Benefits of Microwave-Assisted Chemical Demulsification	45 45 46 47 52 53
2.7	Others	s Demulsification of Crude Oil Emulsion	55
	2.7.1 2.7.2	Ultrasonic Emulsion Separation Electrical Demulsification	55 56
2.8	Sumn	nary	59
CHA	PTER 3	B MATERIALS AND METHODS	60
3.1	Introd	uction	60
3.2	Prepa	ration of water-in-crude oil emulsions	61
	3.2.1	Type of Emulsifier	61

	3.2.2 3.2.3	Fluids and their physicochemical characteristics Characterization of emulsions 3.2.2.1 Microscopic analysis 3.2.2.2 Calorimetric analysis	62 62 63 64
3.3	Exper	imental Setup	65
	3.3.1 3.3.2 3.3.3 3.3.4	Apparatus Materials Equipment Experimental procedure 3.3.4.1 Flow Chart of the Experimental Procedure 3.3.4.2 Description of the Experimental Procedure	65 65 66 68 68 69
	3.3.5	Calculations 3.3.5.1 Calculations for Emulsion Preparation 3.3.5.2 Calculations for Demulsification Preparation 3.3.5.3 Detail Steps	70 70 71 72
3.4	Summ	nary	74
СНА	APTER 4	4 RESULTS AND DISCUSSIONS	75
4.1	Obser	vations	75
	4.1.1	Quantitative Observations 4.1.1.1 Emulsions of 50%-50% (w/o) 4.1.1.2 Emulsions of 30%-70% (w/o) 4.1.1.3 Demulsifications of 50%-50% (w/o) 4.1.1.4 Demulsifications of 30%-70% (w/o)	75 75 85 94 112
	4.1.2	Qualitative Observations 4.1.2.1 Observation 1 4.1.2.2 Observation 2 4.1.2.3 Observation 3 4.1.2.4 Observation 4 4.1.2.5 Observation 5 4.1.2.6 Observation 6 4.1.2.7 Observation 7 4.1.2.8 Observation 8 4.1.2.9 Observation 9	130 130 131 132 132 132 133 134 134 134
4.2	Result	ts	136
	4.2.1 4.2.2 4.2.3 4.2.4 4.2.5	Emulsion w/o (50%-50%) Emulsion w/o (30%-70%) Demulsification (50%-50%) Demulsification (30%-70%) Microwave Heating Properties	136 141 147 150 153

СНА	PTER 5	5 CONCLUSION AND RECOMMENDATIONS	230
4.4	Summ	hary	229
	4.3.4	Surface Tension and Interfacial Tension	229
		Pure Chemical and Microwave-Assisted Chemical for 30%-70% Emulsion	213
		Pure Chemical and Microwave-Assisted Chemical for 50%-50% Emulsion 4 3 3 2 Comparison of Percentage of Water Separation between	197
	4.3.3	Demulsification 4 3 3 1 Comparison of Percentage of Water Separation between	197
		4.3.2.8 Emulsion 30%-70% for Emulsifier 0.5v%	195
		4.3.2.7 Emulsion 50%-50% for Emulsifier 0.5v%	193
		4.3.2.6 Emulsion 30%-70% for Emulsifier 0.5v% RPM 1500	191
		4.3.2.5 Emulsion 30%-70% for Emulsifier 0.3v% RPM 1500	189
		4 3 2 4 Emulsion 30%-70% for Emulsifier 0 1v% RPM 1500	187
		4 3 2 3 Emulsion 50%-50% for Emulsifier 0.5v% RPM 1500	185
		4.3.2.1 Emulsion 50%-50% for Emulsifier 0.3v% RPM 1500	101
	4.3.2	Emulsion Gravitational Stability Test	101
	422	4.3.1.10 Discussion on Shear Stress versus Shear Rate	1/9 101
		4.3.1.9 Shear Stress versus Shear Rate	177
		4.3.1.8 Discussion on Viscosity versus Shear Rate	175
		4.3.1.7 Viscosity versus Shear Rate	174
		(Brookfield)	171
		4.3.1.5 Viscosity versus Agitation Speed (Brookheid)	168
		4.3.1.4 Discussion on Viscosity versus Concentration of Emulsifie	16/
		4.3.1.3 Viscosity versus Concentration of Emulsifier	163
		4.3.1.2 Discussion on Viscosity versus Temperature	160
		4.3.1.1 Viscosity versus Temperature	156
	4.3.1	Brookfield Analysis	156
4.3	Data A	Analysis	156
		4.2.6.3 Surface Tension 30%-70% 4.2.6.4 Interfacial Tension 30%-70%	155 156
		4.2.6.2 Interfacial Tension 50%-50%	155
		4.2.6.1 Surface Tension 50%-50%	155
	4.2.6	Surface Tension and Interfacial Tension	155
		4.2.5.2 Microwave-Assisted Chemical Demulsification 30%-70%	154
		4.2.3.1 MICIOWAVC-ASSISTED CHEMICAL DEMUISINGATION 50/0-50/0	155

	5.1.1	Introduction	230
	5.1.2	Stabilization/Emulsification	231
	5.1.3	Destabilization/Demulsification	232
	5.1.4	Summary	233
5.2	Recon	nmendations	234
	5.2.1	Introduction	234
	5.2.2	Stabilization/Emulsification	235
	5.2.3	Destabilization/Demulsification	238
	5.2.4	Summary	240
REFE	RENC	ES	242

APPENDIX

248

LIST OF TABLES

Table No.	Title	Page
2.1	SARA fractionation of Malaysian crude oil Source: Ariany (2001)	12
2.2	Physical properties of Malaysian crude oils Source: Ariany (2001)	12
2.3	The Chemical demulsifiers used in demulsification tests Source: Abdurahman, H. N. et al (2007)	40
2.4	Selected HLB Group Numbers Source: Adopt from Mc Clements (2005)	44
2.5	Comparison Of Functional Attributes Of Different General Classes Of Emulsifiers Source: Adopt from Mc Clements (2005)	45
3.1	The Artificial emulsifiers used in emulsions	61
3.2	The Chemical demulsifiers used in demulsification tests Source: Suggested from Abdurahman, H. N. et al (2007)	66
3.3	Information of Calculations for Emulsion Preparation	70
3.4	Information of Calculations for Demulsification Preparatio	71
4.1	Observation of w/o Emulsion (50%-50%)	75
4.2	Observation of w/o Emulsion (30%-70%)	85
4.3	Observation of w/o Demulsification of Pure Chemical	94
4.4	Observation of w/o Demulsification of Microwave-Assisted Chemical	103
4.5	Observation of w/o Demulsification of Pure Chemical	112
4.6	Observation of w/o Demulsification of Microwave-Assisted Chemical	121
4.7	Water separation, v/v % of 0.1 v% of Emulsifiers on 50-50% w/o emulsion stability at different mixing speed	136

4.8	Water separation, v/v % of 0.3 v% of Emulsifiers on 50-50% w/o emulsion stability at different mixing speed	136
4.9	Water separation, v/v % of 0.5 v% of Emulsifiers on 50-50% w/o emulsion stability at different mixing speed	137
4.10	Brookfield Test (Emulsion50%-50%)	138
4.11	Emulsion Stability Test(Emulsion50%-50%)	139
4.12	Droplet Size(Emulsion50%-50%)	140
4.13	Droplet Size Distribution(Emulsion50%-50%)	140
4.14	Water separation, v/v % of 0.1 v% of Emulsifiers on 30-70% w/o emulsion stability at different mixing speed	141
4.15	Water separation, v/v % of 0.3 v% of Emulsifiers on 30-70% w/o emulsion stability at different mixing speed	142
4.16	Water separation, v/v % of 0.5 v% of Emulsifiers on 30-70% w/o emulsion stability at different mixing speed	142
4.17	Brookfield Test(Emulsion30%-70%)	143
4.18	Emulsion Stability Test(Emulsion30%-70%)	144
4.19	Droplet Size Distribution(Emulsion30%-70%)	145
4.20	Droplet Size Distribution(Emulsion30%-70%)	146
4.21	Water separation, v/v % of 0.1 v% of Pure Demulsifiers on 50-50% w/o emulsion stability at different mixing speed	147
4.22	Water separation, v/v % of 0.1 v% of Microwave-Assisted Demulsifiers on 50-50% w/o emulsion stability at different mixing speed	147
4.23	Water separation, v/v % of 0.3 v% of Pure Demulsifiers on 50-50% w/o emulsion stability at different mixing speed	148
4.24	Water separation, v/v % of 0.3 v% of Microwave-Assisted Demulsifiers on 50-50% w/o emulsion stability at different mixing speed	148
4.25	Water separation, v/v % of 0.5 v% of Pure Demulsifiers on	

	50-50% w/o emulsion stability at different mixing speed	149
4.26	Water separation, v/v % of 0.5 v% of Microwave-Assisted Demulsifiers on 50-50% w/o emulsion stability at different mixing speed	149
4.27	Water separation, v/v % of 0.1 v% of Pure Demulsifiers on $30-70\%$ w/o emulsion stability at different mixing speed	150
4.28	Water separation, v/v % of 0.1 v% of Microwave-Assisted Demulsifiers on 30-70% w/o emulsion stability at different mixing speed	150
4.29	Water separation, v/v % of 0.3 v% of Pure Demulsifiers on $30-70\%$ w/o emulsion stability at different mixing speed	151
4.30	Water separation, v/v % of 0.3 v% of Microwave-Assisted Demulsifiers on 30-70% w/o emulsion stability at different mixing speed	151
4.31	Water separation, v/v % of 0.5 v% of Pure Demulsifiers on 30-70% w/o emulsion stability at different mixing speed	152
4.32	Water separation, v/v % of 0.5 v% of Microwave-Assisted Demulsifiers on 30-70% w/o emulsion stability at different mixing speed	152
4.33	Microwaves-Assisted Chemical Demulsification 50%-50% Properties for 0.3v% Hexylamine at RPM 500	153
4.34	Microwave-Assisted Chemical Demulsification 30%-70% Properties for 0.3v% Cocoamine at RPM 1000	154
4.35	Surface Tension of Water and Air and Oil and Air	155
4.36	Interfacial Tension of Water and Oil	155
4.37	Surface Tension of Water and Air and Oil and Air	155
4.38	Interfacial Tension of Water and Oil	156
4.39	Emulsion 50%-50% for Emulsifier of RPM 1500 at Ambient Temperature	172
4.40	Emulsion 30%-70% for Emulsifier of RPM 1500 at Ambient Temperature	173

LIST OF FIGURES

Figure No.	Title				
2.1	Photomicrograph of a w/o Emulsion				
2.2	Schematic of SARA fractionation of crude oils Source: Auflem (2002)				
2.3	Permission Hypothetical structure of a petroleum asphaltene Source: Speight and Moschopedis (1981)				
2.4	3D representation of a Venezuelan asphaltene molecule Source: Courtesy of J. Murgich and A. Mansoori				
2.5	"Long diagram" shows that the asphaltenes include the crude oil material highest in molecular weight, polarity, and/or aromaticity Source: After Long (1981)	15			
2.6	Examples of the appearance (magnified about 15 times) of asphaltenes separated fromMars-P crude oil with an excess of (a) n pentane (n-C5) and (b) n-heptane (n-C7)	16			
2.7	Asphaltene-resin micelle	16			
2.8	Schematic of a surfactant molecule and formation of micelles				
2.9	Mechanism of emulsion stabilization by asphaltenes	18			
2.10	Hypothetical representation of an average resin molecule Source: Gafonova (2000)	20			
2.11	Photomicrograph of an o/w emulsion	24			
2.12	Photomicrograph of a w/o/w emulsion	25			
2.13	Typical flow curves of shear stress versus shear rate. Source: Adopted from Schramm (2005)	28			
2.14	Typical curves of viscosity versus shear rate. Source: Adopted from Schramm (2005)				
2.15	Illustration of time-dependent types of rheological behavior Source: Adopted from Schramm (2005)	31			

2.16	Creaming, Sedimentation, Flocculation, Coalescence Source: Mc Clement (2005)	37
2.17	The level of demulsification process of water in oil Emulsion (Separation of water from water in oil emulsion by gravity force) Source: Hanapi et al (2006)	38
2.18	Basic structure of demulsifier Source: Porter (1994)	41
2.19	Multiple Pass Propagation and Absorption of Microwaves within Emulsion Source: Adopted from Fang and Lai (1995)	48
2.20	The desalting system employed in petroleum refineries Source: Antonio (2010)	58
2.21	Discharge of the emulsion between the electrodes and forces that act upon the droplets Source: Antonio (2010)	59
3.1	Digital photograph of a sample of water-in-crude oil emulsion taken with an optical microscope optical microscope with increase of $10 \times (a) 50\%$ -50% and (b) 30%-70%	63
3.2	Flow Chart of the Experimental Procedure	68
4.1	Droplet Size Distribution(Emulsion50%-50%)	141
4.2	Droplet Size Distribution(Emulsion30%-70%)	146
4.3	Viscosity Versus Temperature at RPM 100 (Brookfield)	156
4.4	Viscosity Versus Temperature at RPM 150 (Brookfield)	157
4.5	Viscosity Versus Temperature at RPM 200 (Brookfield)	157
4.6	Viscosity Versus Temperature at RPM 250 (Brookfield)	158
4.7	Viscosity Versus Temperature at RPM 100 (Brookfield)	158
4.8	Viscosity Versus Temperature at RPM 150 (Brookfield)	159
4.9 4.10	Viscosity Versus Temperature at RPM 200 (Brookfield) Viscosity Versus Temperature at RPM 250 (Brookfield)	159 160

4.11	Viscosity Versus Concentration of Emulsifier at RPM 100 (Brookfield)	163
4.12	Viscosity Versus Concentration of Emulsifier at RPM 150 (Brookfield)	163
4.13	Viscosity Versus Concentration of Emulsifier at RPM 200 (Brookfield)	164
4.14	Viscosity Versus Concentration of Emulsifier at RPM 250 (Brookfield)	164
4.15	Viscosity Versus Concentration of Emulsifier at RPM 100 (Brookfield)	165
4.16	Viscosity Versus Concentration of Emulsifier at RPM 150 (Brookfield)	165
4.17	Viscosity Versus Concentration of Emulsifier at RPM 200 (Brookfield)	166
4.18	Viscosity Versus Concentration of Emulsifier at RPM 250 (Brookfield)	166
4.19	Viscosity Versus Agitation Speed of 0.1v% at Ambient $\$ Temperature	168
4.20	Viscosity Versus Agitation Speed of 0.3v% at Ambient Temperature	168
4.21	Viscosity Versus Agitation Speed of 0.5v% at Ambient Temperature	169
4.22	Viscosity Versus Agitation Speed of 0.1v% at Ambient Temperature	169
4.23	Viscosity Versus Agitation Speed of 0.3v% at Ambient Temperature	170
4.24	Viscosity Versus Agitation Speed of 0.5v% at Ambient Temperature	170
4.25	Viscosity Versus Shear Rate at Ambient Temperature	174
4.26	Viscosity Versus Shear Rate at Ambient Temperature	174

4.27	Pseudoplastic behavior portrays as Viscosity versus Shear Rate Source: Adopted from Scott Bader	176		
4.28	Dilatancy behavior portrays as Viscosity versus Shear Rate Source: Adopted from Scott Bader			
4.29	Shear Stress Versus Shear Rate compare with Newtonian at Ambient Temperature	177		
4.30	Shear Stress Versus Shear Rate without compare with Newtonian at Ambient Temperature	178		
4.31	Shear Stress Versus Shear Rate compare with Newtonian at Ambient Temperature	178		
4.32	Shear Stress Versus Shear Rate without compare with Newtonian at Ambient Temperature	179		
4.33	Pseudoplastic behavior portrays as Shear Stress versus Shear Rate Source: Adopted from Scott Bader	180		
4.34	Percentage of Water Separation versus Time	181		
4.35	Percentage of Oil Separation versus Time	181		
4.36	Percentage of Water Separation versus Time	183		
4.37	Percentage of Oil Separation versus Time	183		
4.38	Percentage of Water Separation versus Time	185		
4.39	Percentage of Oil Separation versus Time	185		
4.40	Percentage of Water Separation versus Time	187		
4.41	Percentage of Oil Separation versus Time	188		
4.42	Percentage of Water Separation versus Time	189		
4.43	Percentage of Oil Separation versus Time	190		
4.44	Percentage of Water Separation versus Time	191		
4.45 4.46	Percentage of Oil Separation versus Time Percentage of Water Separation versus Agitation Speed	192		

	after 2 days	193
4.47	Percentage of Oil Separation versus Agitation Speed after 2 days	194
4.48	Percentage of Water Separation versus Agitation Speed after 2 days	195
4.49	Percentage of Oil Separation versus Agitation Speed after 2 days	196
4.50	Percentage of Water Separation versus Time with 0.1v% Pure Demulsifier	197
4.51	Percentage of Oil Separation versus Time with 0.1v% Pure Demulsifier	198
4.52	Percentage of Water Separation versus Time with 0.1v% Microwave assisted Demulsifier	198
4.53	Percentage of Oil Separation versus Time with 0.1v% Microwave Assisted Demulsifier	199
4.54	Percentage of Water Separation versus Time with 0.3v% Pure Demulsifier	200
4.55	Percentage of Oil Separation versus Time with 0.3v% Pure Demulsifier	201
4.56	Percentage of Water Separation versus Time with 0.3v% Microwave Assisted Demulsifier	201
4.57	Percentage of Oil Separation versus Time with 0.3v% Microwave Assisted Demulsifier	202
4.58	Percentage of Water Separation versus Time with 0.5v% Pure Demulsifier	203
4.59	Percentage of Oil Separation versus Time with 0.5v% Pure Demulsifier	204
4.60	Percentage of Water Separation versus Time with 0.5v% Microwave Assisted Demulsifier	204
4.61	Percentage of Oil Separation versus Time with 0.5v% Microwave Assisted Demulsifier	205
4.62	Percentage of Water Separation versus Time with Pure	

	Demulsifier at RPM 500	206
4.63	Percentage of Oil Separation versus Time with Pure Demulsifier at RPM 500	206
4.64	Percentage of Water Separation versus Time with Microwave Assisted Demulsifier at RPM 500	207
4.65	Percentage of Oil Separation versus Time with Microwave Assisted Demulsifier at RPM 500	207
4.66	Percentage of Water Separation versus Time with Pure Demulsifier at RPM 1000	208
4.67	Percentage of Oil Separation versus Time with Pure Demulsifier at RPM 1000	209
4.68	Percentage of Water Separation versus Time with Microwave Assisted Demulsifier at RPM 1000	209
4.69	Percentage of Oil Separation versus Time with Microwave Assisted Demulsifier at RPM 1000	210
4.70	Percentage of Water Separation versus Time with Pure Demulsifier at RPM 1500	211
4.71	Percentage of Oil Separation versus Time with Pure Demulsifier at RPM 1500	211
4.72	Percentage of Water Separation versus Time with Microwave Assisted Demulsifier at RPM 1500	212
4.73	Percentage of Oil Separation versus Time with Microwave Assisted Demulsifier at RPM 1500	212
4.74	Percentage of Water Separation versus Time with 0.1v% Pure Demulsifier	213
4.75	Percentage of Oil Separation versus Time with 0.1v% Pure Demulsifier	214
4.76	Percentage of Water Separation versus Time with 0.1v% Microwave Assisted Demulsifier	214
4.77	Percentage of Oil Separation versus Time with 0.1v% Microwave Assisted Demulsifier	215

xxiv

4.78	Percentage of Water Separation versus Time with 0.3v% Pure Demulsifier	216
4.79	Percentage of Oil Separation versus Time with 0.3v% Pure Demulsifier	216
4.80	Percentage of Water Separation versus Time with 0.3v% Microwave Assisted Demulsifier	217
4.81	Percentage of Oil Separation versus Time with 0.3v% Microwave Assisted Demulsifier	217
4.82	Percentage of Water Separation versus Time with 0.5v% Pure Demulsifier	218
4.83	Percentage of Oil Separation versus Time with 0.5v% Pure Demulsifier	219
4.84	Percentage of Water Separation versus Time with 0.5v% Microwave Assisted Demulsifier	219
4.85	Percentage of Oil Separation versus Time with 0.5v% Microwave Assisted Demulsifier	220
4.86	Percentage of Water Separation versus Time with Pure Demulsifier at RPM 500	221
4.87	Percentage of Oil Separation versus Time with Pure Demulsifier at RPM 500	221
4.88	Percentage of Water Separation versus Time with Microwave Assisted Demulsifier at RPM 500	222
4.89	Percentage of Oil Separation versus Time with Microwave Assisted Demulsifier at RPM 500	222
4.90	Percentage of Water Separation versus Time with Pure Demulsifier at RPM 1000	223
4.91	Percentage of Oil Separation versus Time with Pure Demulsifier at RPM 1000	224
4.92	Percentage of Water Separation versus Time with Microwave Assisted Demulsifier at RPM 1000	224
4.93	Percentage of Oil Separation versus Time with	

	Microwave Assisted Demulsifier at RPM 1000	225
4.94	Percentage of Water Separation versus Time with Pure Demulsifier at RPM 1500	226
4.95	Percentage of Oil Separation versus Time with Pure Demulsifier at RPM 1500	227
4.96	Percentage of Water Separation versus Time with Microwave Assisted Demulsifier at RPM 1500	227
4.97	Percentage of Oil Separation versus Time with Microwave Assisted Demulsifier at RPM 1500	228

LIST OF SYMBOLS

HLB	-	Hydrophile-Lipophile Balance		
Σ	-	Summation		
$arepsilon_{r,w}^{'}$	-	Dielectric constant of water		
$arepsilon_{r,w}^{''}$	-	Dielectric loss of water		
$arepsilon_{r,o}^{'}$	-	Dielectric constant of crude oil		
$ an \delta_o$	-	Loss tangent of crude oil		
$q_{MW,z}$	-	The volume rate of heat generation		
P _(z)	-	Local time-average microwave power flux at the surface of container (watts/cm ²)		
m	-	Mass (g) of the sample		
А	-	Sample container's area		
P _(o)	-	Microwave power flux at z=0 (watts/cm ²)		
$lpha_E$	-	Attenuation factor		
f_o	-	Frequency of incident microwave		
c	-	Electromagnetic wave velocity = speed of light		
Z	-	Pathlength (R-r)		
R	-	Radius of sample container, cm		
r	-	Radial coordinate, cm		
$q_{MW,(n)}$	-	The volume rate of heat generation by the n-th forward and reflected passes		
$\pi R^2 H$	-	The volume of irradiated emulsion.		
Н	-	Height of container, cm		

h	-	Convective heat transfer coefficient, cal/s.cm ² .°C
А	-	Convective heat transfer area, cm ²
V	-	Volume of irradiated emulsion, cm ³
T _m	-	Temperature of emulsion, °C
T _a	-	Ambient Temperature, °C
3	-	emissivity of surface
σ	-	Stefan-Boltzmann constant= $5.672 \times 10^{-8} \text{ W/m}^2$.K ⁴
ρ	-	Density of emulsion, g/cm ³
C _p	-	Heat capacity at constant pressure, cal/g.°C
$\frac{dT}{dt}$	-	Rate of temperature increase in °C/s
$ ho_m$	-	Density of emulsion, g/cm ³
$ ho_w$	-	Density of water, g/cm ³
ρ_{o}	-	Density of crude oil, g/cm ³
$C_{p,m}$	-	Heat capacity of emulsion, cal/g.ºC
$C_{p,w}$	-	Heat capacity of water, cal/g.ºC
C _{p,o}	-	Heat capacity of crude oil, cal/g.°C
Φ	-	Volume fraction of emulsified water
D _P	-	Penetration depth, within a sample for a
λ_{m}	-	Wavelength
q _{мw}	-	Average volume rate of heat generation induced by microwaves, cal/s.cm ³
$q_{\rm MW,w}$	-	Water volume rate of heat generation induced by microwaves, cal/s.cm ³
q _{MW,o}	-	Crude oil volume rate of heat generation induced

by microwaves, cal/s.cm³

% water separation	-	Percentage of water separation
V	-	Volume of water layer (mL)
V ₀	-	Original amount of water (mL)
υ	-	Settling velocity of the water droplets
D	-	Diameter of droplets
G	-	Acceleration caused by of gravity
μ	-	Oil viscosity

LIST OF ABBREVIATIONS

w/o	-	water-in-crude oil
o/w	-	crude oil-in-water
w/o/w	-	water-in-crude oil-in-water
DC	-	Direct Current
AC	-	Alternating Current
Triton-X-100	-	Octyl phenol ethoxylate
Span 80/83	-	Sorbitan monooleate
Tween 20/80	-	Polyorbates
SDDS	-	Sodium Dodecyl Sulfide
Cocamide DEA	-	Cocamide Diethanolamine
BS&W	-	Basic Sediment and Water
HLB	-	Hydrophile-Lipophile Balance
H/C	-	Hydrogen/Carbon
AFM	-	Atomic Force Microscopy
PIT	-	Phase Inversion Temperature
PEG-600	-	Polyethylene glycol 600

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

From the era of globalization, the demands of crude oil in the world increases sharply but the resources are limited. In addition, the crude oil obtained from deep sea is normally emulsified with the water which decreases the quality and quantity of the crude oil in the process. Crude oil is composed of mostly hydrocarbons, both aliphatic and aromatic, as well as some molecules that naturally occurring surfactants in crude oil (asphaltenses and resins) have been identified as largely responsible for the stability of these emulsions. An emulsion may be tight (difficult to break) or loose (easy to break), whether an emulsion is tight or loose depends on a number of factors such as the percentages of oil and water found in the emulsion, the amount of agitation, the types and amounts of emulsifying agents present, as well as the properties of oil and water (Ali and Algam, 2000) (in Abdurahman and Rosli, 2006)

Demulsification is introduced which is to break the emulsion water-in-crude oil (w/o). Demulsification is very essential industrial process which is to remove the water in the crude oil which to improve the quality and quantity of the crude oil that need to be commercialized. There are many techniques which have been used as to demulsify the water-in-crude oil emulsions. For instances, chemical demulsifier, microwave heating, electrostatic demulsification, centrifugation technique, sedimentation technique and many on.

Based on the previous research, chemical demulsifier is the widely used method to demulsify the emulsion and the efficiency is considered quite high. Moreover, chemical demulsifier is easier to obtain but it will create another environmental issues. The w/o emulsions is normally has low Hydrophile-Lipophile Balance (HLB) number which has high affinity to the oil or it can be refer as lipophilic or hydrophobic. Hence, water soluble chemical demulsifiers are frequently used to demulsify the w/o emulsions. These emulsion are moderate (2000-50,000) molecular weight, polydispersed interfacially active polymers. The method of production of oil soluble demulsifiers in most cases involves handling of dangerous chemicals like ethylene and propylene oxide. It would be highly desirable to have demulsifier that are water soluble but as effective as their oil soluble counterpart (Bhattacharyya, 1992) with the ability to reduce the environment problems.

Furthermore, microwave heating also another technique that is widely used and it comes out as alternative to solve for the chemical demulsifier's environmental issues. Microwave heating is more economical and the device is available and is easily obtained. Besides, the procedures are users friendly and heating is more rapidly and uniformly (Abdurahman, Rosli, and Azhary, 2010) compares with conventional heating. The theory of microwave demulsification was first introduced by Klaila (1983) and Wolf (1986) in their patent applications. Chih and Yeong (2002), Fang *et al.* (1989) and Fang and Lai (1995) reported demulsification of w/o emulsions by microwave radiation. **(in Abdurahman, Rosli and Anwaruddin, 2006)**

1.2 SIGNIFICANCE OF THE STUDY

The world nowadays concern is to save planet from any pollution, therefore in the application of chemical with microwave-assisted, the environmental problems can be decreased in a significant way as in this method, the usage of pure chemical is reduced with the help of microwave and at the same time it can maximize the efficiency. In addition, the pure chemical used is designed or planned to be environmental friendly, this can definitely help to minimize the environmental problems while increases the production of pure crude oil to meet the high demand in market.

Furthermore, the application of chemical with microwave-assisted can also reduce the operational cost and production cost. This is because the water in the crude oil which will provoke the corrosion of the pipe is extracted. The usage of pipeline is minimize, the cost of operational or maintenance can also be decreased. Besides, the efficiency is high by using this method which can increase the production and reduces the production cost as there is unnecessary to demulsify w/o in multi-stages to separate them.

1.3 PROBLEM STATEMENT

In the need of crude oil in the world basis, emulsions are completely undesirable because the volume of dispersed water occupies space in the processing equipment and pipelines, increased operating and capital costs. Moreover, the characteristics and physical properties of oil change notably upon emulsification. The density of emulsion can increase from 800 kg/m³ for the original oil to 1030 kg/m³ for the emulsion. The most significant change is observed in viscosity, which typically increases from a few mPa·s or less to about 1000 mPa·s (Fingas et al., 1993). **(In Hanapi et al, 2006)**

Other than that, the existence of the water in the crude oil will cause a lot of undesirable problem such as it can interfere with refining operations, provoke corrosions, increase heat capacity and reduce the handling capacity of refining equipments and pipelines (Selvarajan et al., 2001). The water in the crude oil is provoking corrosions in pipeline in water as there is carbon dioxide (CO₂) in the water. The CO₂ in the water will react with water to form carbonic acid H_2CO_3 . H_2CO_3 is acidic and will react with the pipeline and in a long run the pipe will become rust and it cost million of money to repair the pipeline. At the same time, it causes operational problems as the rust will contaminate the crude oil and require another separation process to treat the contaminated crude oil. These increases the cost of the production of

pure crude oil and it is not economically. Hence demulsification is very important to be applied to avoid the corrosion and to minimize the usage of the pipeline by removing the water in the crude oil.

Besides, the coproduction of the water with crude oil may give rise of the expense of pumping or transporting water via pipeline or tanker; the corrosion of pumps, production equipment and downstream overhead distillates columns and poisoning of downstream refinery catalysts. These will increase the operating cost which is the biggest problem facing by oil industries.

1.4 RESEARCH OBJECTIVES

- 1. To investigate the emulsion stabilization and destabilization of w/o emulsions by microwave-assisted chemical method
- 2. To compare the performance of microwave-assisted chemical method with conventional method for w/o emulsion demulsification.
- 3. To find environmentally friendly chemicals for crude oils emulsion breaking.
- To investigate overall performance of microwave-assisted chemicals for w/o emulsions demulsification.

1.5 SCOPE OF RESEARCH

- 1. Characterization of emulsions in terms of physical and chemical properties.
- 2. To examine the demulsification of w/o emulsions by chemical method.
- 3. To examine the demulsification of w/o emulsion by microwave-assisted chemical.
- 4. Comparison of the performance of microwave-assisted chemical method with conventional method for w/o emulsion demulsification.

The first scopes of research is Characterization of emulsions in terms of physical

and chemical properties. We need to investigate the physical and chemical properties is because we need to identify the natural emulsifiers which exist in the w/o emulsions. This natural emulsifiers are the main concern which cause the w/o emulsions to be very stable and create problem to destabilizing them. We do not need any water in the crude oil as it will generate many operational and production problem which will affect the cost of pure crude oil.

The second scope is to examine the demulsification of w/o emulsions by chemical method. This is the main method that will be implemented in this research to demulsify the w/o emulsion by using a more environmental friendly, economic competitive, and biological degradable chemicals which will minimize the environmental issues which is the main concern in nowadays world.

The third scope is to examine the demulsification of w/o emulsion by microwave-assisted chemical. This is the combination method that will be implemented in this research to demulsify the w/o emulsion as by using chemicals are already very efficient in destabilizing the w/o emulsions, then with microwave-assisted there will be a high performance of the demulsification process. This is because with microwave-assisted chemical demulsification, the process will be accelerated which will increase the efficiency of the destabilizing process.

The final scope of research is comparison of the performance of microwaveassisted chemical method with conventional method for w/o emulsion demulsification. Through this research, it is desired to observe whether the microwave-assisted chemicals for w/o emulsions demulsification will up to the desired performance that it wish to be. This is because in this research, there should be high performance as with both conventional methods which are pure chemicals and pure microwave heating only for w/o emulsions demulsification, the efficiency is considered high. Hence, it is necessary to compare the overall performance, so that it would be helpful and practical to produce a big amount of pure crude oil in the limited time to meet the high demand from the market.

1.6 RESEARCH QUESTIONS

- 1. How to investigate the emulsion stabilization and destabilization of w/o emulsions by microwave-assisted chemical method
- Why do we have to compare the performance of microwave-assisted chemical method with conventional method for w/o emulsion demulsification.
- Why do we have to find environmentally friendly chemicals for crude oils emulsion breaking.
- How to investigate overall performance of microwave-assisted chemicals for w/o emulsions demulsification.

1.7 SUMMARY

In a nutshell, the demulsification of the w/o emulsions is very crucial in high demand market of the crude oil. Hence, to increase the amount of pure crude oil, the method chosen to maximize the efficiency of the demulsification is the main keys to meet the demand. Procedure to choose the most suitable methods is essential so as to increase production while reducing the cost of production. Therefore, understanding of each method is very important to avoid any failure of the research which is time wasted. Finally, detail information of the method chosen will be discussed deeply in the next chapter which is Literature Review.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

In the production of the crude oil from the reservoir rock; bottom hole perforations/pump, crude oil is seldom produced alone because it generally is commingled with water. The water creates several problems and usually increases the unit cost of oil production as the water which contains carbon dioxide, CO₂ will cause corrosion of the pipeline and maximize the usage of pipeline and it requires frequently maintenance. In addition, the corrosion caused by the water will also contaminate the crude oil, extra treatment of the crude oil is needed and it increases the cost of operation and directly increases the cost of production. Therefore, the produced water must be separated from the oil, treated, and disposed of properly. All these steps increase costs.

Produced water may be produced as "free" water (i.e., water that will settle out fairly and rapidly), and it may be produced in the form of an emulsion. A regular oilfield emulsion is water droplets dispersion in oil. Emulsions can be difficult to treat and may cause several operational problems in wet-crude handling facilities and gas/oil separating plants. Emulsions can create high-pressure drops in flow lines, lead to an increase in demulsifier use, and sometimes cause trips or upsets in wet-crude handling facilities. The problem is usually at its worst during the winter because of lower surface temperatures. These emulsions must be treated to remove the dispersed water and associated inorganic salts to meet crude specifications for transportation, storage, and export and to reduce corrosion and catalyst poisoning in downstream processing facilities (Kokal and Aramco, 2006). Catalyst poisoning will increase the cost as the catalyst needed to be replace and it cannot be reactivated or regenerated to reuse again. This is due to the catalyst is contaminated and cannot function properly.



Figure 2.1: Photomicrograph of a w/o Emulsion

Crude oil is a complex fluid that containing asphaltenes, resins and napthenic acid which exist as natural emulsifiers. They influence the stability of the w/o emulsions and make it an obstacle to demulsify the w/o emulsions. As mentioned, asphaltenes is the heaviest and most polar fraction in the crude oil and responsible in rising up the variety of nuisances and stabilized the water in oil emulsion that occurred during crude oil production. It is widely known that deposition and flocculation of asphaltenes may be occurred when the thermodynamic equilibrium is disturbed (Auflem, 2002). The ratio of the asphaltenes and resins which are the natural emulsifiers in crude oil which cause the w/o emulsions to occur will affect the degree of demulsification. The ratio of asphaltenes to resins should not be exceed much as it will cause a lot of demulsifiers usage needed to demulsify the w/o emulsions.

Emulsion problems in crude oil productions resulted by a demand for expensive emulsion separation equipment such as water treaters, separators and coalescers. Hence,
chemical with microwave assisted demulsification is the suitable method from both operational and economic point of view to break the crude oil emulsion. A chemical agent typically acts on the interfacial film by either reacting chemically with the polar crude oil components or by modifying the environment of the demulsification. Among chemical agents, interfacial-active demulsifiers, which weaken the stabilizing films to enhance droplets coalescence, are preferred due to lower additions rates needed (Hanapi et al, 2006). Microwave is act as a 'motivater' which to increase the efficiency of chemical demulsification and in the same time reduce the usage of the chemical which will help reduce the problems of environmental issues. This is due to normally in nature inappropriate waste treatment of the chemical will be taken by factory to make their work uncomplicated and reduce the cost which is indeed irresponsible acts.

2.2 CRUDE OIL EMULSION COMPOSITION

2.2.1 Natural Emulsifiers (SARA)

In nature, the crude oil produced is always accompany by the water which wellmixed together and the emulsions is very stable that need demulsifiers to separate them. The stability of the emulsion is due to the composition of natural emulsifiers co-exist with the w/o and make the impossible to break without addition of demulsifiers. Since some of these substances contain ionizable groups, the water-phase pH can be expected to affect their ionization in the interfacial films, producing radical changes of the physical properties of the films and also the solubility of some polar organic compounds toward the water phase (Kokal, 2005) (in Fortuny, M. et al, 2007). The natural emulsifiers are saturates (including waxes), aromatics, resins and asphaltenes are called SARA fractionation.

The basis method to eliminate asphaltenes is by precipitation in paraffinic solvent such as n-pentane. Chromatographic fractionation method is used to separate the deasphalted oil into saturates, aromatics and resins (Aske et al., 2001). From the four classes of compounds, only the saturated is easily discernible from the rest of the

hydrocarbons in the mixture. This is because of the absence of π -bonds, which allows them to be readily differentiated from the aromatic components by asset of the difference in their polarity. The balance of the oil is contained aromatics and heteroatomic compounds of varying degree of functionalism, alkyl substitution and condensation.

However, the asphaltene content of petroleum is an important aspect of fluid process ability and the ratio of asphaltene and resins in the crude oil also play an important role in the stability of the w/o emulsions. Hence, both compounds will be discussed detail in the following sections.



Figure 2.2: Schematic of SARA fractionation of crude oils

Source: Auflem (2002)

Types of	SARA Fractionation			
Malaysian Crude Oil	Asphaltenes (wt%)	Resins (wt%)	Aromatics (wt%)	Saturates (wt%)
Semangkok	1.31	35.32	17.43	70.62
Tabu	1.23	36.43	15.46	81.59
Irong Barat	0.37	32.01	45.95	45.63
Seligi	0.32	20.94	16.18	80.47
Tapis	0.11	29.81	18.14	77.51
Guntung	0.45	21.50	20.74	75.42

Table 2.1: SARA fractionation of Malaysian crude oil

Source: Ariany (2001)

Table 2.2: Physica	properties of	of Malaysian	crude oils
--------------------	---------------	--------------	------------

Types of	Physical Properties				
Malaysian crude oils	Density (g/cm3), 25°C	Viscosity (cP) 30°C/50°C	рН, (26°С)	Surface Tension (mN/m)	Interfacial Tension (mN/m)
Semangkok	0.8131	4.56/3.0	7.04	27.2	27.7
Tabu	0.8120	6.48/3.6	6.10	25.6	35.7
Irong Barat	0.8648	8.76/6.5	7.03	29.6	32.8
Seligi	0.7816	3.48/2.9	7.09	25.3	29.6
Tapis	0.7947	3.60/2.9	6.94	25.7	33.8
Guntung	0.8222	5.40/4.3	6.54	26.4	36.7

Source: Ariany (2001)

2.2.2 Asphaltenes

Asphaltenes are complex polyaromatic molecules defined to be soluble in benzene/ethyl acetate and insoluble in low-molecular-weight n-alkanes. They are dark brown to black friable solids with no specific melting point. Asphaltenes are considered to consist of condensed aromatic sheets with alkyl and alicyclic side chains and heteroatoms (nitrogen, oxygen, sulfur, and trace metals like vanadium and nickel) scattered throughout. **Figure 2.3** shows the hypothetical structure of a petroleum asphaltene, and **Figure 2.4** shows a 3D representation.



Figure 2.3: Permission Hypothetical structure of a petroleum asphaltene

Source: Speight and Moschopedis (1981)



Figure 2.4: 3D representation of a Venezuelan asphaltene molecule

Source: Courtesy of J. Murgich and A. Mansoori

Moreover, asphaltenes are the non-volatile and polar fraction of petroleum that is insoluble in n-alkanes such as n-pentane or n-heptane. So, asphaltenes represent of crude oil components, rather than a chemical class. The polarity, molecular weight and aromaticity of precipitated asphaltenes are rise linearly with carbon number of n-alkane precipitant. **Figure 2.5** represents the range of heavy compounds precipitated by mixing crude oil with n-pentane and n-heptane.



Figure 2.5: "Long diagram" shows that the asphaltenes include the crude oil material highest in molecular weight, polarity, and/or aromaticity

Source: After Long (1981).

There are many definitions of asphaltenes. Strictly speaking, asphaltenes are the components of crude oil that meet some procedural definition. A general definition is that asphaltenes are the material that is (1) insoluble in n-pentane (or n-heptane) at a dilution ratio of 40 parts alkane to 1 part crude oil and (2) re-dissolves in toluene. **Figure 2.6** shows that the asphaltenes separated from Mars-P crude oil with an excess of (a) n pentane (n-C5) and (b) n-heptane (n-C7).



(a) n-C; asphaltenes

(b) n-C7 asphaltenes

Figure 2.6: Examples of the appearance (magnified about 15 times) of asphaltenes separated fromMars-P crude oil with an excess of (a) n pentane (n-C5) and (b) n-heptane (n-C7).

Asphaltene molecules can have carbon numbers from 30 and over and molecular weights from 500 to more than 10,000. They are characterized by a fairly constant hydrogen/carbon ratio of 1.15 with a specific gravity near one. The asphaltenes nature in the crude oil is still a subject of debate. The asphaltenes are believed to exist in oil as a colloidal suspension and to be stabilized by resins adsorbed on their surface. In this regard, the resins act as peptizing agents for asphaltenes and together form clusters called micelles (**Figure 2.7**).



Figure 2.7: Asphaltene-resin micelle

Kokal and Aramco, 2006 stated that these micelles or colloids contain most of the polar material found in the crude oil and possess surface-active properties (interfacially active material). The surface-active properties are the result of the sulfur, nitrogen, oxygen, and metal containing entities in asphaltenes molecules that form polar groups such as aldehydes, carbonyl, carboxylic, amine, and amides.

It is this surface-active behavior of asphaltenes that make them good emulsifiers. Surfactants are compounds that have a polar part with an affinity to water and a nonpolar part with an affinity to oil (**Figure 2.8**). This dual affinity is satisfied when they are positioned (or adsorbed) at the oil/water interface with the polar part immersed in water and the nonpolar part in oil. This orientation results in a decrease in the system thermodynamic free energy. The high-molecular-weight substances accumulation at the interface results in the formation of the rigid film. **Figure 2.9** shows an asphaltene-stabilized water droplet. When such a film forms, it acts as a barrier to drop coalescence. For two drops to coalesce, the film must be drained and ruptured. The presence of the asphaltenes can retard the drainage of this film naturally. The primary mechanism involved in the retardation is the steric repulsion or hindrance (Kokal and Aramco, 2006)



Figure 2.8: Schematic of a surfactant molecule and formation of micelles



Figure 2.9: Mechanism of emulsion stabilization by asphaltenes.

These substances of interfacially active exist predominantly in the crude oil colloids, which consist of asphaltenes and resins. The asphaltenes consist in part of cycloaliphatic naphthenic acids and polycyclic or of their oil-soluble calcium and magnesium salts, substituted phenols, and steroid carbonic acids. Most of the inorganic bonds of the crude are in the asphaltenes (Oetter et al, 1994). The interfacially active components of asphaltenes are most active either directly before or during the start of flocculation (Kessel, Neumann, and Rahimian, 1993). (in the Schorling, P.C. et all, 1999)

In a nutshell, because of these properties make that a asphaltenes a good emulsifier which stabilize the w/o emulsions. However, it causes a problems to demulsify the w/o which require many of methods to demulsify it which will be further discuss in the demulsification sections.

2.2.3 Resins

Resins are black or dark brown semi solid, have a specific gravity near unity, molar mass ranging from 500 to 2000 g/mol and very adhesive materials (Gafonova, 2000). The content of resin in crude oils ranges from 2-40 wt%. From the **Table 2.1**, the content of resin in crude oil is higher compared to asphaltenes composition. Crude oil with a small amount or no asphaltenes is generally has a lower concentration of resin if compared to those with larger amount of asphaltenes.

Resins are defined as the non volatile and polar fraction of crude oil that is soluble in n-pentane, n-heptane and aromatic solvents such as toluene but insoluble in methanol and propanol. The molecular species within the resin are same as to those in the aromatics. But, resins species have higher molar mass, greater polarity, higher heteroatom content and lower H/C ratio compared to aromatics. The resin portion consists of carbon, hydrogen, oxygen, nitrogen and napthenic acids. The content of these elements in resin of various type of crude varies over a narrow range. The widest range is observed in sulfur content (Speight, 1991).

Resins have a much higher H/C ratio compared to asphaltenes, indicating that they are less aromatic than asphaltenes. Asphaltenes are assumed to be maturation products of resin; in the maturation process the cyclic portion of resin molecules undergoes aromatization (Speight, 1991). It is commonly believed that resin molecules are composed of a highly polar end group, which may incorporate sulfur, oxygen or nitrogen, and a long non-polar end group. Nitrogen is present in resins in the form of pyrolle and indole groups. Infrared spectroscopic data indicates the presence of ester, ketone and acid functional groups. Sulfur is present in the form of cyclic sulfides (Gafonova, 2000). However, resin molecules structural studies have not been as intensive as they have been for asphaltenes. Resins were presented either as long paraffinic chain molecules with naphtenic rings in the center, or as condensed aromatic and naphtenic ring systems with heteroatoms scattered in different location. The molecular structure of resin is shown in **Figure 2.10** (Gafonova, 2000).



Figure 2.10: Hypothetical representation of an average resin molecule

Source: Gafonova (2000)

Resins are complex high-molecular-weight compounds that are insoluble in ethylacetate but are soluble in n-heptane. They are heterocompounds, like asphaltenes, that contain oxygen, nitrogen, and sulfur atoms. Molecular weights of resins range from 500 to 2,000. As **Figure 2.7** shows, resins have a high tendency to associate with asphaltenes, and together they form a micelle. The asphaltene-resin micelle plays a key role in stabilizing emulsions. It appears that the asphaltene-resin ratio in the crude oil is responsible for the type of film formed (solid or mobile) and, therefore, is directly linked to the stability of the emulsion. (Kokal and Aramco, 2006)

Resins in crude oil consist mostly of naphthenic aromatic hydrocarbons, generally aromatic ring systems with alicyclic chains. The crude oil resins are to a extent interfacially active and they are predominantly effective as a dispersant asphaltenes (Schorling, et. al., 1999)

2.2.4 Waxes

There are a few of waxes definitions which according to Kokal and Aramco (2006) waxes are high-molecular-weight alkanes naturally present in the crude oil that crystallize when the oil is cooled below its "cloud point." They are insoluble in acetone and dichloromethane at 30°C. There are two types of petroleum waxes: paraffin and microcrystalline. Paraffin waxes are high-molecular-weight normal alkanes, and microcrystalline waxes are high-molecular-weight iso-alkanes that have melting points greater than 50°C. On the other hand, waxes have been defined as esters of long-chain (C16 and above), monohydric (one hydroxyl group), or alcohols with long-chain (C16 and above) fatty acids. Actually, the natural waxes are mixtures of esters and frequently contain hydrocarbon as well according to Becker (1997).

Waxes by themselves are soluble in oil and, in the absence of asphaltenes, do not form stable emulsions in model oils (Bobra, 1990). However, the addition of a small amount of asphaltenes (an amount insufficient by itself to produce emulsions) to oils containing wax can lead to the formation of stable emulsions. Therefore, waxes can interact synergistically with asphaltenes to stabilize emulsions. The physical state of the wax in the crude oil also plays an important role in emulsion stabilization. Waxes are more appropriate to form a stable emulsion when they are present as fine solids in the emulsion; thus, waxy emulsions are more likely at lower temperatures. Waxes which are being oil-wet have a tendency to stabilize water-in-oil emulsions. Crudes that have a high cloud point generally have a greater tendency to form stable and tight emulsions than crudes with low cloud points. Similarly, lower temperatures generally enhance the emulsion forming tendencies of crude oils (Kokal and Aramco, 2006)

2.2.5 Solids

Fine solid particles present in the crude oil are capable of effectively stabilizing emulsions. These solids effectiveness in stabilizing emulsions depends on factors such as the particle size of the solid, interparticle interactions, and the wettability of the solids (Tambe and Sharma, 1993; Menon, Nikolov, and Wasan, 1988; Levine. and Sanford, 1985). Solid particles stabilize emulsions by diffusing to the oil/water interface, where they form rigid films that can sterically inhibit the coalescence of emulsion droplets. Furthermore, solid particles at the interface may be electrically charged, which may also enhance the stability of the emulsion (Kokal and Aramco, 2006)

Particles must be much smaller than the size of the emulsion droplets to act as emulsion stabilizers. Typically these solid particles are submicron to a few microns in diameter (Tambe and Sharma, 1993). The wettability of the particles plays an very important role in stabilizing the emulsions. Wettability is the degree to which a solid is wetted by oil or water when both are present.

The role of colloidal solid particles in emulsions stability and the mechanisms involved are summarized in the following points (Tambe and Sharma, 1993).

- The particles must be present at the oil/water interface before any stabilization can take place. The ability of the particles to diffuse to the interface and adsorb at the interface depends on its size, wettability, and the state of dispersion of the solids (whether flocculated or not).
- The ability of the solids to form a rigid, protective film encapsulating the water droplets is important for stabilizing these emulsions.
- Water-wet particles are likely to stabilize o/w emulsions, and oil-wet particles stabilize w/o emulsions.
- Some degree of particle interaction is required for effective stabilization.

The effectiveness of colloidal particles in stabilizing the emulsions depends largely on the formation of a densely packed layer of solid particles (film) at the oil/water interface. This film provides steric obstruction to the water droplets coalescence. The presence of solids at the interface also changes the rheological properties of the interface that exhibits viscoelastic behavior. This affects the rate of film drainage between droplets and also affects the displacement of particles at the interface. It has also been established in Bobra (1990) that for asphaltenes and waxes to be effective emulsifiers, they must be present in the form of finely divided submicron particles.

2.3 CRUDE OIL EMULSION FORMATIONS AND STABILITY

2.3.1 Classification of Emulsions

Emulsions are systems made of dispersion of liquid droplets in another nonmiscible liquid. They are referred to as either w/o emulsions, droplets of water dispersed in oil medium, or o/w emulsions, oil droplets dispersed in an aqueous medium. They are either the desired result of a mechanical process or the spontaneous result of favorable conditions of formation (Clausse et al, 2005). In another explanation, emulsions are a particular form of colloidal dispersion in which a liquid is distributed in a continuous water phase of different compositions. Separation of water and oil from emulsified solutions, in the process termed demulsification, indicates breakage of the emulsified film surrounding oil or water droplets to allow coalescence or gravitational settling of the oil (Kuoa and Lee, 2010).In reality, it is possible also to emulsify the w/o to be o/w to reduce the operational problems. It is because water is denser than the oil and when it needs to be transport to the chemical laboratory, emulsification of o/w is required.

Hence, the type of emulsion which is formed depends upon a number of factors. If the ratio of phase volumes is very large or very small, then the phase having the smaller volume is frequently the dispersed phase. If the ratio is closer to 1, the other factors determine the type of emulsion formed. Or in the simpler explanation, the dominant phase volume will be the solution while the other will be a solute in the solution.

Produced oilfield emulsions can be classified into three broad groups: water-inoil, oil-in-water, and multiple or complex emulsions. Water-in-oil emulsions consist of water droplets in a continuous oil phase, and oil-in-water emulsions consist of oil droplets in a water-continuous phase. **Figures 2.1 and 2.11** show the two basic (waterin-oil and oil-in-water respectively) types of emulsions. In the oil industry, water-in-oil emulsions are more common (most produced oilfield emulsions are of this kind); therefore, the oil-in-water emulsions are sometimes referred to as "reverse" emulsions.



Figure 2.11: Photomicrograph of an o/w emulsion.

Multiple emulsions are more complex and complicated; they consist of tiny droplets suspended in bigger droplets that are suspended in a continuous phase. For example, a water-in-oil-in-water emulsion consists of water droplets suspended in larger oil droplets that, in turn, are suspended in a continuous water phase. **Figure 2.12** shows an example of a multiple emulsion.



Figure 2.12: Photomicrograph of a w/o/w emulsion.

Given the oil and water phases, the type of emulsion formed depends on several factors. As a rule of thumb, when the volume fraction of one phase is very small compared with the other, the phase that has the smaller fraction is the dispersed phase and the other is the continuous phase. When the volume-phase ratio is close to 1 which is 50:50 in ratio, then other factors determine the type of emulsion formed. Emulsions are also classified by the droplets size in the continuous phase. When the dispersed droplets are larger than 0.1 µm, the emulsion is a macroemulsion. Emulsions of this kind are normally thermodynamically unstable which indicates that the two phases will separate over time because of a tendency for the emulsion to reduce its interfacial energy by coalescence and separation. However, droplet coalescence can be minimize or even eliminated through a stabilization mechanism. Most oilfield emulsions belong in this category. In contrast to macroemulsions, there is a second class of emulsions known as microemulsions. These emulsions form spontaneously when two immiscible phases are brought together because of their extremely low interfacial energy. Microemulsions have very small in droplet sizes, less than 10 nm, and are considered thermodynamically stable. Microemulsions are fundamentally different from macroemulsions in their formation and stability (Kokal and Aramco, 2006).

2.3.2 Emulsion Stability

Stability of water-in-crude oil emulsions is attributed to asphaltenes and resins, which prevent droplet coalescence by forming a rigid film or skin at the interface (Mc Lean, Kilpatrick, 1997) and (Gafanova, Yarranton, 2001). Asphaltenes and resins have the same chemical composition but their molecular weight is different. Asphaltenes are defined as the crude oil fraction insoluble in *n*-heptane or *n*pentane but soluble in toluene while resins are soluble in aliphatic and aromatic solvents (except in methanol). They both contain hydrophobic and hydrophilic moieties, which confer the amphiphilic character and respective surface active properties. In crude oil, aggregates of asphaltenes are kept in dispersed state by resins but when crude oil is suddenly brought in contact with water, asphaltenes and resins compete for the water/oil interface (Sjoblom, Johnsen et al, 2001). Resins, which are lighter than asphaltenes, are the first entities to reach the water/oil interface; this provokes a change in asphaltene solubility resulting in accumulation of the asphaltene entities around the water droplets. The emulsion stability is known to be related to the state of the asphaltene aggregates but the form in which asphaltenes stabilize water-in-oil emulsions still remains controversial. It is now admitted that the emulsion stability is due to an asphaltenic network, containing also smaller native surfactants such as resins and naphtenic acids. It is generally believed that the presence of resin decreases film rigidity and diminish emulsion stability (Daniel-David et al, 2008). Ese et al. showed by AFM that the addition of resins into asphaltene monolayers caused the opening of the rigid asphaltene structure

According to NRT Science & Technology Committee (1997), emulsion can be categorized into stable, unstable and meso-stable emulsions according to stability and operational definitions:

• Stable emulsions will persist for days, weeks and longer. They showed the viscoelastic properties and viscosities are at least three orders of magnitude greater than that of the starting oil. In addition, stable emulsion will increase with viscosity over time. It has been postulated that the stability is derived from the strong viscoelastic that were caused by asphaltenes and perhaps along with resins. Increasing alignment of asphaltenes at the oil-water interface may cause the increasing of viscosity.

- Unstable emulsions usually persist for only a few hours after mixing stops. These emulsions are ready to separate into oil and water due to insufficient water particle interactions. However, the oil may retain small amounts of water, especially if the oil is viscous.
- Meso-stable emulsions are most likely the most common emulsion that was formed in the fields. These emulsions can be red or black in appearance. This emulsion has the properties between stable and unstable emulsions. It is suspected that these emulsions contained either insufficient asphaltenes to render them completely stable or contained too many destabilizing materials such as smaller aromatics. The viscosity of the oil may be high enough to stabilize some water droplets for a period of time. Meso-stable emulsions may also degrade to form layers of oil and stable emulsions.

2.3.3 Colloid Rheology

2.3.3.1 Non-Newtonian Flow Properties

For Non-Newtonian fluids the coefficient of viscosity is not a constant, but s itself a function of the shear rate. Some convenient way to summarize the flow properties of fluids are by plotting curves(flow curves) of shear stress versus shear rate (τ versus γ) as shown in **Figure 2.13** or by plotting viscosity versus shear rate as shown in **Figure 2.14**. These curves can be categorized into several rheological classifications, although that colloidal system can exhibit several of the following characteristics aat once.



Figure 2.13: Typical flow curves of shear stress versus shear rate.

Source: Adopted from Schramm (2005)



Figure 2.14: Typical curves of viscosity versus shear rate.

Source: Adopted from Schramm (2005)

2.3.3.2 Pseudoplastic

As shear rate increases, the viscosity of many colloidal dispersions decreases. Such systems are termed pseudoplastic, or shear thinning. For such dispersions, the viscosity decreases the faster material is pumped through a pipe, sprayed out of a nozzle, or mixed with a mixer. Pseudoplastic behavior in dispersions can be cuased by alignment, stretching, deformation, or peptization of dispersed material while being sheared. To refer to the viscosity of a Non-newtonian fluid or dispersions one must also cite the shear rate to which it applies. Examples of pseudoplastic fluids include many emulsions, foams, and suspensions. At very low shear rates, some pseudoplastic dispersions will behave like a Newtonian fluid because the Brownian motion of dispersed species counteracts the orienting effects of the applied shear. Above a certain shear rate, the shear effects then dominate and pseudoplastic flow is observed. In many dispersions exhibiting pseudoplastic flow the effect will be reversible, sometimes after some time lag as Thixotropy which in **Section 2.3.3.5** (Schramm, 2005).

2.3.3.3 Dilatancy

As the shear rate increases, the viscosity of some dispersions actually increases. This is called dilatancy, or shear-thickening. Dilatancy can be due to the dense packing of particles in very concentrated dispersions for which at low shear, the particles can just move past each other but at high shear they become wedged together such that the fluid cannot fill (lubricate) the increased void volume, and the viscosity increases. Examples of this effect are concentrated suspensions (plastisols) of polyvinyl chrolide (PVC) particles in plasticizer liquid and the commercial novelty product Silly Putty® (which is a silicone material) (Schramm, 2005).

2.3.3.4 Plasticity/Pseudoplasticity with Yield Stress

In some colloidal dispersions, the shear rate (flow) remains at zero until a threshold shear stress is reached, termed the yield stress (τ_Y), and then Newtonian or pseudoplastic flow begins. A common cause of this behavior is the existence of an interparticle or intermolecular network which initially acts like a solid and offers resistance to any positional changes of the volume elements. In this case flow only occurs when the applied stress exceeds the strength of the network and what was a solid becomes instead of fluid. Examples included oil-well drilling muds, greases, lipstick, toothpaste, and natural rubber polymers (Schramm, 2005).

2.3.3.5 Thixotropy

Thixotropy refers to pseudoplastic flow that is time dependent. At a constant applied shear rate, the viscosity decreases, as shown in **Figure 2.15**. In a flow curve, hysteresis occurs; here the interparticle or intermolecular alignments are not only

influenced by the magnitude of the applied shear but also by the time interval over which the shear is applied. Thixotropy arises because, after the shear is applied, it takes some time for the interparticle or intermolecular alignments to be altered, and after the shear rate is reduced it takes some time for the original alignments to be restored. If the sheared system is allowed to stand it will eventually regain its original structure. Examples are lipstick (pseudoplastic and thixotropic), paint (plastic and thixotropic) and others can be found in ceramics, foods, cosmetics, and pharmaceuticals (Schramm, 2005). Scott Bader states that for thixotropic liquids the viscosity decreases over time for a given shear rate until a minimum is reached. Once the shearing force is stopped the viscosity recovers over time.



Figure 2.15: Illustration of time-dependent types of rheological behavior

Source: Adopted from Schramm (2005)

2.3.3.6 Rheopexy

Rheopexy refers to dilatants flow which is time dependent. At a constant applied shear rate viscosity increases, as shown in **Figure 2.15**. In a flow curve, hysteresis occurs (but opposite to the thixotropic case). An example of the rheopectic system is a bentonite clay "gel" system which sets slowly on standing, but sets quickly when gently agitated (Schramm, 2005). While Scott Bader states rheopexy increase in viscosity over time for a given shear force until a maximum is reached followed by a viscosity reduction over time when the shear is stopped. This type of behavior is extremely rare.

2.4 DEMULSIFICATION OF CRUDE OIL EMULSION

2.4.1 Demulsification (Destabilizing or Breaking of Emulsion)

Demulsification is the breaking or destabilizing of a crude oil emulsion into oil and water phases. From a process point of view, the oil producer is interested in three aspects of demulsification: the rate or the speed at which this separation takes place, the amount of water left in the crude oil after separation, and the quality of separated water for disposal. A fast rate of separation, a low value of residual water in the crude oil, and a low value of oil in the disposal water are obviously desirable. Produced oil usually has to meet company and pipeline specifications. For example, the oil shipped from wetcrude handling facilities must not contain more than 0.2% BS&W and 10 pounds of salt per thousand barrels of crude oil. This standard depends on company and pipeline specifications. The salt is insoluble in oil and associated with residual water in the treated crude. Low basic sediment and water (BS&W) and salt content are required to reduce corrosion and deposition of salts. The major concern in refineries is to remove inorganic salts from the crude oil before they cause corrosion or other detrimental effects in refinery equipment. The salts are removed by washing or desalting the crude oil with relatively fresh water (Kokal and Aramco, 2006)

2.4.2 Destabilizing Emulsions

As mentioned previously, produced oilfield emulsions possess some kinetic stability. This stability arises from the formation of interfacial films that encapsulate the water droplets. To separate this emulsion into oil and water, the interfacial film must be destroyed and the droplets made to coalesce. Therefore, destabilizing or breaking emulsions is linked directly to the removal of this interfacial film. The factors that affect the interfacial film and, consequently, the stability of the emulsions were discussed earlier. The factors that enhance or speed up emulsion breaking are discussed here.

There are a lot of techniques to destabilize the w/o emulsions which are temperature, agitation or shear, residence or retention time, solids removal, control of emulsifying agents and retrofitting

The first technique used to destabilize w/o emulsions is temperature. Application of heat promotes w/o separation and accelerates the treating process. An increase in temperature has the following effects which are

- Decreases the viscosity of the oil.
- Increases the mobility of the water droplets.
- Increases the settling rate of water droplets.
- Increases droplet collisions and favors coalescence.
- Weakens or ruptures the film on water droplets because of water expansion and enhances film drainage and coalescence.
- Increases the difference in densities of the fluids that further enhances water-settling time and separation.

All of these effects favor emulsion destabilization and oil/water separation; however, heat by itself is not a thoroughly solve the problem and even has several disadvantages For instance, loss of light ends from the crude oil. An economic analysis should be conducted that takes into consideration factors such as heating costs, reduced treating time, and residual water in the crude. An increase in temperature can also be achieved by burying crude-oil pipelines or by insulating them. These factors should be evaluated carefully during development, especially at facilities where emulsion problems are anticipated. Furthermore, if the temperature is too high it will damage the properties of the crude oil and affect the quality of the crude oil and directly the value of the crude oil will also be affected. Careful control and modify of the temperature is needed and it need detail calculation to make sure it will not cause any undesirable problems to happen.

Second techniques are agitation or shear. Generally, reducing agitation or shear reduces emulsion stability. Very high shear is detrimental and should be avoided. High shear causes violent mixing of oil and water and leads to smaller droplet sizes and this will cause the separation even harder to be conducted. This is due to the smaller droplets are relatively more stable than larger droplets; therefore, measures that increase shearing of the crude oil, for example, mechanical chokes, valves, flow obstructions, and pressure drops should be avoided or minimized where possible. However, a certain amount of shear is required for mixing the chemical demulsifier into the bulk of the emulsion.

Thirdly is residence or retention time. The period of time that the emulsion is held at the treating temperature is the residence, retention, or treating time. This typically and normally is between 10 to 30 minutes for normal crude oil production. However, it may need to be much longer to treat tight and stable emulsions effectively. An increase in residence time increases the separation efficiency and reduces the residual amount of water in the crude oil. Increasing residence time, however, comes at the expense of high separator-equipment costs as the longer the residence time of the process, to prolong the operation is higher and the tray or stages inside the separator column has to be increased to a better separation.

Fourth is solids removal which solids have a strong tendency to stabilize emulsions, especially if they are present as fines or when they are wetted by both oil and water. Removing the solids or their source is sometimes all that is required or needed for eliminating or minimizing the w/o emulsions problems. Oil wet solids stabilize water-in-oil emulsions. Water-wet solids can also be made oil-wet with a coating of heavy polar materials and can participate effectively in the stabilization of w/o emulsions (Kokal, S. and Al-Juraid, 1998). The presence of solid asphaltenes and waxes has a definite detrimental effect on the emulsion problem, and every effort should be made to eliminate their presence in the crude oil. The solids can be removed by dispersing them into the oil or can be water-wetted and removed with the water.

Fifth technique is control of emulsifying agents. Due to emulsifying agents are necessary in the stabilization of emulsions, controlling them allows for their destabilization and resolution. Some of the ways to control emulsifiers include in the following processes which are

- Careful selection of chemicals that are injected during oil production. The chemicals include, for example, acids and additives during acidization, corrosion inhibitors for corrosion protection, surfactants and dispersants for organic-deposition control and inorganicdeposition control, and polymers and blocking agents for waterproduction control. Laboratory compatibility testing of these chemicals should be conducted before field injection to avoid tight emulsions.
- Avoiding incompatible crude-oil blends. A crude-oil blend is incompatible if it results in the precipitation of solids for organic and inorganic. This occurs, for example, when an asphaltic crude oil is mixed with a paraffinic crude oil, resulting in the precipitation of asphaltenes. Again, laboratory testing can identify incompatible crudes.
- Utilize of dispersants for controlling the precipitation of asphaltenes and the use of pour point depressants for controlling waxes.

Alternatively, emulsion stability can be controlled by raising the temperature of the crude above its cloud point.

• Neutralizing or reducing the effect of stabilizing film encapsulating the water droplets by demulsifiers. These chemicals promote coalescence of water droplets and accelerate water separation. (Kokal and Aramco, 2006)

The final techniques that are appropriate to destabilize the w/o emulsions is retrofitting. By retrofitting the existing equipment, additional water separation can be achieved. Invariably, emulsion problems increase after the separation equipment has been installed because of field aging, increased water cuts, improper design, or several other reasons which cause the emulsions cannot be separated properly due to the inefficiency of the separator. Additional equipment like free-water knockout drums and heater treaters can be installed to assist in the breaking of oilfield emulsions. Internals can also be installed or retrofitted in production separation traps or increases the sieve tray or stages to maximize the separation. The most common retrofitting is the installation of a coalescer section that assists in coalescing water droplets.

2.4.3 Demulsification Mechanisms

Emulsions may become unstable through a diversity of physical mechanisms, including creaming, sedimentation, flocculation, coalescence which schematic diagrams are shown in **Figure 2.16**



Figure 2.16: Creaming, Sedimentation, Flocculation, Coalescence

Source: Mc Clement (2005)

Sedimentation and creaming are both forms of gravitational separation. Sedimentation is the process in which water droplets settle down in an emulsion because of their higher density. Sedimentation can be defined as the downward movement of droplets due to the fact that they have higher density than the surrounding liquid whereas its inverse process, creaming, is the rising of oil droplets in the water phase or can be described as the upward movement of droplets due to the fact that they have a lower density than the surrounding liquid.. Sedimentation and creaming are driven by the density difference between oil and water and may not result in the breaking of an emulsion.

Demulsification, the separation of an emulsion into its component phases, is a two-step process. The first step is flocculation (aggregation, agglomeration, or coagulation). The second step is coalescence. Any of these steps can be the rate-determining step in emulsion breaking (Kokal and Aramco, 2006). The level of demulsification process of water in oil emulsion is shown in **Figure 2.17**.



Figure 2.17: The level of demulsification process of water in oil emulsion (Separation of water from water in oil emulsion by gravity force)

Source: Hanapi et al (2006)

Flocculation or aggregation is the first step in demulsification. During flocculation, the droplets clump together which will lead into forming of aggregates. The droplets are close to each other, even contacting at certain points, but do not lose their identity and retain their individual integrity which indicates they may not coalesce.

Coalescence is the second step in demulsification. During coalescence, water droplets will fuse or coalesce together to form a larger drop which they will lose their identity and cannot retain their individual integrity. This is an irreversible process that leads to a decrease in the number of water droplets and eventually to complete demulsification. Based on Mc Clement, 2005, coalescence is the process whereby two or more droplets merge together to form a single larger droplet and extensive droplet coalescence can eventually lead to the formation of a separate layer of oil on top of the sample which is known as "oiling-off".

2.5 CHEMICAL DEMULSIFICATION OF CRUDE OIL EMULSION

2.5.1 Factors that affect Chemical Demulsification

Chemical demulsification is the most broadly applied method of treating waterin-oil and oil-in-water emulsions and involves the use of chemical additives to accelerate the emulsion breaking process. The stability of emulsions is largely affected by the nature of the interface/film and surfactant adsorption mechanisms (Kim, 1995). In addition, chemicals used in the demulsification are readily available and easily obtained. It need not to use any expensive machine to undergo the experiment as it involves only mixing and it does not require high voltage or thermal to undergo the demulsification so as it is simple and easy apply method.

The optimization of the amount and type of chemical employed, contributes to reduce the oil content in the produced water offshore. The development and use of environmentally friendly chemicals is facilitated through building up more fundamental knowledge concerning the process involved in stabilizing and breaking the emulsions. Success of chemical demulsifying methods dependent upon the following:

- (i) An adequate quantity of a properly selected chemical must enter the emulsion.
- (ii) Thorough mixing of the chemical in the emulsion must occur
- (iii) Sufficient heat may be required to facilitate or fully resolve an emulsion.
- (iv) Sufficient residence time must exist in treating vessels to permit settling of demulsified water droplets. (Hanapi et al, 2006)

Chemical Selection of the right demulsifier is crucial to emulsion breaking. The selection process for chemicals is still viewed as an art rather than a science. However, with the increasing understanding of emulsion mechanisms, the availability of new and improved chemicals, and new technology, research, and development efforts, selection of the right chemical is becoming more scientific. Many of the failures of the past have

been eliminated. Recently, the world is saving the earth from pollution and environmental issues also take into consideration and therefore chemical demulsifiers that are environmental friendly are needed and favoured in order to save the planet from being destroyed continuously.

2.5.2 Types of Demulsifiers for Demulsification

Table 2.3: The Chemical demulsifiers used in demulsification tests

Group	Demulsifier	
A/ Polymeric	Polyethylene block PEG	
	Poly PO terminated	
	Polyethylene Oxide (PEO) 600,000	
	Polyethylene Oxide (PEO) 1000,000	
B/ Polyhydric alcohols	Polyethylene glycol (PEG) 600	
	Ethylene glycol (EG)	
	Propylene glycol (PG)	
	Polyethylene glycol (PEG) 1000	
C/ Amines	Hexylamine	
	Trioctylamine	
	Dioctylamine	
	Octylamine	
	Pentylamine	
	Propylamine	
	Decylamine	
D/ Sulphonate	Sodium di-2-ethylhexyl sulphosuccinate (AOT)	
	Dodecyl benzene sulphonic acid (DBSA)	
	Sodium dodecyl benzene sulphonic (NaDBS)	

Source: Abdurahman, H. N. et al (2007)

2.5.2.1 Physical and Chemical Properties of Demulsifiers

Since demulsifiers are surfactants, understanding the role of demulsifiers as a surface active agents are very important. Basically, there are two groups in the demulsifier molecule which are hydrophobic (water haters) group and a hydrophilic group (water lover). A demulsifier molecule can be shown as in **Figure 2.18**. The hydrophobic group such as long chain alkyl group is not repelled by water, since the attraction of the hydrocarbon chain for water is approximately the same as itself. In fact, at very low concentration of demulsifier in the water the hydrocarbon chains will lie flat on the surface.



Figure 2.18: Basic structure of demulsifier

Source: Porter (1994)

The hydrophilic effect is referred to the water-preferring nature of species (atom, molecule, droplet and particle). Hydrophilic usually means that a species prefers the aqueous phase rather than the oil phase. In this sense, hydrophilic has the same meaning of oleophobic or lipophobic. Hydrophilic molecules are believed to decrease the degree of order in water molecules around them. So, ions in solution are hydrophilic such as carboxylate, sulphate, phosphate, sulphonate and quaternary ammonium. Primary

amines, amine oxides, phosphine oxide and sulphoxides are polar groups with a highly electronegative character which shown strong electrophilic properties (Porter, 1994). This will affect the degree of the demulsification in choosing the chemical demulsifier as the longer the chain of hydrophilic the better as the water is absorb by the demulsifier without affect the crude oil composition.

If the molecules contain electronegative atoms capable of associating with the hydrogen-bonding network in water, these molecules are considered as hydrophilic. The examples of molecules that include in this group are ethers, aldehydes, amides, esters, oxygen atom in alcohol, nitrogen atom in amides, amines, ketones and nitroalkanes. This effect sometimes can be diminished when the molecules, which contain the hydrophilic effect, are attached to the hydrophobic group. But this phenomenon will not be happened if a number of such nonpolar groups are attached to the hydrophobic groups, so that limited or entire water solubility can be achieved, depending upon the relative size of the hydrophobic effect and the number of hydrophilic groups. (Hanapi et al, 2006)

Beside that, there are a lot of water soluble polymeric demulsifiers such as the emulsion tetrapolymer of methylmethacrylate, butyl acrylate, acrylic acid and methacrylic acid and dispersions of water soluble cationic polymers (Bhattacharyya, 1992). The hydrophobic effect is referred to the water-avoiding nature of a species (atom, molecule, droplet, and particle). Hydrophobic usually means that a species prefers the oil phase to the aqueous phase. In this sense, hydrophobic has the same meaning as oleophilic or lipophilic. Oil soluble demulsifiers are also known as hydrophobic groups. But this kind of oil soluble demulsifier is less prefer in w/o emulsions but is prefer in o/w emulsion. The choosing of appropriate chemical demulsifier is based on the nature of the emulsions.

There are a lot of reasons that causes the insolubility of the hydrogen chain in water. These reasons include the mechanism that involves both entropic and enthalpic contributions and the unique multiple hydrogen bonding capability of water (Porter, 1994). There is a reorientation and restructuring of water around nonpolar solutes, which disrupts the existing water structure and imposes a new and more ordered structure on the surrounding water molecules. This will result the decreasing in entropy value. Hydrophobic groups tend to increase the degree of order in water molecules around them but it is undesirable in the w/o emulsions which we need is increase the degree of order in oil molecules around them and the oil is our main focus and the water is the problems we need to solve in order to produce pure crude oil that are ready to sell. The aqueous solubility of alone demulsifier molecule will depend upon the relative strengths of the hydrophobic and hydrophilic effects. They are not independent, since both rely on the structure of the hydrogen bonds around the hydrophilic and hydrophobic groups. (Hanapi et al, 2006)

2.5.2.2 Hydrophilic Lipophilic Balance

Hydrophile-Lipophile Balance (HLB) is a technique of characterizing surfactant based on their relative affinity for water and oil. In general, lower HLB numbers are assigned to surfactants which are more lipophilic. The lower HLB is normally less than 5.0. If the HLB is more than 5.0 is considered as High HLB. For higher HLB numbers, they are assigned to surfactants with a high affinity for water. In many cases blends containing two or more surfactants may be used to provide optimum performance. Often, higher HLB number surfactants will stabilize o/w emulsions and lower HLB number of demulsifier to destabilize it while lower HLB number surfactants will stabilize w/o emulsions and demulsifier with higher HLB number is needed to destabilize it. (MacPherson et. al., 2005).

A widely used semiempirical method of calculating the HLB number of a surfactant is as follows (Davis, 1994b):

HLB =
$$7 + \Sigma$$
(hydrophilic group numbers) – Σ (lipophilic group numbers) (2.1)

Group numbers have been assigned to many different types of hydrophilic and lipophilic groups (**Table 2.4**). The sums of the group numbers of all the lipophilic groups and hydrophilic groups are substituted into the above equation and the HLB number is calculated.

Hydrophilic Group	Group Number	Lipophilic	Group Number
		Group	
$-SO_4^-Na^+$	38.7	—СН —	0.475
-COO ⁻ H ⁺	21.2	-CH ₂ -	0.475
Tertiary amine	9.4	$-CH_{3} -$	0.475
Sorbitan ester	6.8	-CH =	0.475
Glyceryl ester	5.25		
-СООН	2.1		
—ОН	1.9		
-0 -	1.3		
$-CH_2 - CH_2 - 0) - $	0.33		

Table 2.4: Selected HLB Group Numbers

Source: Adopt from Mc Clements (2005)

The HLB number of a surfactant gives a useful indication of its solubility in either the oil and/ or water phase, and can be used to predict the type of emulsion that will be formed by surfactant as shown in **Table 2.5**. Below is the table of comparison of functional attributes of different general classes of emulsifiers.
Table 2.5: Comparison Of Functional Attributes Of Different General Classes Of Emulsifiers

Chemical	Solubility	Emulsion	Usage	pН	Salt	Temperature				
Name		Туре	Level	Stability	Stability					
			(g/g_{oil})							
		S	Surfactants							
Nonionic	Oil	W/O	~0.05	Good	Good	-				
(Low HLB)										
Nonionic	Water	O/W	~0.05	Good	Good	Poor at				
(High HLB)						T~PIT				
Ionic	Water	O/W	~0.05	Good	Poor at	Poor at				
					I>CFC	T~PIT				
Proteins										
	Water	O/W	~0.05	Poor at	Poor at	Poor at				
				IEP	I>CFC	T>T _m				
Polysaccharide	Polysaccharides									
	Water	O/W	~1-1.15	Good	Good	Good				

Source: Adopt from Mc Clements (2005)

2.6 MICROWAVE DEMULSIFICATION OF CRUDE OIL EMULSION

2.6.1 Theory of Microwave Heating

2.6.1.1 Dielectric Properties

There are three dielectric properties involve in microwave heating which are

- i. Dielectric constant
- ii. Dielectric loss

iii. Loss tangent (Ratio of Dielectric constant to Dielectric loss

Dielectric constant and dielectric loss of water used in this research were given by Wolf (1986) respectively as below:-

$$\varepsilon_{r,w}' = 85.215 - 0.33583T \tag{2.2}$$

$$\varepsilon_{r,w}^{\prime\prime} = 320.658T^{-1.0268} \tag{2.3}$$

Von Hippel (1954) proposed equation for dielectric properties of various petroleum oils, in this regards, dielectric constant and loss tangent of crude oil for the this study calculated from the equations respectively as follow:-

$$\varepsilon_{r,o}' = 2.24 - 0.000727T \tag{2.4}$$

$$\tan \delta_o = (0.527T + 4.82) * 10^{-4} \tag{2.5}$$

2.6.1.2 Attenuation Factor

Beer-Lambert's equation (Atkins, 1986) in physical chemistry states that loss of electromagnetic energy, including microwaves, is proportional to the energy intensity and pathlength. This equation will be used to calculate the rate of heat generation by microwave radiation. Considering that the lost microwave energy is converted to thermal energy (heat), the volume rate of heat generation is given by the following equation:

$$q_{MW,z} = \frac{2\alpha_E}{4.184} P_{(z)} \tag{2.6}$$

where $P_{(z)}$ is local time-average microwave power flux at the surface of container (watts/cm²) is given by the integrated form of the Beer -Lambert's equation; that is:-

$$P_{(z)} = P_{(o)}e^{-2\alpha_E z}$$
(2.7)

$$P_{(o)} = \frac{453.2 + 59.8 \ln(m)}{A} \tag{2.8}$$

m = Mass (g) of the sample A = sample container's area $P_{(0)}$ = microwave power flux at z=0 (watts/cm²)

The combination of both equation (2.6) and (2.7) gives the local volume rate of heat generation in terms of incoming microwave flux $P_{(o)}$.

The attenuation factor can be calculated from the following equation given by the electromagnetic field theory (Von Hippel, 1954):

$$\alpha_E = \frac{2\pi f_o}{c} \left[\frac{\varepsilon'_r}{2} \left(\sqrt{1 + \tan^2 \delta} - 1 \right) \right]^{1/2}$$
(2.9)

where

 f_o = frequency of incident microwave c = electromagnetic wave velocity = speed of light = 3 x 10⁸ m/s = 3 x 10¹¹ cm/s

The attenuation factor of water varies from 0.465cm⁻¹ at 15°C to 0.085cm⁻¹at 95°C. Therefore, under the same intensity of microwave power, water generates less heat at higher temperatures.

2.6.1.3 Volume Rate of Heat Generation

In the research, the dispersed phase is water while the continuous phase is the crude oil which has small dielectric constant and low dielectric loss factor, it is relatively "transparent" to microwave (Fang and Lai, 1995). The dielectric constant and

where

loss tangent of crude oil are in the ranges of 2.0 to 2.2 and 0.001 to 0.005, respectively according to Von Hippel (1954). By developing the following equation, microwave may go through the entire thickness of emulsion sample was included.

Microwave should reach the other side of microwave cavity if they go through the w/o emulsion as shown in the **Figure 2.19**.



Figure 2.19: Multiple Pass Propagation and Absorption of Microwaves within Emulsion

Source: Adopted from Fang and Lai (1995)

The volume rate of microwave heat generation can be developed as follow if the emulsions are placed in the centre of the microwave oven and the container is in a cylindrical shape glass with its top and bottom ends are covered with aluminium foil as shown in **Figure 2.19**. The microwave propagation process is repeated in many times till the discontinuing of the radiation. As a first approximation, considering microwave propagate only in radial direction, the pathlength of microwave in the first forward pass

of microwave before reaching the element is R-r (z = R-r). Hence, equation (2.10) is developed from equation (2.6) to be further developed to equation (2.11) which is to obtain the first forward pass of microwave before reaching the element equation

$$q_{MW,z} = \frac{2\alpha_E}{4.184} P_{(o)} e^{-2\alpha_E z}$$
(2.10)

$$q_{MW,(R-r)} = \frac{2\alpha_E}{4.184} P_{(R)} e^{-2\alpha_E(R-r)}$$
(2.11)

where

the local microwave flux is at the location r
z = pathlength (R-r)
R = radius of sample container, cm
r = radial coordinate, cm

The microwave propagation continuously moves to the pathlength R+r which is inside the emulsion to reach the cavity wall. Then, it reflected back by the wall, and travel another r+R to return to the element. Hence the pathlength of r+R+R+r attenuates the returning microwave power reaching the element. The volume rate of heat generation by the first backward pass of microwave in the element is:-

$$\frac{2\alpha_E}{4.184} P_{(R)} e^{-2\alpha_E(R-r)} e^{-2\alpha_E(r+R+R+r)}$$
(2.12)

The same method is used to generate subsequent forward and reflected passes of microwave.

The combine volume rate of heat generated by the n-th forward and reflected passes is:

$$q_{MW,(n)} = \frac{2\alpha_E}{4.184} \{ P_{(R)} e^{-2\alpha_E[R+4(n-1)R-r]} + P_{(R)} e^{-2\alpha_E[3R+4(n-1)R+r]} \}$$
(2.13)

The intensity of the microwave will decrease each time microwaves pass the element.

According to Fang and Lai (1995) the average volume rate of heat generation can be generated by integration of the local volume rate over the entire volume of emulsion. That is:

$$q_{MW} = \frac{1}{\pi R^2 H} \int_0^R 2\pi r H \sum_{n+1}^\infty q_{MW,(n)} dr$$
(2.14)

where

 $\pi R^2 H$ = the volume of irradiated emulsion. H = height of container, cm

After integration

$$q_{MW} = \frac{2\alpha_E}{4.184} P_{(R)} \frac{2}{(2\alpha_E R)^2} \sum_{n=1}^{\infty} \{ [1 + e^{2\alpha_E R(2\alpha_E R - 1)}] e^{-2\alpha_E [R + 4(n-1)R]} + [1 - (2\alpha_E R + 1)e^{-2\alpha_E R}] e^{-2\alpha_E [3R + 4(n-1)R]} \}$$
(2.15)

According to Abdurahman et. al. (2010) the volume rate of microwave heat generation from energy balance equation is as follow:

$$q_{MW} = g_{MW} = \frac{hA}{V} (T_m - T_a) + \frac{\varepsilon A\sigma}{V} [(T_m + 273.15)^4 - (T_a + 273.15)^4] + \rho C_p \frac{dT}{dt}$$
(2.16)

where Convection Heat Transfer = $\frac{hA}{V}(T_m - T_a)$ h= convective heat transfer coefficient, cal/s.cm².°C A= convective heat transfer area, cm² V= Volume of irradiated emulsion, cm³ T_m = Temperature of emulsion, °C T_a = Ambient Temperature, °C

Radiation Heat Transfer =
$$\frac{\varepsilon A \sigma}{v} [(T_m + 273.15)^4 - (T_a + 273.15)^4]$$

 ε = emissivity of surface
 σ = Stefan-Boltzmann constant
= 5.672 x 10⁻⁸ W/m².K⁴

Conduction Heat Transfer = $\rho C_p \frac{dT}{dt}$ ρ = density of emulsion, g/cm³ C_p = heat capacity at constant pressure, cal/g.°C $\frac{dT}{dt}$ = rate of temperature increase in °C/s

From the research result, the effect of convection term is very small as well as radiation term than the conduction heat transfer term in the sample. The heat generated by the glass container is very small and can be negligible because of its small dielectric constant and small mass. The density (ρ) and heat capacity (C_p) of the emulsion can be calculated from mixing rules as follow:

$$\rho_m = \rho_w \Phi + \rho_o (1 - \Phi) \tag{2.17}$$

$$C_{p,m} = C_{p,w} \Phi + C_{p,o} (1 - \Phi)$$
(2.18)

where
$$\rho_m = \text{density of emulsion, g/cm}^3$$

 $\rho_w = \text{density of water, g/cm}^3$
 $\rho_o = \text{density of crude oil, g/cm}^3$
 $C_{p,m} = \text{heat capacity of emulsion, cal/g.}^{\circ}C$
 $C_{p,w} = \text{heat capacity of water, cal/g.}^{\circ}C$
 $C_{p,o} = \text{heat capacity of crude oil, cal/g.}^{\circ}C$
 $\Phi = \text{volume fraction of emulsified water}$

Based on Abdurahman et al., 2010, if the dielectric properties are assumed to be independent of temperature at frequency 2450 MHz, the penetration depth D_P , and wavelength λ_m within a sample for a radiation of the above frequency (2450 MHz) are related to dielectric constant $\epsilon'r$ and dielectric loss $\epsilon''r$ as follows:

$$D_{p} = \frac{c}{2\pi f} \left[\frac{\varepsilon' \left(\sqrt{1 + \left(\frac{\varepsilon''}{\varepsilon'}\right)^{2}} - 1 \right)}{2} \right]^{-1/2}$$
(2.19)
$$\lambda_{m} = \frac{c}{f} \left[\frac{\varepsilon' \left(\sqrt{1 + \left(\frac{\varepsilon''}{\varepsilon'}\right)^{2}} + 1 \right)}{2} \right]^{-1/2}$$
(2.20)

where

where

c = Speed of light f = Frequency

2.6.1.4 Temperature Increase

The temperature increase of irradiated emulsion is of great interest in design and operation of microwave heating and separation processes if it is able to be predicted

$$\frac{\Delta T}{\Delta t} = \frac{q_{MW}}{c_p \rho} - \frac{hA}{c_p \rho V} (T_m - T_a) - \frac{\varepsilon \sigma A}{c_p \rho V} [(T_m + 273.15)^4 - (T_a + 273.15)^4]$$
(2.21)

$$\Delta T = T_{i,j+1} - T_{i,j}$$
$$\frac{\Delta T}{\Delta t} = \frac{dT}{dt} = \text{rate of temperature increase, }^{\circ}C/s$$

Besides, it can be considered that emulsion is a heterogeneous mixture of water and oil which the heat generated separately. The total volume rate of heat generation of emulsion is as follow:

$$q_{MW} = q_{MW,w} \Phi + q_{MW,o} (1 - \Phi)$$
(2.22)

where

2.6.2 Benefits of Microwave-Assisted Chemical Demulsification

The concept of microwave demulsification was first introduced by Klaila (1978) and Wolf (1986) in patent documents. When usage of microwave irradiation is applied, two principal mechanisms are simultaneously operative. One of these is a rapid increase in temperature, which reduces emulsion viscosity and breaks the outer film of droplets. The other is molecular rotation, which neutralizes the Zeta potential owing to rearrangement of electrical charges surrounding water molecules, resulting in movement of ions around droplets. A synthesis of these two mechanisms results in separation of an emulsion without addition of any chemical agent (Fang et al, 1988). Thus, oil recovered from an emulsion can be reused and secondary environmental pollution caused by facilitating chemicals is avoided. (in Kuo and Lee, 2010)

For all of the reasons discussed above, it is therefore of interest to investigate alternative separation procedures able to demulsify water-in-highly viscous crude oils at short times that are inexpensive, easy to implement, without time-consuming calibrations, and widely applicable a (Fortuny, M. et al, 2007) and it can decrease the usage of chemical so that it can minimize the environmental issues that are hotly discussed. The method is microwave which can increase the efficiency of the chemical

demulsification while helping to rescue the planet and saving the cost of operation and production.

A lot of activity has been developed recently regarding the use of microwave irradiation for demulsification purposes. This is because the microwave irradiation offers a clean, low-cost, and convenient method of heating, which often results in higher yields and shorter reaction times (Roussy, G.; Pearce, J. A., 1995). It has been known that the acceleration of reactions by exposure to microwaves results from material-wave interactions, leading to thermal effects easily estimated by temperature measurements (the so-called dielectric heating) and specific effects (not purely thermal) generally associated with the selective absorption of microwave energy by polar molecules (Perreux, L.; Loupy, 2002). In particular, materials dissipate microwave energy by two main mechanisms: dipole rotation, which is related to the alignment of molecules that have permanent or induced dipoles with the electric-field component of the radiation, and ionic conduction, which refers to the migration of dissolved ions with the oscillating electric field.

The objective of the present study is conducted to examine the influences oil soluble surfactant (Triton-X-100), sorbitan monooleate (Span 80/83), Polyorbates (Tween 20/80) and Sodium Dodecyl Sulfide (SDDS) on emulsion stabilization and microwave demulsification of w/o emulsions. The findings showed that emulsion stability is related to surfactant concentrations, stirring time, temperature, water-oil phase ratio and agitation speed, The demulsification rate was significantly accelerated by microwave radiation (Abdurahman H. Nour and Rosli M. Yunus, 2006)

The demulsification or coalescence rate was measured by the ratio of the volume of water separated to the total water content. The demulsification efficiency reaches 90% in a very short time under microwave radiation. The percentage of water separation was calculated from volume measurements as follows:

% water separation =
$$\frac{Volume \ of \ water \ layer, V(ml)}{Original \ amount \ of \ water, V_0(ml)} * 100\%$$
(2.23)

2.7 OTHERS DEMULSIFICATION OF CRUDE OIL EMULSION

2.7.1 Ultrasonic Emulsion Separation

Phase-separation methods based on the use of ultrasonic fields have received increasing attention in the demulsification process. The force on a particle, droplet or a bubble in an acoustic field is related to the difference in density and speed of sound within the particle and the host fluid or solvent that the particle suspended inside. Particles migrate to either pressure nodes or antinodes of the standing acoustic wave field as a result of this primary acoustic force. Subsequent agglomeration of particles or droplets or bubbles coalescence is induced as a result of attractive secondary interparticle acoustic forces. These methods exploit the difference in density and speed of sound within dispersed and continuous phases, which is naturally present in most dispersions. Thus the constraints regarding the type of 2 materials that can be separated are minimal. In fact, these methods can be used to separate the dispersed phase even from neutrally buoyant dispersions as long as the speed of sound through the two phases is different. Besides, the dimensions of the devices that operate on this method can range from one-half wavelength of sound to several wavelengths, based on the need. These devices are easily to scale and contain no moving parts. Besides, these methods typically use acoustic fields that are very gentle on particles and this makes them suitable for the use in various biological applications (Pangu, 2006).

Ideas to apply ultrasound for emulsion breaking are found in patents and very limited numbers of scientific papers. 20 kHz ultrasound attempts were applying to crude oil emulsions (Gou, S. et al, 2005), irradiation of 200 kHz to 3 MHz ultrasound to the reaction mixture for biodiesel production (Maeda, Y. et al, 2005), separation of a stable O/W emulsion of the wastewater from washing raw wool by using 20 kHz followed by

electrolysis (Stack, L. et al, 2005). Pangu and Feke, 2004 used an acoustic chamber filled with porous medium for the separation of dilute dispersion of oil and water. The irradiation enhances the separation. However, explanation of the enhancement effect was made with the comparison between on and off of ultrasound and sometimes the comparison was qualitative. Effort has been lacking to quantify the change of the degree of separation in ultrasonic emulsion breaking. Therefore, no systematic discussion has been made on the effect of irradiation conditions on the separation degree. The difficulty in quantifying the separation is probably cause by the complexity of the separation phenomena under ultrasonic irradiation. It has been understood that emulsion breaking is a result of the combination of three basic processes of creaming, coagulation and coalescence. In addition to the force for aggregating droplets, ultrasonic irradiation causes various side effects to the emulsion samples. Rise of the temperature of the emulsion sample due to the absorption of ultra sonic energy can cause the instability of the emulsion and as mention before if too high of temperature will destroy the properties of the crude oil and decrease the quality of the crude oil and decrease the value of the valuable crude oil¹. Streaming of acoustic disturbs the emulsion and the mixing suppresses the splitting. (Susumu, Kikumoto and Tokuyama, 2009)

2.7.2 Electrical Demulsification

Among the many different methods of demulsification, for instance, centrifugation technique and sedimentation technique, the electrostatic demulsification method in a high-voltage field is one of the most effective and simplest demulsification methods. Electrostatic forces cause the coalescence of the fall readily due to electric forces or gravity. These forces increase dramatically as the distance between the dispersed water droplets becomes lesser. An efficient demulsification process can be achieved with both Direct Current (DC) and Alternating Current (AC) fields. In DC fields, the electrophoretic droplet motion enhances the probability of coalescence, whereas in AC fields, the greater motion in the bulk fluids is necessary to increase the coalescence. Therefore, the AC field is more suitable for the continuous demulsification

process which will decrease the cost of production as it is continuous without have to stop frequently. The following parameters are considered to have the effect on the demulsification kinetics: (operating conditions) voltage, frequency, temperature, degree of mixing, shape, and distance of two electrodes; (emulsion properties) density, viscosity, interfacial tension, water drop size, holdup, surfactant concentration in oil phase, electrolyte concentration in water phase (Kim, B.Y. et al, 2002).

Furthermore, electrostatic grids are sometimes used for emulsion treatment. High voltage electricity (electrostatic grids) is often an effective means of breaking or destabilizing emulsions. It is generally theorized that water droplets have an associated net charge, and when an electric field is applied, the droplets move about rapidly and collide with each other more frequently and coalesce. The electric field also disturbs the interfacial film by rearranging the polar molecules, thereby weakening the rigid film and enhancing coalescence. The electrical system consists of a transformer and electrodes that provide high-voltage alternating current. The electrodes are placed to provide an electric field that is perpendicular to the direction of flow. The distance between the electrodes is often adjustable so that the voltage can be varied to meet the requirement and degree of stability of the emulsion being treated. Electrostatic dehydration usually is used with chemical and heat addition. Invariably, the use of electrostatic dehydration results in reduced heat requirements. Lower temperatures result in fuel economy, reduced problems with scale and corrosion formation, and reduced light-end loss. It also can reduce the damage of the crude oil and affect the quality of the crude oil. Electrostatic grids can also lead to a reduction in the use of emulsion-breaking chemicals which will help reduce the environmental issues and help save the earth. The one limitation of electrostatic dehydration is shorting (arcing), which normally happens when excess water is present. Recent designs in electrostatic grids have eliminated shorting (arcing) (Kokal and Aramco, 2006).

The industrial system of petroleum desalting comprises of two desalting stages, including water recycling, as shown in **Figure 2.20** which picture the desalting system employed in petroleum refineries These are normally modular, high-speed desalting units, to which an external electric field is applied, and where the emulsion is injected

into the space between the electrodes. The fluid flow from the continuous phase is considered to be horizontal in the volume between the electrodes and vertical after it passes the region around the electrodes, as shown in Figure 2.21 which picture the discharge of the emulsion between the electrodes and forces that act upon the droplets. The small droplets are affected by both the action of the electric field and gravitational force. They then agglutinate and are separated from the continuous phase. The smaller droplets that are not large enough to be decanted remain in the petroleum that exits the desalting unit. The time in which the emulsion remains under the influence of the electric field is calculated by the equation for the speed of the horizontal discharge from the continuous phase, from the moment the emulsion exits the central distributor until it leaves the group of electrodes. The balance of forces that act upon the droplets leads to the formulation of a mathematical model which enables the calculation of the time between collisions, the speeds immediately before collisions and the trajectory of the droplets. The operational variables that have the most influence in this process are the operating temperature, the electric power gradient, the quantity of water in the mixture and the density and viscosity of the petroleum. The formulated model enables the study of the influence of these variables on the efficiency of the separation of the mixture, hence enabling the process to be optimized. (Bresciani. et al. 2010)



Figure 2.20: The desalting system employed in petroleum refineries.

Source: Antonio (2010)



Figure 2.21: Discharge of the emulsion between the electrodes and forces that act upon the droplets

Source: Antonio (2010).

2.8 SUMMARY

In a nutshell, demulsification of the w/o emulsion is fully depend on the stability of the emulsion cause by natural emulsify or additive emulsify. Hence different methods have been introduced to separate w/o emulsions and every method has it own advantages and disadvantages to improve the separation efficiency. Therefore, the method chosen has to be relate to environmental issues, choosing the method which has the least impact to environment is the better way to preserve our earth while meeting the market demand. Because of that chemical with microwave-assisted demulsification method is chosen as a method to conduct the experiment as through a lot of deliberation and consideration related to environment and production, it meet on both issues concern.

Detail methodology and material needed to conduct the experiment will be fully explained in the next chapter which is Chapter 3 Methodology.

CHAPTER 3

MATERIALS AND METHODS

3.1 INTRODUCTION

In this chapter, detail materials used and needed and experiment procedures will be listed out in order to conduct the research. In addition, in this chapter the detail information of the research scopes will be explained clearly based on the method we used.

This chapter will list out the preparation of water-in-crude oil emulsions by using various emulsifiers base on the characteristics of emulsions in forms of physical and chemical properties that are typically obtained in the oilfield in order to produce the composition of w/o we needed to analyze and conduct the experiment.

Next, the equipments needed to analyze the w/o emulsions also will be listed out and are briefly introduced the purpose of choosing the equipments. In addition, the process to undergo the demulsification process will be detail explain in order to demulsify the w/o emulsions which have been prepared before by using several pure chemical demulsifiers. The demulsification of w/o emulsions by pure chemical method and pure chemical with microwave-assisted will be examined. Then, the overall performance will be investigated after the demulsification process has been done. . The effectiveness of the demulsification is crucial in the research and therefore in this chapter the experimental procedures will be explained in detail and assisted by a flow chart.

3.2 PREPARATION OF WATER-IN-CRUDE OIL EMULSIONS

3.2.1 Type of Emulsifiers

The emulsifiers are used for the preparation of w/o emulsions, this is very crucial in choosing the right emulsifiers to prepare the w/o emulsions as the emulsifier is used to stabilize the w/o emulsions, so that we can analyze the right composition of w/o emulsions which same as the crude oil which is extract from oilfield in oil industries.

A stable w/o emulsion is required as it enables to test the real and precise degree of effectiveness of demulsification process by applying pure chemical or pure chemical with microwave-assisted methods. In addition, artificial or manufacture emulsifiers are used as the pure crude oil in laboratory does not contain natural emulsifier like (including waxes), aromatics, resins and asphaltenes (SARA). Below is the type of emulsifiers needed to prepare w/o emulsions:

Table 3.1: The Artificial emulsifiers used in emulsions

Emulsifier	Emulsifier (Scientific)			
Non-ionic water soluble surfactant	Triton-X-100			
Sorbitan monooleate	Span 83			
Cocamide	DEA			

3.2.2 Fluids and Their Physicochemical Characteristics

As the research is under the supervision of Mr Abdurahman H. Nour who is very famous in this demulsification process and has been receiving awards and attended many well-known conferences and is a very talented lecturer, hence the crude oil will be provided or suggested by Mr. Abdurahman. Abdurahman et al, 2007 suggested that the crude oil samples are obtained from Petronas Refinery.

Some physicochemical properties of the fluids, such as density, viscosity, shear rate, shear stress, temperature, surface tension (γ s) and interfacial tension (γ i) are chosen to identify the characteristic of the crude oil samples from Petronas Refinery in order obtained a clearer behavior of the w/o emulsions and can easily design a method to demulsify it . Densities of liquids, viscosity, shear rate, shear stress, and temperature were obtained by applying Brookfield. Measurement of the surface tensions and interfacial tension will be carried out using Tension Meter which will be explained in detail in Section 3.3.3.

3.2.3 Characterization of Emulsions

The droplets size of water-in-crude oil emulsions which is the water as droplets and the crude oil as continuous phase will be analyze in order to observe the stability of w/o emulsions. We are proposed w/o emulsions that to be processed is analyzed in a light field optical microscope (ZEISS). The images were magnified 10 times to identify the mean diameter distribution of the water droplets in the mixture. The droplet size distribution graph will indicates that the mean diameter of the droplets of the mixture studied, which characterizes an emulsion whose droplet diameter normally exceeds 0.1 μ m.



Figure 3.1: Digital photograph of a sample of water-in-crude oil emulsion taken with an optical microscope optical microscope with increase of 10× (a) 50%-50% and (b) 30%-70%

Another method to observe the water droplet in the crude oil is that by detection of droplet freezing through the energy released by using a calorimeter. The theoretical determination of the relationship is difficult to obtain due to unknown parameters, as is shown in the later. Hence, an experimental determination involving microscopic observation of a limited number (1000) of droplets was performed. Detail information which this determination is done will be clearly described in **Section 3.2.1**. **Section 3.2.2** is devoted to the calorimetric method. (Adapted from Clausse et al., 2005)

The microscope used maybe change due to the availability in the laboratory.

3.2.2.1 Microscopic Analysis

One drop of emulsion samples is taken and gently deposited on a perfectly clean and smooth microscopic slide. The drop of emulsion is allowed to leak out on the plate without any exterior operation. No cover glass is placed on the sample emulsion to avoid any perturbation of the emulsion. Border areas pictures wherein the density of water droplets is low are taken. This was likely to observe that the number of droplets included was between 200 and 1000 depending on size. The pictures were analyzed with specific software. Present the results obtained as histograms showing either the number distribution of droplet size or the volume distribution. (Adapted from Clausse et al., 2005).

3.2.2.2 Calorimetric Analysis

The fundamental principle of this technique is that dispersed and bulk aqueous phases have different solidification features. A great number of research works dealing with undercooling phenomena (Broto, F., D. Clausse, 1976) have shown that the smaller the sample is, the lower is the solidification probability at any temperature below the melting temperature of the referred material. Therefore, it is estimated that during steady cooling, bulk and dispersed phases of an emulsion solidify at different temperatures and determination of these temperatures is a way to point out bulk and dispersed phases.

The masses that are concerned are determined through the corresponding energy released. Thermo grams are provided, and from their analysis, it is possible to obtain information about droplet sizes. By doing so, information on the sizes of a very large number of droplets, from 5×106 to 200×106 depending on droplets size and the volume of the emulsion sample under study, is obtained. This provides a great advantage in comparison with a simple and classic test for which a very small number of droplets are considered and they have to be diluted.

As seen before, the theoretical correlation between the most possible solidification temperature of a droplet (T^*) and its size (R_d) depends only on the properties of the aqueous phase (γ , Vi, Lm, and Tm) and on the rate of temperature decrease. In this work, we study a real and complex system, i.e., crude oil and production water. Because of salts are present in the aqueous phase, its properties are different from those of pure water. For the rate of temperature decrease, we used the same value (1 °C/min) for all tests, so the correlation we obtain in this study is usable only for our aqueous system and for the same rate of freezing.

Section 3.2.2.1 and 3.2.2.2 are adapted from Clausse et al., 2005

3.3 EXPERIMENTAL SETUP

3.3.1 Apparatus

The apparatus we needed in the demulsification of w/o emulsions is that we need 1 of 10L tank which will be used to fill the crude oil that is needed to conduct the experiment throughout the whole semester.

In addition we need also about 15 of 50 ml measuring cylinders and 15 of 200 ml measuring cylinders to undergo the emulsification with several different conditions for example the composition of water and crude oil. Meanwhile, we need plastic measuring jar as it is for mixing purpose as we need to mix the crude oil and water by adding emulsifier in the measuring cylinder. This is to mix the water and crude oil in a proper way

Besides, we need 15 of 50 ml measuring cylinders, 15 of 200 ml measuring cylinders and 5 of 250 ml beakers to undergo the demulsification with several different conditions for example the composition of water and crude oil with or without microwave-assisted.

3.3.2 Materials

The materials we require in the research are several types of demulsifiers to demulsify the different composition of w/o emulsions that we have prepared before by using several artificial emulsifiers. The demulsifiers are used to break the emulsions so that we can obtain pure crude oil that we want. While breaking the emulsion we can identify or test the emulsion to measure the efficiency of demulsifiers in demulsifying the w/o emulsions.

The types of materials which are demulsifiers are listed below:

Group	Demulsifier			
Coco Amine	Coco Amine			
Amines	Hexylamine			
Polyhydric alcohols	PEG-600			

Table 3.2: The Chemical demulsifiers used in demulsification tests

Source: Suggested from Abdurahman, H. N.

3.3.3 Equipment

There are several equipments needed to analyze the w/o emulsions so as we can determine the exact method to destabilize the emulsions and tabulate the data into a list to smoothen the work.

First equipment is Three Plate Propellers which is used to homogenize the emulsion and agitate the emulsion in emulsion preparation and demulsication preparation.

Second equipment is Brookfield which is used to measure the density, viscosity, shear rate, shear stress, temperature and revolution per minute (RPM). Density is very important to be taken into consideration as the density of the w/o emulsions will determine the amount of chemical demulsifier we need to break the emulsions. Besides, viscosity is also important to decide the precise method as the viscosity will affect the effectiveness or the performance of the demulsification process. All Brookfield laboratory viscometers are accurate within +/-1.0% of the measurement range in use and have a repeatability with +/-0.2% (Brookfield Inc.). Based on Scott Bader, the Brookfield viscometer is a very common type that is simple to operate and is often used as a QC tool to check a single viscosity measurement at a specified temperature, and they can also be used to get a basic rheology profile under lower shear conditions.

Third equipment that will be used is Tension Meter. Tension Meter is an instruments used to measure the surface tension (air and oil) and interfacial tension (oil and water) which influence the stability of the w/o emulsions and we need to examine the tension in order to break the emulsions with chemical demulsifiers effectively.

Fourth equipment is Microwave oven. Microwave oven is used as this research is microwave-assisted with chemical demulsification. Microwave oven is to improve or increase the performance of the demulsification so that the process can be conducted in the least of chemical usage but achieve the high efficiency.

Fifth is using the microscope which is used for droplets size measurement. Droplets size measurement is crucial as the smaller the droplets size the tighter the emulsions and the harder the demulsification can be carried out or the more stable is the w/o emulsions and vice versa. The types of microscopes suggested are listed in **Section 3.2.3**.

3.3.4 Experimental Procedure

3.3.4.1 Flow Chart of the Experimental Procedure



Figure 3.2 Flow Chart of the Experimental Procedure

3.3.4.2 Description of the Experimental Procedure

Experiment procedure is that first we have to mix the pure crude oil into the distilled water to emulsify the water into crude oil to produce the w/o emulsions into the compositions needed. Before that, we mix some emulsifiers with the crude oil to dissolve the emulsifiers into the oil to a homogeneous condition so that it can form an interfacial film on the surface of crude oil to encapsulate the water droplets to stabilize the emulsion in order to produce the specification of w/o emulsions as obtain from the oilfield.

Next, we have to test the emulsions to observe or check the emulsion is w/o or o/w with filter paper method or test tube method. We need w/o emulsions and we need to test the stability so as it is really in stable condition to allow the demulsification to take place. If phase inversion, we have to repeat from first step to obtain the w/o with stable condition.

Then, after the phase is what it is required, the demulsification can be carried out by adding pure chemical only and chemical with microwave-assisted to compare the effectiveness or performance of the demulsification so as we can tabulate the data into Result and Discussion. Several experiments have to be conducted to achieve the average results. This will enable to obtain the optimum results.

3.3.5 Calculations

3.3.5.1 Calculations for Emulsion Preparation

Specification	Justification				
Concentration	0.1 v%, 0.3 v%, 0.5 v%				
Emulsifier	(i) Span 83(ii) Triton X-100(iii) Cocamide DEA				
Sample of Crude oil	(i) 50-50% (w/o) (ii) 30-70% (w/o)				
Amount	70mL				
Agitation Speed	(i) RPM 500 (ii) RPM 1000 (iii) RPM 1500				
Calculation	2x3x3x3 = 54 samples				
For 50-50%(200mL)	Crude oil needed= $54/2 \times 0.5 \times 70$ mL = 945 mL = 0.945 L				
For 30-70%(200mL)	Crude oil needed= $54/2 \ge 0.7 \ge 70$ mL = 1323 mL = 1.323 L				
Total Crude oil needed for Emulsion Preparation	0.945L + 1.323L = 2.268L				

Table 3.3: Information of Calculations for Emulsion Preparation

3.3.5.2 Calculations for Demulsification Preparation

Specification	Justification
Concentration	0.1v%, 0.3 v%, 0.5 v%
Demulsifier	(i) Cocoamine(ii) Hexylamine(iii) PEG-600
Sample of Crude oil	(i) 50-50% (w/o) (ii) 30-70% (w/o)
Amount	50ml and 200mL
Method	(i) Pure Demulsifier(ii) Pure Demulsifier + Microwave
Agitation Speed	(i) RPM 500 (ii) RPM 1000 (iii) RPM 1500
Calculation	1x2x6x3x3 = 108 samples
For 50-50%(50mL)	Crude oil needed= $108/4 \ge 0.5 \ge 50$ mL = 675 mL = 0.675 L
For 30-70%(50mL)	Crude oil needed= 108/4 x 0.7 x 50mL = 945mL = 0.945L
For 50-50%(200mL)	Crude oil needed= $108/4 \ge 0.5 \ge 200$ mL = 2700 mL = 2.7 L
For 30-70%(200mL)	Crude oil needed= 108/4 x 0.7 x 200mL = 3780mL = 3.78L
Total Crude oil needed for Demulsification Preparation	0.675L + 0.945L + 2.7L + 3.78L = 8.1L

Table 3.4: Information of Calculations for Demulsification Preparation

Total Volume of Crude Oil needed for the entire research (roughly)

= 2.268L + 8.1L

= 10.368L

Volume of emulsifier or demulsifier needed is

= v % x 50ml or 70ml or 200mL (generally)

3.3.5.3 Detail Steps

- 1. First, we have to prepare the emulsions that the composition we wanted which is w/o emulsions 50%-50% and 30%-70%.
- 2. When preparing for the w/o emulsions, we need to use synthetic emulsifiers to prepare the w/o emulsions we wanted. We need to prepare 3 different concentrations of emulsifiers which are 0.1v%, 0.3 v% and 0.5 v% to emulsify the water into crude oil. We will use 3 different type of emulsifiers such as:-
 - (i) Span 83(ii) Triton X-100(iii)Cocamide DEA
- 3. After that, we emulsify the two different compositions of w/o emulsions with the 3 emulsifiers with 3 different concentrations. Next, we need to agitate them by using three plate propellers device with 3 different rpm which are:-
 - (i) RPM 500(ii) RPM 1000(iii) RPM 1500
- 4. After we add the emulsifier into the crude oil, we need to agitate the solution slowly using three plate propellers for about 2 minutes to dissolve the emulsifier into crude oil in order for it to form an interfacial film at the surface of the oil in order to encapsulate the water droplets.
- 5. Then only we add the ultra purified water slowly into the solution to homogenize the solution for about 2 minutes with higher agitation but not to vigorous which is below RPM 200.
- 6. Next, we turn to the agitation we need as Step 3 stated for about 3 minutes to produce the emulsion we wanted.
- Right after that, test the emulsion using filter paper and test tube method to ensure the emulsion is w/o and not o/w. If w/o, we can proceed, if not repeat Step 4 to 6.
- 8. After that, we need to use the Tension Meter to measure the surface tension which is the tension between atmosphere air with crude oil and the interfacial tension which is the tension between the crude oil and the water droplets.

- 9. Afterward, we will put the samples (total up 54 samples) to settle down to obtain the best w/o emulsions.
- 10. Next, we will examine the droplets size of w/o emulsions with the rest of the samples prepared by using microscope and we need to take a picture of the droplet size as shown in Figure 3.1. Then, the picture taken will be analyzed using software AxioVision Rel. 4.8 to obtain the droplet size distribution.We will use the following formula, Stokes' Law to observe the stability of the w/o emulsions to calculate the settling velocity by taking the mean droplets size calculated from the droplet size distribution analysis:-

$$v = \frac{(\rho_w - \rho_o) D^2 g}{18\mu}$$
(3.1)

where

υ	= settling velocity of the water droplets
$\rho_{\rm w}$	= density of water
ρ_o	= density of oil
D	= diameter of droplets
g	= acceleration caused by of gravity
μ	= oil viscosity

This formula can also be used to test the appropriate or optimum agitation (rpm). Agitation is very crucial for emulsion stability. Agitation will cause the emulsion breaking, the particles will move faster and velocity, υ increases when come to demulsification.

11. After that, we will take the rest of the samples prepared for Brookfield device to measure the viscosity, shear rate, shear stress, and torque which will be used to examine the emulsion behavior in Newtonian or Non-Newtonian motion. For the Brookfield test, we need to 5 to 7ml for every temperature. The parameters like viscosity, shear rate, shear stress, and torque need to be tested at

(i) Temperature (°C) : Ambient Temperature, 50, 70, 90

- (ii) Agittion Speed (rpm) : 100, 150, 200, 250
- 12. Then, when the w/o emulsions samples are chosen. The Demulsification process can be conducted. There are 3 different demulsifiers which are

(i) Cocoamine

(ii) Hexylamine (iii)PEG-600

Next, there are 6 ways to demulsify the w/o emulsions which 3 pure chemical demulsifiers and 3 pure chemical demulsifiers plus microwave-assisted. In addition, there are 3 different concentrations required which are 0.1v%, 0.3 v% and 0.5 v% for the demulsifiers. Furthermore, the agitation required is RPM 500, RPM 1000 and RPM 1500. Hence total up there are 108 samples.

- 13. When conduct the demulsification, repeat Step 4 till 7 to prepare the emulsion but for the Step 6 the agitation is the agitation of the two samples which have been chosen in 50%-50% and 30%-70% as the most stable emulsion.
- 14. Afterward, put the demulsifiers inside the emulsion and agitate using the agitation stated in Step 12 for 3 minutes.
- 15. For demulsification with microwave assisted, after 3 minutes, it is put into microwave with three detector at top, middle and bottom to examine their temperature using Pico® Log Recorder. The emulsion is being micro waved for 2-3 minutes with Power 60% (540 Watts).
- 16. Then, the demulsification of w/o emulsions are left to settle down in the measuring cylinder. After that, we will observe the separation by naked eyes.
- 17. Finally, the data are collected and tabulated into tables for Result and critical Discussion to obtain the overall effectiveness performance of the demulsification of w/o emulsions.

3.4 SUMMARY

In a nutshell, in this chapter the materials and the methods are clearly stated so that when conducting the experiment, there is a clear guideline to lead one to conduct the experiment accordingly. The result is collected and tabulated into tables and discussions will be covered in Chapter 4 Results and Discussions in PSM II.

CHAPTER 4

RESULT AND DISCUSSION

4.1 **OBSERVATIONS**

4.1.1 Quantitative Observations

4.1.1.1 Emulsions of 50%-50% (w/o)

Picture of Separation		Water		Oil		
After 2 days	Amount	Time	Clearity	Amount	Time	Clearity
(Water/Emulsion/Oil	Separated	Start to		Separated	Start to	
Layer, ml)	(%)	Separate		(%)	Separate	
40ml Sample		(min)			(min)	
AND CLARKS	0	-	-	75	720	Clear
0						
(0/23/17)						
Two Layers						
	Picture of Separation After 2 days (Water/Emulsion/Oil Layer, ml) 40ml Sample International Content of the second	Picture of SeparationAfter 2 daysAmount(Water/Emulsion/OilSeparatedLayer, ml)(%)40ml Sample0Image: Separation of the second se	Picture of SeparationWaterAfter 2 daysAmountTime(Water/Emulsion/OilSeparatedStart toLayer, ml)(%)Separate40ml Sample(min)0-Image: Separate s	Picture of SeparationWaterAfter 2 daysAmountTimeClearity(Water/Emulsion/OilSeparatedStart toImage: ClearityLayer, ml)(%)SeparateImage: Clearity40ml Sample(min)Image: ClearityImage: Clearity0Image: Clearity0Image: Clearity0Image: Clearity0Image: Clearity0Image: ClearityImage: ClearityImage: ClearityImage: Clearity0Image: Clearity0Image: Clearity0Image: Clearity0Image: Clearity0Image: Clearity0Image: Clearity0Image: Clearity11Image: Clearity<	Picture of SeparationWaterManountTimeClearityAmountAfter 2 daysAmountSeparatedStart toSeparatedSeparated(Water/Emulsion/OilSeparated(%)Separate(%)(%)40ml Sample(%)Separate(min)-75Image: Separate	Picture of SeparationWaterClearityAmountTimeAfter 2 daysAmountTimeClearityAmountTime(Water/Emulsion/OilSeparatedStart toSeparatedSeparatedSeparatedLayer, ml)(%)Separate(min)(%)Separate(%)40ml Sample(min)75720Image: Separate sepa

Table 4.1: Observation of w/o Emulsion (50%-50%)

Sample 10 Cocamide DEA 0.1v% RPM 500 (Mean Droplet Size = 0.5467 μ m)	(15/6/19) Three Layers	75	30	Clear with little oil suspended	95	1440	Clear
Sample 19 Triton X- 100 0.1v% RPM 500 (Mean Droplet Size = 0.853 μ m)	(17/22/1) Three Layers	85	30	Very clear			Clear
Sample 4 Span 83 0.3v% RPM 500 (Mean Droplet Size = 1.1313 μ m)	(3/20/17) Three Layer	15	2880	Cloudy	85	120	Clear

Sample 13 Cocamide DEA 0.3v% RPM 500 (Mean Droplet Size = 0.56 μ m)	(15/10/15) Three Layers	75	30	Cloudy	75	360	Clear with water suspended
Sample 22 Triton X- 100 0.3v% RPM 500 (Mean Droplet Size = 0.8203 μ m)	(17/21/2) Three Layers	85	30	Clear	10	2160	Clear
Sample 7 Span 83 0.5v% RPM 500 (Mean Droplet Size = 0.901 μ m)	(0.5/28.5/11) Three Layers	2.5	2880	Cloudy	55	360	Clear

Sample		80	30	Cloudy	90	360	Clear with
16 Cocamide	16						little water
DEA	Section 1						suspended
0.5v% RPM 500							
(Mean							
Droplet							
Size =	100 C						
0.7497	1 73						
μm)							
	(16/6/18)						
	Three Layers						
Sample		82.5	30	Clear with	30	2160	Clear with
25 Triton X-				little oil			water
100				suspended			suspended
0.5v% RPM 500							
(Mean							
Droplet							
Size =							
0.57	and the second						
μm)							
	(16.5/17.5/6)						
	Three Layers						
Sample 2		0	-	-	60	240	Clear
0.1v%							
RPM							
(Mean							
Droplet	and the second						
Size =							
0.2233							
um)							
, piii)	100 -						
	(0/28/12)						
	Two Layers						

Sample 11 Cocamide DEA 0.1v% RPM 1000 (Mean Droplet Size = 0.4777 μ m)	(20/0/20)	100	30	Cloudy	100	720	Clear with water suspended
	Three Layers (Thin layer of Extra Heavy Oil)						
Sample 20 Triton X-100 0.1v% RPM 1000 (Mean Droplet Size = 0.387 μ m)	(20/0/20) Three Layers (Thin layer of Extra Heavy Oil)	100	30	Clear with little oil suspended	100	240	Clear with little discoloured

Sample 5 Span 83 0.3v% RPM 1000 (Mean Droplet Size = 0.15 μ m)	(0/33/7) Two Layers	0	_	_	35	60	Clear
Sample 14 Cocamide DEA 0.3v% RPM 1000 (Mean Droplet Size = 0.2067 μ m)	(17/20/3) Three Layers	85	30	Cloudy	15	120	Cloudy
Sample 23 Triton X- 100 0.3v% RPM 1000 (Mean Droplet Size = 0.35 μ m)	(17/23/0) Three Layers (4ml Clear Water)	85	30	Cloudy	0	-	-
Sample 8 Span 83 0.5v% RPM 1000 (Mean Droplet Size = 0.175 μ m)	(0/35/5) Two Layers	0	_	_	25	1440	Clear
---	--	------	----	--------------------------------	----	------	--------
Sample 17 Cocamide DEA 0.5v% RPM 1000 (Mean Droplet Size = 0.2933 μ m)	(15/8/17) Three Layers	75	30	Cloudy	85	2880	Cloudy
Sample 26 26 Triton X- 100 0.5v% RPM 1000 (Mean Droplet Size = 0.2533 μ m)	(18.5/21.5/0) Three Layers (3ml Clear Water)	92.5	30	Clear with oil suspended	0	-	-

Sample 3 Span 83 0.1v% RPM 1500 (Mean Droplet Size = 0.1123 μ m)	(0/30/10) Two Layers	0	-	-	50	120	Clear
Sample 12 Cocamide DEA 0.1v% RPM 1500 (Mean Droplet Size = 0.2433 μ m)	(18/9/13) Three Layers	90	30	Cloudy	65	360	Cloudy
Sample 21 Triton X- 100 0.1v% RPM 1500 (Mean Droplet Size = 0.387 μ m)	(16/9/15) Three Layers	80	30	Very clear with little oil suspended	75	60	Cloudy

0 1 (and the second s	0			22.5	(0	<u>C1</u>
Sample o Span 83 0.3v% RPM 1500 (Mean Droplet Size = 0.13 μ m)	(0/35.5/4.5) Two Layers	U	-	-	22.5	00	Ciear
Sample 15 Cocamide DEA 0.3v% RPM 1500 (Mean Droplet Size = 0.2333 μ m)	(18.5/21.5/0) Three Layers (Thin layer of Extra Heavy Oil)	92.5	30	Cloudy	0	-	-
Sample 24 Triton X- 100 0.3v% RPM 1500 (Mean Droplet Size = 0.1783 μ m)	(17/23/0) Three Layer (1ml Clear Water)	85	30	Cloudy	0	-	-

0 1 0		0			10	240	01
Sample 9 Span 83 0.5v% RPM 1500 (Mean Droplet Size = 0.09 μ m)	(0/38/2) Two Layers	0	-	-	10	240	Clear
Sample 18 Cocamide DEA 0.5v% RPM 1500 (Mean Droplet Size = 0.1183 μ m)	(17/23/0) Four Layers (2ml Clear Water and Thin Layer of Extra Heavy Oil)	85	30	Cloudy	0	-	-
Sample 27 Triton X- 100 0.5v% RPM 1500 (Mean Droplet Size = 0.1467 μ m)	(17.5/22.5/0) Three Layer (0.5ml Clear Water)	87.5	30	Cloudy	0	-	-

4.1.1.2 Emulsions of 30%-70% (w/o)

Sample	Picture of Separation	Water			Oil			
(Mean	After 2 days	Amount	Time	Clearity	Amount	Time	Clearity	
Droplet	(Water/Emulsion/Oil	Separated	Start to		Separated	Start to		
Size, µm)	Layer, ml)	(%)	Separate		(%)	Separate		
	40ml Sample		(min)			(min)		
Sample	A DA	0	-	-	89.29	720	Clear	
28								
Span 83	14							
0.1v%								
RPM 500	and the second							
(0.91								
μm)	(0/15/25)							
	Two Layers							
Sample 37 Cocamide DEA 0.1v% RPM 500 (1.024 µm)	(0/13/27) Two Layers	0	-	-	96.43	720	Clear	
Sample		83.33	120	Clear	89.29	360	Clear	
46 Triton X- 100 0.1v% RPM 500 (0.3833 μm)	(10/5/25) Three Layers							

Table 4.2: Observation of w/o Emulsion (30%-70%)

Sample		0	-	-	96.43	240	Brownish
31 Span 83	Prove of						Clear
0.3v%							
(Mean							
Droplet							
Size =							
1.1833	(0/13/27)						
μm)	Four Layers						
	(Thin layer of Extra						
	Heavy Oil and						
	Bright Layer of						
	Emulsion)						
Sample		0	-	-	92.86	60	Clear
Cocamide							
DEA	Frank I						
RPM 500							
(Mean							
Droplet	Sec. 1						
Size =							
0.7953	(0/14/26)						
μm)	Three Layers						
	(A White layer is						
	formed at 3ml)						
Sample		83.33	60	Cloudy	0	-	-
49 Triton X-							
100							
0.3v% RPM 500	100 M						
(Mean							
Droplet							
Size =							
0.5167	(10/30/0)						
μm)	Two Layers						

Sample		0	-	-	96.43	240	Brownish
34 Span 83							Clear
0.5v%	Contraction of the local division of the loc						
RPM 500	1 Della						
(Mean							
Droplet	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1						
$S_{1Ze} =$							
0.7433							
μm)	(0/13/27)						
	Four Layers						
	(Thin layer of Extra						
	Heavy Oil and						
	Bright Layer of						
	Emulsion)						
Sample	1.2	16.67	2880	Cloudy	85.71	120	Clear
Cocamide							
DEA							
RPM 500	Z						
(Mean							
Droplet	ALC: NO. OF TAXABLE PARTY.						
Size =							
0.48							
μm)	(2/14/24)						
	Three Layers						
Sample		100	30	Clear	100	720	Clear
Triton X-	<u>.</u>						
100							
0.3V% RPM 500	2						
(Mean							
Droplet	1						
Size =	The second s						
0.6433	deally .						
μm)	(12/0/28)						
	Two Layers						

Sample		0	-	-	78.57	240	Clear
29 Span 83 0.1v%							
RPM 1000							
(Mean							
Droplet							
Size =							
0.3033	C.S.						
μm)	(0/18/22)						
	Two Layers						
Sample 38		0	-	-	80.36	720	Clear
Cocamide	4						
DEA 0.1v%							
RPM							
(Mean							
Droplet							
Size =							
0.4567	(0/17, 5/22, 5)						
μm)	Two Layers						
Sample		75	30	Clear	89.29	720	Clear
47 Triton X-							
100	The Lot of Lot o						
0.1v% RPM							
1000							
(Mean							
Droplet	State of the second						
Size =	es,						
0.2367	(9/6/25)						
μm)	Three Layers						

Sample	4.4	0	-	-	85.71	720	Brownish
32 Spap 83	12						Clear
0.3v%							
RPM	No. No.						
1000							
(Mean							
Droplet	See 1						
Size =							
0.3167							
μm)	(0/16/24)						
	Three Layers						
	(Thin layer of Extra						
	Heavy Oil)						
Sample		0	-	-	73.21	30	Clear
Cocamide	- C.						
DEA							
0.3v% RPM	TONIS!						
1000							
(Mean	and the second s						
Droplet	and the second second						
Size =							
0.3577	(0/19.5/20.5)						
μm)	Two Layers						
Sample		66.67	120	Clear	92.86	720	Clear
50							
Triton X-							
0.3v%	A PART OF						
RPM							
1000 (Maan	and the second						
Droplat	2						
Size -	18 C 1 1						
	the second						
0.3033	(8/6/26)						
μm)	Three Layers						

Sample		0	-	-	85.71	1440	Brownish
35 Span 83							Clear
0.5v%							
RPM							
(Mean							
Droplet							
Size =	34 J / 3						
0.2567							
μm)	(0/16/24)						
	Three Layers						
	(Thin layer of Extra						
	Heavy Oil)						
Sample		58.33	2160	Cloudy	85.71	30	Clear
44 Cocamide							
DEA	BINT						
0.5v% RPM							
1000							
(Mean	Section in the section of						
Droplet							
Size =	0						
0.2167	(7/9/24)						
μm)	Three Layers						
Sample		87.5	30	Clear	53.57	360	Clear
53 Triton V	P.						
100 Inton X-							
0.5v%							
RPM 1000							
(Mean	And a second						
Droplet							
Size =	and the second second						
0.22							
μm)	(10.5/14.5/15)						
. ,	Three Layers						

Sample 30 Span 83 0.1v% RPM 1500 (Mean Droplet Size = 0.1867 μ m)	(0/21.5/18.5) Two Layers	0	-	_	66.07	120	Clear
Sample 39 Cocamide DEA 0.1v% RPM 1500 (Mean Droplet Size = 0.2633 μ m)	(0/19.5/20.5) Two Layers	0	-	-	73.21	360	Clear
Sample 48 Triton X- 100 0.1v% RPM 1500 (Mean Droplet Size = 0.1867 μ m)	(9/7/24) Three Layers	75	30	Clear	85.71	720	Clear

Sample 33 Span 83 0.3v% RPM 1500 (Mean Droplet Size = 0.1833 μ m)	(0/20/20) Two Layers	0	_	_	71.43	720	Clear
Sample 42 Cocamide DEA 0.3v% RPM 1500 (Mean Droplet Size = 0.18 μ m)	(0/21/19) Two Layers	0	-	-	67.86	30	Clear
Sample 51 Triton X- 100 0.3v% RPM 1500 (Mean Droplet Size = 0.1967 µm)	(11.5/4.5/24) Three Layers	95.83	120	Cloudy	85.71	360	Clear

Sample		0	-	-	67.86	1440	Brownish
36 Span 83							Clear
0.5v%							
1500	ZAAD						
(Mean							
Droplet							
Size =							
0.16							
μm)	(0/21/19)						
	Three Layers						
	(Thin layer of Extra						
	Heavy Oil)						
Sample		41.67	2160	Cloudy	71.43	30	Clear
45 Cocamide	S The						
DEA							
RPM							
1500 (Mean							
Dronlet							
Size =							
0.1583	(5/15/20)						
um)	(5/15/20)						
	Three Layers	02.22	20	C1 1		2.40	<u></u>
Sample 54	1	83.33	30	Cloudy	75	240	Clear
Triton X-							
100 0.5v%	Part of the						
RPM							
1500 (Mean							
Droplet	all the						
Size =							
0.1783							
μm)	(10/9/21)						
. /	Three Layers						

4.1.1.3 Demulsifications of 50%-50% (w/o)

Sample	Picture of Separation	Water				Oil			
(Span 83	After 2 days	Amount	Time	Clearity	Amount	Time	Clearity		
0.5v% RPM	(Water/Emulsion/Oil	Separated	Start to		Separated	Start to			
1500)	Layer, ml)	(%)	Separate		(%)	Separate			
	40ml Sample		(min)			(min)			
Sample C1 PEG-600 0.1v%, RPM 500	(0/30/10) Two Layers	0	-	-	49.5	720	Clear		
Sample C10 Hexylamine 0.1v%, RPM 500	(0/38/2) Two Layers	0	-	-	9.9	360	Clear		
Sample C19 Cocoamine 0.1v%, RPM 500	(0/37/3) Two Layers	0	-	-	14.85	360	Clear		

Table 4.3: Observation of w/o Demulsification of Pure Chemical

Sample C4 PEG-600 0.3v%, RPM 500	(0/34/6)	0	-	-	29.7	1440	Clear
	Two Layers						
Sample C13 Hexylamine 0.3v%, RPM 500	(V/28/2)	0	-	-	9.9	720	Clear
	(0/38/2)						
	Two Layers						
	(With some						
	coagulation of water						
	but not significant)	05.04	2000	X 7			CI
Sample C22 Cocoamine 0.3v%, RPM 500	(17/7/16) Three Layers	85.86	2880	Very Clear with a lot of emulsion suspended	79.21	60	Clear

Sample	F. 8073	0			50 / 1	120	Clear
C7 PEG-600 0.5v%, RPM 500	(0/28/12) Two Layers				39.41	120	Cicai
Sample		0	-	-	14.85	360	Clear
C16							
Hexylamine							
0.5v%,							
RPM 500	(0/37/3)						
	Two Layers						
Sample C25 Cocoamine 0.5v%, RPM 500	(0/36/4)	0	-	-	19.8	240	Clear
	(U/36/4)						
	Two Layers						

Sample		0			0.0	1440	Clear
C2 PEG-600 0.1v%, RPM 1000	(0/38/2) Two Layers				7.7	1440	Ciedi
Sample C11 Hexylamine 0.1v%, RPM 1000	(0/37/3) Two Layers	0	-	-	14.85	1440	Clear
Sample C20 Cocoamine 0.1v%, RPM 1000	(0/37/3) Two Layers	0	-	-	14.85	720	Clear

Q		0			20.7	720	Class
C5 PEG-600 0.3v%, RPM 1000	(0/34/6) Two Layers				29.1	/20	Clear
Sample	uni.	0	-	-	24.75	720	Clear
C14							
Hexylamine	HINE IS						
0.3v%,	\mathcal{H}						
RPM 1000							
	(0/35/5)						
	Two Layers						
Sample		75.76	2880	Very	74.26	120	Clear
C23				Clear with			
Cocoamine	AN D			a lot of			
0.3v%,				emulsion			
RPM 1000				suspended			
	(15/10/15)						
	Three Layers						

Sample	Sale -	0	-	-	29.7	240	Clear
C8 PEG-600 0.5v%, RPM 1000	(0/34/6)						
		0.5.0.5	• • • • •				<u></u>
Sample C17 Hexylamine 0.5v%, RPM 1000	(19/6/15) Three Layers	95.96	2880	Very Clear with a little of oil suspended	74.26	720	Clear
Sample C26 Cocoamine 0.5v%, RPM 1000	(0/37/3) Two Layers	0	-	-	9.9	240	Clear

Sample C3 PEG-600 0.1v%, RPM 1500	(0/37.5/2.5) Two Layers	0	-	_	12.38	1440	Clear
Sample C12 Hexylamine 0.1v%, RPM 1500	(0/35/5) Two Layers	0	-	-	24.75	720	Clear
Sample C21 Cocoamine 0.1v%, RPM 1500	(0/37/3) Two Layers	0	-	_	14.85	120	Clear

Sample C6 PEG-600 0.3v%, RPM 1500	(0/33.5/6.5) Two Layers	0	-	-	32.18	240	Clear
Sample C15 Hexylamine 0.3v%, RPM 1500	(0.05/38.45/1.5) Two Layers (With some coagulation of water with not significant layer)	0.25	2880	Very Clear	7.43	360	Clear
Sample C24 Cocoamine 0.3v%, RPM 1500	(0/35.5/4.5) Two Layers	0	-	-	22.28	360	Clear

Sample	20	0	_	_	37.13	240	Clear
CO					57.15	210	Cioui
PEG-000							
0.50%,	-						
RPM 1500							
	and the second						
	(0/32.5/7.5)						
	Two Layers						
Sample		0	-	-	19.8	720	Clear
C18							
Hexylamine	VIII 1						
0.5v%,							
RPM 1500							
	States of States						
	AND AND ADD.						
	(0/36/4)						
	Two Layers						
Sample	G	0	-	-	19.8	240	Clear
C27	and the second se						
Cocoamine	ET I						
0.5v%,							
RPM 1500							
	1.15						
	A Com						
	(0/36/4)						
	Two Layers						

Sample	Picture of Separation		Water			Oil			
(Span 83	After 2 days	Amount	Time	Clearity	Amount	Time	Clearity		
0.5v% RPM	(Water/Emulsion/Oil	Separated	Start to		Separated	Start to			
1500)	Layer, ml)	(%)	Separate		(%)	Separate			
	40ml Sample		(min)			(min)			
Sample MC1 PEG-600 0.1v%, RPM 500	(0/164/18) Two Layers	0	-	-	19.78	30	Clear		
Sample MC10 Hexylamine 0.1v%, RPM 500	(2/166/13) Three Layers	2.21	1440	Very Clear	14.36	15	Clear		
Sample MC19 Cocoamine 0.1v%, RPM 500	(0/160/20) Two Layers	0		_	22.22	15	Clear		

Table 4.4: Observation of w/o Demulsification of Microwave-Assisted Chemical

Sample MC4 PEG-600 0.3v%, RPM 500	(0/142/38) Two Layers	0	-		42.22	15	Clear
Sample MC13 Hexylamine 0.3v%, RPM 500	(90/4/88) Three Layers	98.9	360	Very Clear with a little of oil suspended	96.7	15	Clear
Sample MC22 Cocoamine 0.3v%, RPM 500	(0/136/43) Two Layers	0	-	-	48.04	15	Clear

Sample MC7 PEG-600 0.5v%, RPM 500	(0/145/39)	0	_	_	42.39	15	Clear
	Two Layers						
Sample MC16 Hexylamine 0.5v%, RPM 500	(89/3/88) Three Layers	98.89	240	Very Clear with a little of oil suspended	97.78	15	Clear
Sample MC25 Cocoamine 0.5v%, RPM 500	(83/4/85) Three Layers	96.51	720	Very Clear with a little of oil suspended	98.84	15	Clear

Sample MC2 PEG-600 0.1v%, RPM 1000	(0/160/18) Two Layers	0	-	-	20.22	15	Clear
Sample MC11 Hexylamine 0.1v%, RPM 1000	(1/171/8) Three Layers	1.11	2880	Very Clear	8.89	15	Clear
Sample MC20 Cocoamine 0.1v%, RPM 1000	(0/162/14) Two Layers	0	-	-	15.91	15	Clear

Sample		0	-	-	22.22	15	Clear
MC5							C.cut
PEG-600	A CONTRACTOR						
$0.3v^{0/2}$							
DDM 1000							
	U						
	(0/160/20)						
	Two Layers						
Sample		94.38	720	Very	97.75	30	Clear
MC14				Clear with			
Hexylamine				a little of			
0.3v%,				oil			
RPM 1000				suspended			
	and the second division of the second divisio						
	- 11						
	(84/7/87)						
	Three Layers						
Sample	-	0	-	-	42.22	15	Clear
MC23							
Cocoamine							
0.3v%,							
RPM 1000	6 13						
	a ser						
	(0/142/38)						
	Two Layers						
		1	1		1	1	1

		<u>^</u>	r		21.11		C1
Sample MC8 PEG-600 0.5v%, RPM 1000	(0/152/28) Two Layers	0	-	-	31.11	15	Clear
Sample MC17 Hexylamine 0.5v%, RPM 1000	(88/3/89) Three Layers	97.78	360	Very Clear	98.89	60	Clear
Sample MC26 Cocoamine 0.5v%, RPM 1000	(84/4/84) Three Layers	97.67	120	Very Clear with a little of oil suspended	97.67	15	Clear

Sample		0	-	-	8.99	15	Clear
MC3							
PEG-600	N SALAN						
0.1v%							
RPM 1500	N.						
	0						
	(0/170/8)						
	Two Layers						
Sample		0	-	-	4.49	60	Clear
MC12	and the second						
Hexylamine							
0.1v%,							
RPM 1500							
	(0/174/4)						
	Two Layers						
Sample	and the second second	0	-	-	15.91	15	Clear
MC21	STATISTICS.						
0.1V%,							
RPM 1500	Street, Square,						
	(0/162/14)						
	Two Layers						

Sample		0	-	_	17 78	15	Clear
MC6	7				1,.,0	10	Citur
DEC 600							
$0.2 v^{0/2}$							
0.3V70,	8 11						
KPM 1500							
	(0/164/16)						
	Two Layers						
Sample	-	89.89	2880	Very	96.63	60	Clear
MC15				Clear with			
Hexylamine	The second second			a lot of			
0.3v%,				emulsion			
KI WI 1500				suspended			
	(80/12/86)						
	Three Layers						
Sample	-	0	-	-	29.89	15	Clear
MC24							
Cocoamine							
0.3v%,							
RPM 1500	(0/148/26)						
	(0/148/20)						
	I wo Layers						

	(m			1	Î.	1	1
Sample	In contrast, per time and there is also if this rad call agains, sits rais into its time the time and the intervent again.	0	-	-	13.79	15	Clear
MC9							
PEG-600							
0.5v%							
RPM 1500							
10 W 1500							
	(0/162/12)						
	Two Lovers						
Comula		02.12	720	Varre	00 00	20	Class
Sample		92.15	720	very	90.00	30	Clear
MC18				Clear			
Hexylamine							
0.5v%,							
RPM 1500							
	(82/8/88)						
	Three Lavers						
Coursel.		1.12	2000	Class	(0.(7	15	<u>C1</u>
Sample		1.12	2880	Clear	00.07	15	Clear
MC27							
Cocoamine							
0.5v%,							
RPM 1500							
	(1/122/54)						
	(1/125/34)						
	Three Layers						

4.1.1.4 Demulsifications of 30%-70% (w/o)

Sample	Picture of Separation		Water			Oil				
(Span 83	After 2 days	Amount	Time	Clearity	Amount	Time	Clearity			
0.5v% RPM	(Water/Emulsion/Oil	Separated	Start to		Separated	Start to				
1500)	Layer, ml)	(%)	Separate		(%)	Separate				
	40ml Sample		(min)			(min)				
Sample C28 PEG-600 0.1v%, RPM 500	(0/39/1) Three Layers (2ml of Impurities at bottom)	0	-	-	3.55	240	Clear			
Sample C37 Hexylamine 0.1v%, RPM 500	(0/36/4) (Water-riched and Oil- riched emulsion)	0	-	-	14.18	120	Clear			
Sample C46 Cocoamine 0.1v%, RPM 500	(0/22/18) Two Layers	0	-	-	63.83	60	Clear			

Table 4.5: Observation of w/o Demulsification of Pure Chemical

Sample C31 PEG-600 0.3v%, RPM 500	(0/39/1) Four Layers (5ml of Impurities at bottom and Water- riched emulsion and Oil-riched emulsion)	0	-	_	3.55	240	Clear
Sample C40 Hexylamine 0.3v%, RPM 500	(0/33/7) Three Layers (Water-riched emulsion and Oil- riched emulsion)	0	-	-	24.82	60	Clear
Sample C49 Cocoamine 0.3v%, RPM 500	(0/21/19) Two Layers	0	-	_	67.38	30	Clear

Sampla		0			2 5 5	260	Clear
Sample C34 PEG-600 0.5v%, RPM 500	(0/39/1) Three Layers (2ml of Impurities at bottom)	0			3.55	360	Clear
Sample	643	16.95	2880	Very	28.37	60	Clear
C43	Sec. and			Clear			
Hexylamine	150 177 211						
0.5v%, RPM 500							
	(2/20/0)						
	(2/30/8)						
<u> </u>	I nree Layers	0			5674	20	Class
Sample	20	U	-	-	56.74	30	Clear
Cocoamine							
0.5v%.	-						
RPM 500	1						
	(0/24/16)						
	Two Layers						

Sample C29 PEG-600 0.1v%, RPM 1000	(0/39/1) Three Layers (Water-riched emulsion and Oil- riched emulsion)	0	-	_	3.55	360	Clear
Sample	111	0	-	-	14.18	120	Clear
C38	and and the						
0.1v%.							
RPM 1000							
	(0/36/4)						
	Three Layers						
	(Water-riched						
	emulsion and Oil-						
	riched emulsion)						
Sample C47 Cocoamine 0.1v%,		0	-	-	65.6	30	Clear
RPM 1000							
	(0/21.5/18.5)						
	Two Layers						

Sample C32 PEG-600 0.3v%, RPM 1000	(0/39/1) Three Layers (Water-riched emulsion and Oil- riched emulsion)	0	_	_	3.55	240	Clear
Sample C41 Hexylamine 0.3v%, RPM 1000	(0/33/7) Three Layers (Water-riched emulsion and Oil- riched emulsion)	0	-	-	24.82	120	Clear
Sample C50 Cocoamine 0.3v%, RPM 1000	(0/22/18) Two Layers	0	-	-	63.83	30	Clear
Sample		0	-	-	3.55	360	Clear
------------	-------------------	------	------	-------	-------	-----	-------
C35	145						
PEG-600							
0.5v%,							
RPM 1000							
	(0/39/1)						
	Three Lavers						
	(Water-riched						
	emulsion and Oil-						
	riched emulsion)						
Sample		8.47	2880	Verv	14.18	60	Clear
C44				Clear			
Hexylamine							
0.5v%,	MILLING.						
RPM 1000							
	100						
	(1/35/4)						
	Three Layers						
Sample	1 23	0	-	-	58.51	30	Clear
C53							
Cocoamine							
0.5v%,							
RPM 1000	and the second						
	Alton						
	0						
	(0/23.5/16.5)						
	Two Layers						

	10.0 S - 10.0						
Sample C30 PEG-600 0.1v%, RPM 1500	(0/39/1) Three Layers	0	_	_	3.55	360	Clear
	(Water-riched						
	emulsion and Oil-						
	riched emulsion)						
Sample C39 Hexylamine		0	-	-	10.64	240	Clear
0.1v%, RPM 1500	(0/37/3)						
	Three Lavers						
	(Water-riched						
	emulsion and Oil-						
	riched emulsion)						
Sample C48 Cocoamine 0.1v%, RPM 1500	(0/22/18) Two Layers	0	-	-	63.83	30	Clear

Sample C33 PEG-600 0.3v%, RPM 1500	(0/39/1) Three Lavers	0	-	-	3.55	360	Clear
	(Water-riched						
	emulsion and Oil-						
	riched emulsion)						
Sample C42 Hexylamine 0.3v%, RPM 1500	(0/36/4) Three Layers (Water-riched emulsion and Oil- riched emulsion)	0	-	-	14.18	240	Clear
Sample C51 Cocoamine 0.3v%, RPM 1500	(0/23/17) Two Layers	0		_	60.28	30	Clear

Sample C36 PEG-600 0.5v%, RPM 1500	(0/39/1) Three Layers (Water-riched emulsion and Oil- riched emulsion)	0	_	_	3.55	360	Clear
Sample C45 Hexylamine 0.5v%, RPM 1500	(0.05/37.95/2) Two Layers (With some coagulation of water with not significant layer)	0.42	2880		7.09	120	Clear
Sample C54 Cocoamine 0.5v%, RPM 1500	(0/20.5/19.5) Two Layers	0	-	-	69.15	30	Clear

Sample	Picture of Separation		Water		Oil			
(Span 83	After 2 days	Amount	Time	Clearity	Amount	Time	Clearity	
0.5v% RPM	(Water/Emulsion/Oil	Separated	Start to		Separated	Start to		
1500)	Layer, ml)	(%)	Separate		(%)	Separate		
	40ml Sample		(min)			(min)		
Sample	a a a a a a a a a a a a a a a a a a a	1.85	2880	Clear	70.63	240	Clear	
MC28	TA CAL							
PEG-600	a set							
0.1v%,								
RPM 500								
	(1/90/89)							
	Three Lavers							
Sample		0	_	_	48.67	30	Clear	
MC37	STREET, STREET,							
Hexylamine								
0.1v%.								
RPM 500								
	The same in second							
	(0/120/62)							
	Two Layers							
Sample		72.8	720	Cloudy	50.9	30	Clear	
MC46								
Cocoamine								
0.1v%,								
RPM 500								
	-							
	1. 1. 2							
	(38/74/62)							
	Three Layers							

Table 4.6: Observation of w/o Demulsification of Microwave-Assisted Chemical

Sample MC31 PEG-600 0.3v%, RPM 500	(1/88/91) Three Lavers	1.85	2880	Clear	72.22	30	Clear
Sample MC40 Hexylamine 0.3v%, RPM 500	(32/24/124) Three Layers	59.26	720	Very Clear	98.41	15	Clear
Sample MC49 Cocoamine 0.3v%, RPM 500	(45/35/80) Three Layers	93.75	240	Cloudy	71.43	60	Clear

	and the second se						
Sample MC34 PEG-600 0.5v%, RPM 500	(2/89/88) Three Layers	3.72	1440	Clear	70.23	30	Clear
Sample MC43 Hexylamine 0.5v%, RPM 500	(44/13/127) Three Layers	79.71	240	Very Clear with a little oil suspended	98.6	15	Clear
Sample C52 Cocoamine 0.5v%, RPM 500	(45/53/80) Four Layers (Water-rich and oil- rich emulsion)	84.27	120	Cloudy	64.21	60	Clear

Sample MC29 PEG-600 0.1v%, RPM 1000		0	-	_	74.68	120	Clear
	(0/84/92) Two Layers						
Sample MC38 Hexylamine 0.1v%, RPM 1000	(0/154/25) Two Layers	0	-	-	19.95	30	Clear
Sample MC47 Cocoamine 0.1v%, RPM 1000	(22/120/40) Three Layers	40.29	360	Cloudy	31.4	15	Clear

Sample	-	0	-	-	80.26	15	Clear
MC32							
PEG-600							
0.3v%							
RPM 1000							
	1968 B						
	Carly Di						
	(0/78/100)						
	Two Layers						
Sample		18.52	720	Very	92.06	15	Clear
MC41	ALC: NOT			Clear			
Hexylamine							
0.3v%,							
RPM 1000							
	and the second						
	(10/54/116)						
	Three Layers						
Sample		97.38	120	Cloudy	80.26	120	Clear
MC50							
Cocoamine							
0.3v%,	10 M						
RPM 1000							
	and the second s						
	(52/26/100)						
	Three Layers						

Sample	-10 V	0	-	-	84.42	15	Clear
MC35							
PEG-600	T						
0.5v%,	The second						
RPM 1000							
	(0/72/104)						
	Two Layers						
Sample MC44 Hexylamine 0.5v%, RPM 1000	(30/100/44) Three Layers	57.47	720	Very Clear	36.12	15	Clear
Sample MC53 Cocoamine 0.5v%, RPM 1000	(18/82/76) Three Layers	34.09	120	Cloudy with oil suspended	61.69	15	Clear

Sample MC30 PEG-600 0.1v%, RPM 1500	(0/94/76) Two Layers	0	-	-	63.87	120	Clear
Sample MC39 Hexylamine 0.1v%, RPM 1500	(0/162/16) Two Layers	0	_	_	12.84	15	Clear
Sample MC48 Cocoamine 0.1v%, RPM 1500	(38/54/50) Three Layers	89.2	240	Cloudy	50.3	15	Clear

~ 1			1				
Sample MC33 PEG-600 0.3v%, RPM 1500	(0/88/90) Two Layers				12.23	15	Clear
Sample MC42 Hexylamine 0.3v%, RPM 1500	(9/155/12) Three Layers	17.05	1440	Clear	9.74	15	Clear
Sample MC51 Cocoamine 0.3v%, RPM 1500	(50/36/92) Three Layers	93.63	240	Cloudy	73.84	120	Clear

		1		1		
(0/80/96) Two Layers	0	_	_	77.92	15	Clear
	26.52	720	Very Clear	12.99	30	Clear
(14/146/16) Three Layers						
(45/37/94) Three Layers	85.23	120	Cloudy	76.3	30	Clear
	(0/80/96) Two Layers (14/146/16) Three Layers	0 آ (0/80/96) Two Layers 26.52 (14/146/16) Three Layers 85.23 (45/37/94) Three Layers	0 - 0	0 - - (0/80/96) - - Two Layers 26.52 720 Very Clear Image: Construction of the second	0 - - 77.92 (0/80/96) - - - - Two Layers 26.52 720 Very Clear 12.99 Image: Class of the classes 26.52 720 Very Clear 12.99 Image: Class of the classes 85.23 120 Cloudy 76.3 Image: Class of the classes 85.23 120 Cloudy 76.3 Image: Classes 85.23 120 Cloudy 76.3	0 - - 77.92 15 (080/96) 10 - - 77.92 15 (080/96) 10 - - - 15 (080/96) 100 - - - - 15 (080/96) 100 -

4.1.2 Qualitative Observations

4.1.2.1 Observation 1

For the first observation is that the emulsion has two layers and some have three layers. For the two layers, they are formed either oil and emulsion or water and emulsion or water and oil. These are due to the emulsifier which is either oil soluble or water soluble. For the three layers, it is in the form of water, oil and emulsion or extra heavy oil, water and emulsion or clear water, cloudy water and emulsion.

For the oil and emulsion is due to the ratio of oil and water is the same for 50%-50% emulsion and sometime this is due to the systematic error of the measuring devices and there is a possibility the water or oil is more and the emulsifier is able to form a stable emulsion of the same amount of the oil and the water but for the rest which is more will be separated.

In addition, for the water, oil and emulsion may due to the emulsifier is more to water soluble like Triton X-100 (Shun Chia Industrial Company Limited) and the emulsifier cannot form a interfacial film on the oil surface and it cannot capture the water droplet and maybe instead of being captured and hence the oil, water and emulsion is formed.

Next, it also can form water and oil only due to the emulsifier is water soluble and the crude oil has no effect to form emulsion and the water and oil are separated due to the emulsifier does not play any role in forming interfacial film on oil surface and the water droplets cannot be trapped. This may due to the emulsifier is both oil and water soluble like Cocamide DEA and it enables both water and oil to be evenly dispersed in a solution (Truth in Aging.com). Therefore, the emulsifier forms interfacial film on both crude oil and water surface and this cause both oil and water cannot encapsulating each other and separated as oil and water only without forming any emulsion. In my research I need to test the emulsion stability and therefore water and emulsion will be needed to test the sample stability. So, the emulsifier I used must be oil soluble like Span 83 which it will solute into oil and form a interfacial film to encapsulate the water to form w/o emulsion. The water will be separated is because of the emulsifier is oil soluble and the amount of emulsifier maybe not enough and it is not strong enough to encapsulating the water droplet. This causes the water to be separated. It also can be due to the emulsifier is water soluble and the reasons are mentioned above.

Moreover, the extra heavy oil, water and emulsion occurs is due to there is the existence of the extra heavy oil which is the crude oil of less than 10° API or in other words crude that is heavier than water. 10° API is the gravity of water. Because of this, the extra heavy oil is on top of the solution as it is heavier than the water and crude oil which has API of about 18°. This happens as it cannot penetrate into the solution and ceases to flow although it is liquid at reservoir conditions, above ground, at normal temperature and under atmospheric pressure. Due to this reason it is also classified as 'non-conventional oil'; conventional oil is flowing both in the reservoirs and above ground (Mommer, B., 2004)

Furthermore, clear water, cloudy water and emulsion is occurred because emulsifier may bring some crude oil into the water as it has strong bond between the emulsifier and the crude oil and cause the water to be cloudy instead of clear. In addition, there is suspension of oil droplet in the clear water. This is also cause by the same reason mentioned but it does not cause water to be cloudy.

4.1.2.2 Observation 2

For the second observation is that there is yellowish layer between the emulsion and water layer. This is due to the emulsifier may discolour the crude oil. For instance, like Triton X-100 is a highly effective detergent and offers exceptional performance in hardsurface cleaning applications (Shun Chia Industrial Company Limited). Therefore, it will discolour the crude oil to become lighter colour instead of dark colour and form a separation line between emulsion and water.

4.1.2.3 Observation 3

For the third observation is that when Cocamide DEA is used as the emulsifier to prepare the emulsion with high RPM, there is a lot of foam formed. This is happening because of the Cocamide DEA is an emulsifier, thickener and foaming agent. This ingredient has the ability to increase the foaming capacity and/or stabilize the foam of a surfactant (Truth in Aging.com) and hence a lot of foam is formed when high agitation.

4.1.2.4 Observation 4

For the fourth observation is that by using Cocamide DEA and Triton X-100 in preparing the 50%-50% emulsion, the water separation is very fast although using high speed of agitation. This may be due to the emulsifier is not evenly dispersed or distributed in the crude oil and the interfacial film formed is not entirely and because of it the film cannot encapsulate the droplets firmly and the separation is immediate. In addition, it may be due to internal separation is very fast even though it is in static mode. The droplets are moving fast internally although there is calm outside as the inter-distance between droplets are large the droplets can move faster, the viscosity decreases and coagulation occurs faster and the emulsion become less stable.

4.1.2.5 Observation 5

For the fifth observation is that the water separation for low RPM 500 using Cocoamide DEA and Triton X-100 is slower which is 1 hour later if compare to RPM 1000 and RPM 1500 which water separation occurs right after 30 minutes. This may due to an increase of particles size with increasing of the agitation intensity is obtained proving that high turbulence or high intensity may promote particles coalescence or agglomeration during synthesis as the agitation will increase the collision between droplets and increase coalescence (Oprea and Dodita, 2001).

In fact, the increase of agitation intensity results in an effective breaking-up of droplets into smaller droplets to increase the stability of the emulsion as the smaller the droplets size, the smaller the inter-distance of the droplets, the slower the droplets can move, the higher the viscosity and more stable the emulsion. By further increasing the intensity of hydrodynamic activity will result in larger particle fractions because of flocculation (Oprea and Bulacovschi, 1986; Eliseeva, 1980)

Optimum agitation is necessary to keep the particles in dispersed phase, to prevent flocculation, to improve mass and heat transfer, phenomena that influence the reaction mechanism and kinetics as well as the final product properties (Oprea and Dodita, 2001)

4.1.2.6 Observation 6

The sixth observation is that for demulsification, the oil layer is more visible than the water layer. This may due to the separation may already occur but the separated water will take time to settle down at the bottom of the solution as the viscosity of the emulsion is high and it is difficult for the coalescence water to penetrate and it take longer time than the oil layer which is continuous phase to settle down. In fact, highly viscous interfacial films retard the rate of oil-film drainage during the coalescence of the water droplets by providing a mechanical barrier to coalescence (Kokal and Aramco, 2006).

In addition, the coalescence is affected by the interfacial tension as the tight emulsion has lower interfacial tension. When the separation occurs, the interfacial tension between oil and water is high while there is still emulsion in between oil and water and the interfacial tension is decreased which will slow down the coalescence of the water droplets and it appear slower.

4.1.2.7 Observation 7

The seventh observation is that for demulsification, the separation is much better for RPM500 rather than the RPM1000 and RPM1500. This is due to agitation or shear. Generally, reducing agitation or shear reduces emulsion stability. Very high shear is detrimental and should be avoided. High shear causes violent mixing of oil and water and leads to smaller droplet sizes which are already very small when the emulsion is prepared. Smaller droplets are relatively more stable than larger droplets, even more droplet size will lead to a microemulsion will droplets size is less than 0.1µm; therefore, measures that increase shearing of the crude oil (for example, mechanical chokes, valves, flow obstructions, and pressure drops) should be avoided or minimized where possible. However, a certain amount of shear is required for mixing the chemical demulsifier into the bulk of the emulsion (Kokal and Aramco, 2006).

4.1.2.8 Observation 8

The eighth observation is that for the demulsification, when the demulsifier like Cocoamine and Hexylamine are pipette into the emulsion prepared, the emulsion surface will be spread open. This indicates that the demulsifier is water soluble which they will tend to bond with water rather than oil which is the continuous phase of the emulsion and therefore this situation happens in order to penetrate or dissolve or into the emulsion in order to diffuse to the interface of oil and water to bond with water by disturbing the interfacial film.

The demulsifiers act as a wetting agent which is water-wet agent and change the wettability of the stabilizing particles which is oil-wet agent that form a interfacial film on the surface of oil to trapped water droplets. This will lead to a breakup of the emulsion film (Kokal and Aramco, 2006).

In other words, the demulsifier is neutralizing the effect of stabilizing film or rupture the film which formed by the emulsifier for encapsulating the water droplets and promote coalescence of water droplets and accelerate water separation

4.1.2.9 Observation 9

The ninth observation is that for microwave assisted chemical demulsification. At first the emulsion is pour into the measuring cylinder with the volume recorded but after a while the volume decreases from the volume at the beginning. This happens because of when temperature increases the kinetic energy (velocity) of the molecules increases and the molecules move vigorously because it receives energy from the heat and speedier particles hit the container walls. There will be more collisions among the molecules that cause the molecules to move to more areas in a medium. Volume therefore increases (Stoker, 2010).

When the emulsion is cool down the molecules stop to move and the volume will back to its original volume it should be when it is pour into the measuring cylinder which we can only observe or see after the heat has been released and the molecules have settle down.

4.2 **RESULTS**

4.2.1 Emulsion w/o (50%-50%)

Table 4.7: Water separation,	v/v % of 0.1 v% of	Emulsifiers	on 50-50% v	<i>w</i> /o emulsion
stability at differe	nt mixing speed			

Time		Span 83		С	ocamide DE	ĈA	,	Triton X-100)
(min)	RPM	RPM	RPM	RPM	RPM	RPM	RPM	RPM	RPM
	500	1000	1500	500	1000	1500	500	1000	1500
0	0	0	0	0	0	0	0	0	0
30	0	0	0	50	45	20	75	25	50
60	0	0	0	60	75	35	80	50	55
120	0	0	0	70	90	65	85	90	60
240	0	0	0	70	90	75	85	80	60
360	0	0	0	70	95	85	85	85	65
720	0	0	0	75	100	90	85	95	65
1440	0	0	0	75	-	95	85	100	75
2160	0	0	0	75	-	95	85	-	75
2880	0	0	0	75	-	90	85	-	80

Table 4.8: Water separation, v/v % of 0.3 v% of Emulsifiers on 50-50% w/o emulsionstability at different mixing speed

Time		Span 83		C	ocamide DE	A		Friton X-100)
(min)	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500
0	0	0	0	0	0	0	0	0	0
30	0	0	0	45	20	15	40	35	2.5
60	0	0	0	70	50	30	75	70	10
120	0	0	0	75	65	60	80	70	25
240	0	0	0	80	75	70	80	80	55
360	0	0	0	80	80	75	85	80	65
720	0	0	0	80	90	85	85	82.5	75
1440	0	0	0	85	90	90	85	85	82.5
2160	0	0	0	75	95	90	85	85	82.5
2880	15	0	0	75	85	92.5	85	85	85

	137

Time		Span 83		С	ocamide DE	A	r.	Γriton X-100)
(min)	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500
0	0	0	0	0	0	0	0	0	0
30	0	0	0	55	30	7.5	35	15	2.5
60	0	0	0	75	60	17.5	55	35	15
120	0	0	0	80	75	27.5	65	60	25
240	0	0	0	85	85	45	50	80	50
360	0	0	0	75	90	57.5	77.5	82.5	70
720	0	0	0	75	95	65	80	87.5	77.5
1440	0	0	0	80	95	80	82.5	92.5	87.5
2160	0	0	0	80	95	85	82.5	92.5	87.5
2880	2.5	0	0	80	75	85	82.5	92.5	87.5

Table 4.9: Water separation, v/v % of 0.5 v% of Emulsifiers on 50-50% w/o emulsionstability at different mixing speed

SAMPLE 9 (The most stable emulsion)

- : 50%-50% Ratio Emulsifier : Span 83 Concentration of emulsifier : 0.5v% Amount of Emulsifier : 0.35ml Total amount of sample : 70ml Amount of Water : 35ml Amount of Crude Oil : 35ml Agitation Speed : RPM 1500 Phase Inversion Test : Filter Paper – w/o i.
 - ii. Test Tube w/o

Table 4.10: Brookfield Test (Emulsion50%-50%)

RPM	Viscosity, cp	Shear Stress, D/cm ²	Shear Rate, 1/s	Torque, %
100	107.0	36.47	34.0	35.77
150	106.53	54.4	51.0	53.33
200	104.43	71.07	68.0	69.9
250	102.87	87.43	85.0	85.83

Temperature: Ambient Temperature (20.9°C)

Temperature: 50°C

RPM	Viscosity, cp	Shear Stress, D/cm ²	Shear Rate, 1/s	Torque, %
100	24.9	8.53	34.0	8.33
150	21.87	11.17	51.0	10.97
200	20.67	14.1	68.0	13.73
250	19.63	16.6	85.0	16.33

Temperature: 70°C

RPM	Viscosity, cp	Shear Stress, D/cm ²	Shear Rate, 1/s	Torque, %
100	29.5	10.03	34.0	9.77
150	25.93	13.23	51.0	12.97
200	24.17	16.43	68.0	16.13
250	22.87	19.47	85.0	19.07

Temperature: 90°C

RPM	Viscosity, cp	Shear Stress, D/cm ²	Shear Rate, 1/s	Torque, %
100	20.1	6.83	34.0	6.7
150	16.13	8.19	51.0	8.0
200	14.2	9.69	68.0	9.47
250	13.03	11.07	85.0	10.9

Table 4.11: Emulsion Stability Test(Emulsion50%-50%)

Sample Amount: 40ml

Time (min)	Water/Emulsion/Oil Layer (ml)
30	0/40/0
60	0/40/0
120	0/40/0
240	0/39/1
360	0/39/1
720	0/39/1
1440	0/39/1
2160	0/39/1
2880	0/38/2

% water separation =
$$\frac{Volume \ of \ water \ layer, V(ml)}{Original \ amount \ of \ water, V_0(ml)} * 100\%$$

$$=\frac{0\ ml}{20\ ml}*100\%$$





Table 4.12Droplet Size(Emulsion50%-50%)

No.	Size, µm
1	0.1
2	0.1
3	0.05
4	0.05
5	0.2
6	0.1
7	0.1
8	0.1
9	0.05
10	0.1
11	0.1
12	0.1
13	0.1
14	0.1
15	0.1
16	0.1
17	0.1
18	0.1
19	0.1
20	0.1
21	0.05
22	0.1
23	0.05
24	0.1
25	0.1
26	0.05
27	0.05
28	0.05
29	0.1
30	0.1

 Table 4.13: Droplet Size Distribution(Emulsion50%-50%)

Size, µm	Frequency
0.02	0
0.05	8
0.1	21
0.2	1
0.5	0





Mean	= 0.09 μm
Variance	$= 0.000931034 \ \mu m^2$
Standard Deviation	= 0.030512858 μm

4.2.2 Emulsion w/o (30%-70%)

Table 4.14:	Water separation, v/v % of 0.1 v% of Emulsifiers on 30-70% w/o emulsion
	stability at different mixing speed

Time		Span 83		C	ocamide DE	ĊΑ	,	Triton X-100)
(min)	RPM	RPM	RPM	RPM	RPM	RPM	RPM	RPM	RPM
	500	1000	1500	500	1000	1500	500	1000	1500
0	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	4.166667	8.333333
60	0	0	0	0	0	0	0	12.5	20.83333
120	0	0	0	0	0	0	4.166667	20.83333	33.33333
240	0	0	0	0	0	0	8.333333	29.16667	37.5
360	0	0	0	0	0	0	16.66667	37.5	41.66667
720	0	0	0	0	0	0	37.5	41.66667	58.33333
1440	0	0	0	0	0	0	58.33333	58.33333	66.66667
2160	0	0	0	0	0	0	66.66667	66.66667	66.66667
2880	0	0	0	0	0	0	83.33333	75	75

Time	e Span 83		Cocamide DEA		Triton X-100				
(min)	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500
0	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	4.166667	0	0
120	0	0	0	0	0	0	12.5	4.166667	8.333333
240	0	0	0	0	0	0	37.5	4.166667	29.16667
360	0	0	0	0	0	0	50	8.333333	41.66667
720	0	0	0	0	0	0	66.66667	29.16667	58.33333
1440	0	0	0	0	0	0	75	50	83.33333
2160	0	0	0	0	0	0	83.33333	58.33333	91.66667
2880	0	0	0	0	0	0	83.33333	66.66667	95.83333

Table 4.15: Water separation, v/v % of 0.3 v% of Emulsifiers on 30-70% w/o emulsionstability at different mixing speed

Table 4.16: Water separation, v/v % of 0.5 v% of Emulsifiers on 30-70% w/o emulsionstability at different mixing speed

Time Span 83		Cocamide DEA		Triton X-100					
(min)	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500
0	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	4.166667	4.166667	4.166667
60	0	0	0	0	0	0	4.166667	12.5	8.333333
120	0	0	0	0	0	0	8.333333	29.16667	25
240	0	0	0	0	0	0	25	37.5	41.66667
360	0	0	0	0	0	0	33.33333	41.66667	50
720	0	0	0	0	0	0	75	58.33333	58.33333
1440	0	0	0	0	0	0	91.66667	75	75
2160	0	0	0	0	16.66667	4.166667	95.83333	83.33333	83.33333
2880	0	0	0	16.66667	58.33333	41.66667	100	87.5	83.33333

SAMPLE 36 (The most stable)

Ratio	: 30%-70%
Emulsifier	: Span 83
Concentration of emulsifier	: 0.5v%
Amount of Emulsifier	: 0.35ml
Total amount of sample	: 70ml
Amount of Water	: 21ml
Amount of Crude Oil	: 49ml
Agitation Speed	: RPM 1500
Phase Inversion Test	:
	i. Filter Paper – w/o ii. Test Tube – w/o

Table 4.17: Brookfield Test(Emulsion30%-70%)

Temperature: Ambient Temperature (30.7°C)

RPM	Viscosity, cp	Shear Stress,	Shear Rate, 1/s	Torque, %
		D/cm^2		
100	16.2	5.51	34.0	5.43
150	16.27	8.29	51.0	8.1
200	15.87	10.73	68.0	10.57
250	15.57	13.3	85.0	12.9

Temperature: 50°C

RPM	Viscosity, cp	Shear Stress,	Shear Rate, 1/s	Torque, %
		D/cm^2		_
100	10.8	3.7	34.0	3.67
150	11.2	5.68	51.0	5.63
200	10.73	7.31	68.0	7.23
250	10.8	9.25	85.0	9.1

Temperature: 70°C

RPM	Viscosity, cp	Shear Stress,	Shear Rate, 1/s	Torque, %
		D/cm ²		
100	10.6	3.6	34.0	3.5
150	9.2	4.59	51.0	4.43
200	8.9	5.84	68.0	5.87
250	8.64	7.24	85.0	7.17

Temperature: 90°C

RPM	Viscosity, cp	Shear Stress,	Shear Rate, 1/s	Torque, %
		D/cm^2		
100	8.3	2.86	34.0	2.87
150	6.8	3.54	51.0	3.47
200	7.05	4.76	68.0	4.83
250	6.76	5.71	85.0	5.47

 Table 4.18: Emulsion Stability Test(Emulsion30%-70%)

Sample Amount: 40ml

Time (min)	Water/Emulsion/Oil Layer (ml)
30	0/40/0
60	0/40/0
120	0/40/0
240	0/40/0
360	0/40/0
720	0/40/0
1440	0/21/19
2160	0/21/19
2880	0/21/19

% water separation =
$$\frac{Volume \ of \ water \ layer, V(ml)}{Original \ amount \ of \ water, V_0(ml)} * 100\%$$

$$=\frac{0\ ml}{12\ ml}*100\%$$

= 0 %



 Table 4.19: Droplet Size Distribution(Emulsion30%-70%)

No.	Size, µm
1	0.2
2	0.1
3	0.1
4	0.2
5	0.1
6	0.2
7	0.2
8	0.2
9	0.1
10	0.2
11	0.1
12	0.2
13	0.1
14	0.2
15	0.2
16	0.1
17	0.2
18	0.2
19	0.2
20	0.1
21	0.2

22	0.2
23	0.2
24	0.2
25	0.1
26	0.2
27	0.1
28	0.1
29	0.1
30	0.2

 Table 4.20: Droplet Size Distribution(Emulsion30%-70%)

Size, µm	Frequency
0.05	0
0.1	12
0.2	18
0.5	0



Figure 4.2Droplet Size Distribution(Emulsion30%-70%)

 Mean
 $= 0.16 \ \mu m$

 Variance
 $= 0.002482759 \ \mu m^2$

 Standard Deviation
 $= 0.049827288 \ \mu m$

4.2.3 Demulsification (50%-50%)

Time	PEG-600			Hexylamine			Cocoamine		
(min)	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500
0	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	0	0
120	0	0	0	0	0	0	0	0	0
240	0	0	0	0	0	0	0	0	0
360	0	0	0	0	0	0	0	0	0
720	0	0	0	0	0	0	0	0	0
1440	0	0	0	0	0	0	0	0	0
2880	0	0	0	0	0	0	0	0	0

Table 4.21: Water separation, v/v % of 0.1 v% of Pure Demulsifiers on 50-50% w/oemulsion stability at different mixing speed

Table 4.22:	Water separation, v/v % of 0.1 v% of Microwave-Assisted Demulsifiers on
	50-50% w/o emulsion stability at different mixing speed

Time	PEG-600			Hexylamine		Cocoamine			
(min)	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500
0	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	0	0
120	0	0	0	0	0	0	0	0	0
240	0	0	0	0	0	0	0	0	0
360	0	0	0	0	0	0	0	0	0
720	0	0	0	0	0	0	0	0	0
1440	0	0	0	1.104972	0	0	0	0	0
2880	0	0	0	2.209945	1.111111	0	0	0	0

Time	PEG-600				Hexylamine	2	Cocoamine		
(min)	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500
0	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	0	0
120	0	0	0	0	0	0	0	0	0
240	0	0	0	0	0	0	0	0	0
360	0	0	0	0	0	0	0	0	0
720	0	0	0	0	0	0	0	0	0
1440	0	0	0	0	0	0	0	0	0
2880	0	0	0	0	0	0.252525	85.85859	75.75758	0

Table 4.23: Water separation, v/v % of 0.3 v% of Pure Demulsifiers on 50-50% w/oemulsion stability at different mixing speed

Table 4.24: Water separation, v/v % of 0.3 v% of Microwave-Assisted Demulsifiers on
50-50% w/o emulsion stability at different mixing speed

Time	PEG-600			Hexylamine			Cocoamine		
(min)	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500
0	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	0	0
120	0	0	0	0	0	0	0	0	0
240	0	0	0	0	0	0	0	0	0
360	0	0	0	4.395604	0	0	0	0	0
720	0	0	0	41.75824	11.23596	0	0	0	0
1440	0	0	0	96.7033	89.88764	0	0	0	0
2880	0	0	0	98.9011	94.38202	89.88764	0	0	0

Time	PEG-600				Hexylamine	:	Cocoamine		
(min)	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500
0	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	0	0
120	0	0	0	0	0	0	0	0	0
240	0	0	0	0	0	0	0	0	0
360	0	0	0	0	0	0	0	0	0
720	0	0	0	0	0	0	0	0	0
1440	0	0	0	0	0	0	0	0	0
2880	0	0	0	0	95.9596	0	0	0	0

Table 4.25: Water separation, v/v % of 0.5 v% of Pure Demulsifiers on 50-50% w/oemulsion stability at different mixing speed

Table 4.26: Water separation, v/v % of 0.5 v% of Microwave-Assisted Demulsifiers on
50-50% w/o emulsion stability at different mixing speed

Time	PEG-600				Hexylamine		Cocoamine		
(min)	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500
0	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	0	0
120	0	0	0	0	0	0	0	5.813953	0
240	0	0	0	1.111111	0	0	0	23.25581	0
360	0	0	0	4.44444	0	0	0	62.7907	0
720	0	0	0	82.22222	17.77778	69.66292	60.46512	95.34884	0
1440	0	0	0	95.55556	92.22222	85.39326	95.34884	96.51163	0
2880	0	0	0	98.88889	97.77778	92.13483	96.51163	97.67442	1.123596

4.2.4 Demulsification (30%-70%)

Time	PEG-600				Hexylamine		Cocoamine		
(min)	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500
0	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	0	0
120	0	0	0	0	0	0	0	0	0
240	0	0	0	0	0	0	0	0	0
360	0	0	0	0	0	0	0	0	0
720	0	0	0	0	0	0	0	0	0
1440	0	0	0	0	0	0	0	0	0
2880	0	0	0	0	0	0	0	0	0

Table 4.27:	Water separation, v/v % of 0.1 v% of Pure Demulsifiers on 30-70% w/o
	emulsion stability at different mixing speed

Table 4.28: Water separation, v/v % of 0.1 v% of Microwave-Assisted Demulsifiers on
30-70% w/o emulsion stability at different mixing speed

Time		PEG-600			Hexylamine	2	Cocoamine		
(min)	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500
0	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	0	0
120	0	0	0	0	0	0	0	0	0
240	0	0	0	0	0	0	0	0	35.21127
360	0	0	0	0	0	10.98901	0	0	42.25352
720	0	0	11.49425	0	0	25.64103	0	0	46.94836
1440	0	0	38.31418	0	0	32.96703	0	0	58.68545
2880	1.851852	0	72.79693	0	0	40.29304	0	0	89.20188

Time		PEG-600			Hexylamine		Cocoamine		
(min)	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500
0	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	0	0
120	0	0	0	0	0	0	0	0	0
240	0	0	0	0	0	0	0	0	0
360	0	0	0	0	0	0	0	0	0
720	0	0	0	0	0	0	0	0	0
1440	0	0	0	0	0	0	0	0	0
2880	0	0	0	0	0	0	0	0	0

Table 4.29: Water separation, v/v % of 0.3 v% of Pure Demulsifiers on 30-70% w/oemulsion stability at different mixing speed

Table 4.30: Water separation, v/v % of 0.3 v% of Microwave-Assisted Demulsifiers on30-70% w/o emulsion stability at different mixing speed

Time (min)	P	EG-600			Hexylamine			Cocoamine	
	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500
0	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	0	0
120	0	0	0	0	0	0	0	3.745318	0
240	0	0	0	0	0	0	10.41667	11.23596	14.98127
360	0	0	0	0	0	0	16.66667	28.08989	29.96255
720	0	0	0	7.407407	1.851852	0	31.25	44.94382	59.92509
1440	0	0	0	14.81481	7.407407	3.787879	62.5	67.41573	89.88764
2880	1.851852	0	0	59.25926	18.51852	17.04545	93.75	97.37828	93.63296

Time		PEG-600			Hexylamine	1	Cocoamine			
(min)	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	
0	0	0	0	0	0	0	0	0	0	
15	0	0	0	0	0	0	0	0	0	
30	0	0	0	0	0	0	0	0	0	
60	0	0	0	0	0	0	0	0	0	
120	0	0	0	0	0	0	0	0	0	
240	0	0	0	0	0	0	0	0	0	
360	0	0	0	0	0	0	0	0	0	
720	0	0	0	0	0	0	0	0	0	
1440	0	0	0	0	0	0	0	0	0	
2880	0	0	0	16.94915	8.474576	0.423729	0	0	0	

Table 4.31: Water separation, v/v % of 0.5 v% of Pure Demulsifiers on 30-70% w/oemulsion stability at different mixing speed

Table 4.32: Water separation, v/v % of 0.5 v% of Microwave-Assisted Demulsifiers on
30-70% w/o emulsion stability at different mixing speed

Time (min)	P	EG-600			Hexylamine			Cocoamine		
	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	RPM 500	RPM 1000	RPM 1500	
0	0	0	0	0	0	0	0	0	0	
15	0	0	0	0	0	0	0	0	0	
30	0	0	0	0	0	0	0	0	0	
60	0	0	0	0	0	0	0	0	0	
120	0	0	0	0	0	0	11.23596	3.787879	18.93939	
240	0	0	0	3.623188	0	0	28.08989	7.575758	28.40909	
360	0	0	0	10.86957	0	0	56.17978	11.36364	37.87879	
720	0	0	0	28.98551	11.49425	3.787879	74.90637	15.15152	41.66667	
1440	1.862197	0	0	57.97101	22.98851	7.575758	74.90637	18.93939	75.75758	
2880	3.724395	0	0	79.71014	57.47126	26.51515	84.26966	34.09091	85.22727	
4.2.5 Microwave Heating Properties

4.2.5.1 Microwave-Assisted Chemical Demulsification 50%-50%

Table 4.33: Microwave-Assisted Chemical Demulsification 50%-50% Properties for0.3v% Hexylamine at RPM 500

Time (s)	Temperature Increase,∆T (To=28.9°C)	Rate of Temperature increased, dT/dt (°C/s)	Volume rate of Heat Generation, q (cal/cm ³ .s)	dielectric constant, ε'/dielectric loss, ε" (Water)	Penetration Depth, D _p (cm) (Water)	Wavelength, λ _w (cm) (Water)
15	36.754375	2.450292	1.674958	63.16629124375/4.36592	7.098635	1.539762
30	87.11933333	2.903978	1.985087	46.25222728666667/2.433225	10.8964	1.79986
45	63.243	1.4054	0.960696	54.27061631/3.082706	9.316959	1.66149
60	77.57366667	1.292894	0.88379	49.4579485233334/2.657479	10.31701	1.740526
75	52.61133333	0.701484	0.479517	57.8410489266667/3.496258	8.481286	1.609307
90	69.935	0.777056	0.531176	52.02324195/2.868585	9.802681	1.697038
105	55.03066667	0.524102	0.358263	57.0285642133333/3.392816	8.678142	1.620754
120	95.91233333	0.799269	0.546361	43.29927409666667/2.257381	11.36402	1.860234
135	79.899	0.591844	0.40457	48.67703183/2.599176	10.46478	1.75444
150	73.76433333	0.491762	0.336156	50.7372369366667/2.758776	10.06598	1.718428
165	90.52433333	0.548632	0.375031	45.1087261366667/2.362018	11.08523	1.822536
180	78.946	0.438589	0.299808	48.99707782/2.622762	10.40472	1.748698

4.2.5.2 Microwave-Assisted Chemical Demulsification 30%-70%

Table 4.34: Microwave-Assisted Chemical Demulsification 30%-70% Properties for0.3v% Cocoamine at RPM 1000

Time (s)	Temperature Increase,∆T (To=28.9°C)	Rate of Temperature increased, dT/dt (°C/s)	Volume rate of Heat Generation, q (cal/cm ³ .s)	dielectric constant, ε'/dielectric loss, ε" (Water)	Penetration Depth, D _p (cm) (Water)	Wavelength, λ_w (cm) (Water)
15	8.85	0.59	0.335101	72.5374175/7.706617	4.31297	1.435701
30	28.23733333	0.941244	0.534596	66.0265693466667/5.035431	6.293421	1.505847
45	30.58733333	0.679719	0.386058	65.23736884666667/4.831289	6.519756	1.51499
60	56.218	0.936967	0.532166	56.62982206/3.34423	8.773332	1.62646
75	46.01533333	0.613538	0.348469	60.0561836066667/3.812702	7.925259	1.579275
90	80.696	0.896622	0.509252	48.40937532/2.579769	10.51446	1.759286
105	65.722	0.625924	0.355504	53.43809374/2.999807	9.500621	1.674398
120	118.8586667	0.990489	0.562565	35.5932069733333/1.898214	12.25298	2.051717
135	114.0166667	0.844568	0.479687	37.2192958333333/1.964278	12.10824	2.006412
150	107.3273333	0.715516	0.406389	39.46577464666667/2.063382	11.86938	1.948483
165	122.1053333	0.740032	0.420314	34.50287890666667/1.85632	12.33618	2.08387
180	108.3046667	0.601693	0.341742	39.1375567933333/2.048291	11.90701	1.956635

4.2.6 Surface Tension and Interfacial Tension

4.2.6.1 Surface Tension 50%-50%

Reading	1	2	3	4	Average
Water and Air	56.425	56.086	56.341	56.680	56.383
Oil and Air	24.898	24.664	24.664	24.820	24.762

Table 4.35: Surface Tension of Water and Air and Oil and Air

4.2.6.2 Interfacial Tension 50%-50%

Table 4.36: Interfacial Tension of Water and Oil

Reading	1	2	3	4	Average
Water and Oil	2.931	2.896	2.926	2.896	2.912

4.2.6.3 Surface Tension 30%-70%

Table 4.37: Surface Tension of Water and Air and Oil and Air

Reading	1	2	3	4	Average
Water and Air	53.379	53.547	53.379	53.547	53.463
Oil and Air	27.248	27.799	27.012	26.541	27.150

4.2.6.4 Interfacial Tension 30%-70%

Table 4.38: Interfacial	Tension	of Water	and Oil
-------------------------	---------	----------	---------

Reading	1	2	3	4	Average
Water and Oil	3.963	3.896	3.963	3.886	3.927

4.3 DATA ANALYSIS

4.3.1 Brookfield Analysis

4.3.1.1 Viscosity versus Temperature





Figure 4.3: Viscosity Versus Temperature at RPM 100 (Brookfield)



Figure 4.4: Viscosity Versus Temperature at RPM 150 (Brookfield)



Figure 4.5: Viscosity Versus Temperature at RPM 200 (Brookfield)



Figure 4.6: Viscosity Versus Temperature at RPM 250 (Brookfield)

Emulsion 30%-70% for Emulsifier 0.5v% RPM 1500



Figure 4.7: Viscosity Versus Temperature at RPM 100 (Brookfield)



Figure 4.8: Viscosity Versus Temperature at RPM 150 (Brookfield)



Figure 4.9: Viscosity Versus Temperature at RPM 200 (Brookfield)



Figure 4.10: Viscosity Versus Temperature at RPM 250 (Brookfield)

4.3.1.2 Discussion on Viscosity versus Temperature

From the **Figure 4.2** till **4.10**, it shows that most of the graphs trends are the viscosity is inversely proportional to the temperature which is when temperature increases, the viscosity will decrease. This is because temperature affects the physical properties of oil, water, interfacial films, interfacial viscosity and surfactant solubility in the oil and water phases which in turn, affect the stability of the emulsion. In fact, the most important affect of temperature is on the viscosity of emulsions. This influence is mainly because of a decrease in the oil viscosity. In addition, temperature increases the thermal energy of the droplets and, hence, the droplets will start to move. The interdistance between droplets is increased and the droplets are moving more vigorous and this increases the frequency of drop collisions. It also reduces the interfacial viscosity, which results in a faster film-drainage rate and faster drop coalescence (Kokal and Aramco, 2006).

Based on Jones et. al. who showed that an increase in temperature will lead to a gradual destabilization of the crude oil/water interfacial films which will decrease the

viscosity of the emulsion as the oil and water interfacial tension increases and start to repel each other and move apart to coalescence with their own phase. Temperature influences the interfacial films buildup rate by changing the adsorption rate and characteristics of the interface. It also influences the film compressibility by changing the solubility of the crude oil surfactants in the bulk phase.

However, there are some deviate result which when the temperature is increased, the viscosity of the emulsion is increased also instead of decreasing. This mean the emulsion exhibits o/w emulsion which deviate what we need for w/o emulsion. After reach certain temperature, the emulsion exhibits w/o emulsion which the viscosity decreases with increasing of temperature. This situation happen is due to the phase inversion temperature (PIT).

The emulsion stabilized with a nonionic surfactant is a w/o type at high temperature but an o/w type at low temperature, and a phase inversion in the emulsion takes place at some medium temperature. The existence of a phase inversion temperature (PIT) indicates appreciable changes of the HLB of a nonionic surfactant with temperature. This influence is strong; a change of the HLB of the surfactant or the type of emulsion is obtained with altered temperature; in fact, the effect of phase volume on the phase inversion may be smaller than that of temperature (Shinoda and Friberg, 1986).

Moreover, the hydration forces between the hydrophilic moiety of surfactant and water are stronger at lower temperatures, and the adsorbed monolayer may have a convex curvature towards water. Since a stronger interaction means greater affinity and zero or small interfacial energy, the consequent increase in interface does not result in a large free energy increase of the system. This concept nicely correlates with o/w-type emulsions at low temperature (Shinoda, 1967). On the other hand, the decrease of oil/surfactant interface contributes more efficiently to the free energy decrease of the system at the lower temperature. Thus the convex curvature towards water may be thermodynamically preferable. The dissolution of a nonionic surfactant in an aqueous

phase as micelles below the cloud point is regarded as a similar phenomenan (Shinoda and Friberg, 1986).

Based on Zenitech, when temperature is increased, ethoxylated surfactants like Triton X-100 become less water-soluble. This is due to as the temperature increases the molecules exhibit more movement or vibration. Thus, hydrogen bonding is inhibited; the ethoxylate loses its water solubility and cloudiness results. Therefore, Triton X-100 exhibits o/w emulsion behavior as it is water soluble at ambient temperature and turn to w/o emulsion as loses it solubility in water as shown in the **Figure 4.2** till **4.10**. Hence, Triton X-100 is not prefable to produce a stable emulsion at ambient temperature due to PIT.

While for the Cocamide DEA as shown in the **Figure 4.2** till **4.10**, it exhibits o/w and w/o at ambient temperature and hence it sometime produces a more stable emulsion than Triton X-100 and the other way around. It also not suitable to use to produce an stable emulsion at ambient temperature. Whereas for the Span 83 as shown in the **Figure 4.2** till **4.10**, it exhibits all the time as w/o emulsion at ambient temperature and due to this, it produces the most stable emulsion with the least percentage of water and oil separation.

4.3.1.3 Viscosity versus Concentration of Emulsifier



Emulsion 50%-50% for Emulsifier of RPM 1500 at Ambient Temperature

Figure 4.11: Viscosity Versus Concentration of Emulsifier at RPM 100 (Brookfield)



Figure 4.12: Viscosity Versus Concentration of Emulsifier at RPM 150 (Brookfield)



Figure 4.13: Viscosity Versus Concentration of Emulsifier at RPM 200 (Brookfield)



Figure 4.14: Viscosity Versus Concentration of Emulsifier at RPM 250 (Brookfield)



Emulsion 30%-70% for Emulsifier of RPM 1500 at Ambient Temperature

Figure 4.15: Viscosity Versus Concentration of Emulsifier at RPM 100 (Brookfield)



Figure 4.16: Viscosity Versus Concentration of Emulsifier at RPM 150 (Brookfield)



Figure 4.17: Viscosity Versus Concentration of Emulsifier at RPM 200 (Brookfield)



Figure 4.18: Viscosity Versus Concentration of Emulsifier at RPM 250 (Brookfield)

4.3.1.4 Discussion on Viscosity versus Concentration of Emulsifier

As we can observe from the **Figure 4.11** till **4.18**, the viscosity of the emulsion is increased with increasing of the concentration of the emulsifier. This indicates that the viscosity is definitely influenced by the concentration of emulsifying agent. This is due to the concentration of emulsifying agent will affect the oil and water interface. It is the magnitude of the intermolecular attraction of the interfacial film, which is predominant in determining the viscosity (Sherman, 1959).

However, there is exception that the viscosity is decreased with increasing of the concentration of the emulsifier in 50%-50% emulsions but direct proportional in 30%-70% emulsions. This is due to in concentrated water-in-oil emulsions the emulsifying agent concentration influenced the disperse phase value at which inversion occurred to unstable oil-in-water systems (Sherman, 1950). Based on Ilia Anisa and Abdurahman, 2010, it states that the viscosity of w/o emulsion was strongly augmented by increasing volume of water which the dispersed phase. In addition, part of this effect may be due to the increase in viscosity of the continuous medium. The emulsifying agent is usually dissolved, or dispersed, in the continuous phase so that continuous phase represents the combined viscosity of this substance plus that of the continuous phase. Increase in emulsifier concentration will affect continuous medium to a greater extent in concentrated emulsions than in dilute ones since continuous phase volume is much smaller in the former. (Sherman, 1959)

Figure 4.11 till **4.18** show that Span 83 follows the relationship of viscosity and concentration of the emulsifier and that why the Span 83, 0.5v% produces the most stable emulsion because of it high viscosity at high concentration of the emulsifier in both ratio of emulsion. While for Triton X-100 and Cocamide DEA, the viscosity is changing uncertainly with increasing concentration of the emulsifier and hence base on **Table 4.1** and **4.2**, the water separation which indicates the emulsion stability is fluctuating which is caused by the viscosity fluctuates with concentration of the emulsifier as shown in **Figure 4.11** till **4.18**.

4.3.1.5 Viscosity versus Agitation Speed (Brookfield)



Emulsion 50%-50% for Emulsifier of RPM 1500 at Ambient Temperature

Figure 4.19: Viscosity Versus Agitation Speed of 0.1v% at Ambient Temperature



Figure 4.20: Viscosity Versus Agitation Speed of 0.3v% at Ambient Temperature



Figure 4.21: Viscosity Versus Agitation Speed of 0.5v% at Ambient Temperature





Figure 4.22: Viscosity Versus Agitation Speed of 0.1v% at Ambient Temperature



Figure 4.23: Viscosity Versus Agitation Speed of 0.3v% at Ambient Temperature



Figure 4.24: Viscosity Versus Agitation Speed of 0.5v% at Ambient Temperature

4.3.1.6 Discussion on Viscosity versus Agitation Speed (Brookfield)

From the **Figure 4.19** till **4.24**, they show that viscosity decreases with the increasing of the agitation speed of the Brookfield device. This is due to when the agitation increases, the temperature will increases and therefore the viscosity will decreases which has been discussed in detail in **Section 4.3.1.2**

Besides, from **Figure 4.19** till **4.24**, we can see that the viscosity does not change drastically with increasing agitation speed; it is caused by the droplet sizes which affect the viscosity. An increase in stirring speed generally tends to produce a decrease in droplet size, because it affects more the droplet breaking mechanism than the coalescence rate. Thus, an increase in stirring energy is expected to widen the region where the decreasing tension produces smaller drops (**Salager et. al., 2001**). In addition, this is because also when the agitation increases, the droplets become smaller, the interdistance of the droplets are decreased, the droplets movement becomes slower and the frequency of the collision become less and the viscosity will increase. Hence the viscosity does not change dramatically as the viscosity has to compensate between the effects of both temperature and the droplet size of dispersed phase and since the effect of the temperature is stronger on viscosity, the viscosity decreases with agitation speed but not as vigorous as effect of temperature alone.

As shown in the **Table 4.39** and **4.40** the droplets of emulsion Span 83, 0.5v% produces the very small droplets size and hence it has the highest viscosity in most of the graphs plotted above. Based on Fournanty et. al., 2008 the mean droplet size of the emulsion must not be too large. This is mainly to avoid coalescence and phase separation. However, it must not be too small either, in order to keep the apparent viscosity of the emulsion at a value sufficiently low to allow its flooding. Whereas Triton X-100 show the lowest viscosity in most graphs which this indicates it will not produce a stable emulsion. As for the Cocamide DEA, the viscosity is increased at certain agitation speed and decreased after that with increasing agitation speed, this may

due to the phase inversion temperature (PIT) as discussed in Section 4.3.1.2. This causes the emulsions produce by Cocamide DEA is sometime stable and sometime not.

Original Scale 0.1µm 0.1 µm 01,µm 0.05 µm 0.1 un 0.1 µm 15um 0.1um 0.1 µm 0.05 µm 0.05 µm 1.1 µm 0.1 an 0.2 µm 01.µm 0.05 µm 0.1 ur 0.1 un 0.1 µm 0.1.00 0.1.µm 05 µm 0.1 um 0.1µm 0.1 µm 0.05 un 0.1 µm 01µm = 0.09 µm Mean Variance $= 0.000931034 \ \mu m^2$ Standard Deviation $= 0.030512858 \ \mu m$

Table 4.39: Emulsion 50%-50% for Emulsifier of RPM 1500 at AmbientTemperature



Table 4.40: Emulsion 30%-70% for Emulsifier of RPM 1500 at AmbientTemperature

4.3.1.7 Viscosity versus Shear Rate



Emulsion 50%-50% for Emulsifier 0.5v% RPM 1500 at Ambient Temperature

Figure 4.25: Viscosity Versus Shear Rate at Ambient Temperature

Emulsion 30%-70% for Emulsifier 0.5v% RPM 1500 at Ambient Temperature



Figure 4.26: Viscosity Versus Shear Rate at Ambient Temperature

4.3.1.8 Discussion on Viscosity versus Shear Rate

For the **Figure 4.25** and **4.26**, we can observe that the viscosity of emulsion prepared by Span 83, Cocamide DEA and Triton X-100 in both 50%-50% and 30%-70% are decreased with increasing Shear Rate. These represent that all the emulsions exhibit Non-Newtonian behavior which deviate from Newtonian behavior. The viscosity of a Newtonian fluid is not a function of shear rate or in other words the rate of deformation is directly proportional to the applied force (Scott Bader). The Non-Newtonian behavior is a result of droplet crowding or structural viscosity. A fluid is considered non-Newtonian when its viscosity is a function of shear rate (Kokal and Aramco, 2006).

The type of Non-Newtonian that the emulsions prepared by Span 83, Cocamide DEA and Triton X-100 in both 50%-50% and 30%-70% show is Pseudoplasticity which is a large number of liquids show a large decrease in viscosity when the shear rate is increased and this type of flow is defined as pseudoplastic or shear thinning behavior. Emulsions, suspensions and dispersions are typically pseudoplastic as are many paint, ink and adhesive systems. At higher shear rates the flow behavior becomes more linear (Newtonian). Pseudoplastic behavior in dispersions can be cuased by alignment, stretching, deformation, or peptization of dispersed material while being sheared (Schramm, 2005).



Figure 4.27: Pseudoplastic behavior portrays as Viscosity versus Shear Rate

Source: Adopted from Scott Bader

However for emulsion prepared by Cocamide DEA in 30%-70% shows that at first the viscosity is increased with increasing Shear Rate and decreases afterward when Shear Rate increases. When the viscosity is direct proportional with the Shear Rate, the type of Non-Newtonian behavior shown by the emulsion is Dilatancy. A dilatant fluids show the opposite type of behavior to pseudoplastic systems. For instance, they show an increase in viscosity as the shear rate increases (shear thickening). It is seen in highly concentrated suspensions or slurries (Scott Bader). Based on Schramm, 2005, dilatancy can be due to the dense packing of particles in very concentrated dispersions for which at low shear, the particles can just move past each other but at high shear they become wedged together such that the fluid cannot fill (lubricate) the increased void volume, and the viscosity increases.



Figure 4.28: Dilatancy behavior portrays as Viscosity versus Shear Rate

Source: Adopted from Scott Bader

4.3.1.9 Shear Stress versus Shear Rate

Emulsion 50%-50% for Emulsifier 0.5v% RPM 1500 at Ambient Temperature



Figure 4.29: Shear Stress Versus Shear Rate compare with Newtonian at Ambient Temperature



Figure 4.30: Shear Stress Versus Shear Rate without compare with Newtonian at Ambient Temperature

Emulsion 30%-70% for Emulsifier 0.5v% RPM 1500 at Ambient Temperature



Figure 4.31:Shear Stress Versus Shear Rate compare with Newtonian at Ambient Temperature



Figure 4.32: Shear Stress Versus Shear Rate without compare with Newtonian at Ambient Temperature

4.3.1.10 Discussion on Shear Stress versus Shear Rate

For the **Figure 4.29** till **4.32**, we can see that the Shear Stress of emulsion prepared by Span 83, Cocamide DEA and Triton X-100 in both 50%-50% and 30%-70% are increases with increasing Shear Rate. These represent that all the emulsions exhibit Non-Newtonian behavior which deviate from Newtonian behavior.

The type of Non-Newtonian that the emulsions prepared by Span 83, Cocamide DEA and Triton X-100 in both 50%-50% and 30%-70% show is actually the same as discussed in **Section 4.3.1.8** which is Pseudoplasticity. It shows the behavior of plastic which is initially resist deformation until a certain yield stress is reached. Further than this point the flow is then that of a pseudoplastic fluid (Scott Bader). This type of flow is defined as pseudoplastic or shear thinning behavior. The higher the shear rates the flow behavior, the higher the Shear Stress until certain limit the influence of Shear Rate on Shear Stress will become slower and the trend will almost constant and linear which



is exactly the behavior of the plastic material. Another Pseudoplastic behavior is portrayed below:-

Figure 4.33: Pseudoplastic behavior portrays as Shear Stress versus Shear Rate

Source: Adopted from Scott Bader

If they are compare to **Figure 2.13**, **Figure 4.29** and **Figure 4.31**, we could probably think the emulsions prepared by Span 83, Cocamide DEA and Triton X-100 in both 50%-50% and 30%-70% except Span 83 in 50%-50% exhibit dilatants behavior even though not exactly as the trend of dilatants. However, it is not as the emulsions do show pseudoplastic behavior as the shear stress changes with shear rate shown in **Figure 4.30** and **Figure 4.32** are exactly as the trend shown in **Figure 4.33** and in **Section 4.3.1.8** has discussed that the viscosity of the emulsions prepared by Span 83, Cocamide DEA and Triton X-100 in both 50%-50% and 30%-70% decrease as the shear rate increases which is a pseudoplastic behavior.

4.3.2 Emulsion Gravitational Stability Test



4.3.2.1 Emulsion 50%-50% for Emulsifier 0.1v% RPM 1500

Figure 4.34: Percentage of Water Separation versus Time



Figure 4.35: Percentage of Oil Separation versus Time

From **Figure 4.34**, we can see that the separation of water of Span 83 is none which indicates that the emulsion prepared by using it as emulsifier is the most stable among three emulsifiers. As shown in the **Figure 4.34**, Cocamide DEA has the most water separation although the water start to separate of emulsion prepared by Triton X-100 is the fastest. This is due to the at low concentration of emulsifier, the amount of emulsifier is hardly well-distributed into the oil to form a interfacial film to encapsulating the water droplets and in addition the Cocamide DEA and Triton X-100 is both water and oil soluble and water soluble respectively. The former has the tendency to form interfacial film but weak while the latter will not form interfacial film instead of play no role or dissolve in water to emulsifier the emulsion to produce o/w emulsion rather than w/o emulsion.

Therefore as shown in **Figure 4.35**, the oil separated for emulsion prepared by Triton X-100 is changing drastically as this indicates the emulsifier play no role in the emulsifier and so the oil separate from water very quick as the emulsion form is temporary and no interfacial film to enhance the emulsion and interfacial tension of oil and water increases and they separate faster. For the Cocamide DEA, since it soluble in both oil and water, the interfacial film may form in both oil and water surface and encapsulating each other and hence the oil separated is first high and then decreases. While for the emulsion prepared by Span 83, the oil is separated due to the amount of emulsifier is not enough to be well-distributed on the surface on the crude oil and hence some of the oil does not form emulsion with water droplets and it is separated. This is because of the concentration of emulsifying agent will affect the oil and water interface which is the magnitude of the intermolecular attraction of the interfacial film (Sherman, 1959).



4.3.2.2 Emulsion 50%-50% for Emulsifier 0.3v% RPM 1500

Figure 4.36: Percentage of Water Separation versus Time



Figure 4.37: Percentage of Oil Separation versus Time

From Figure 4.36, we can see that the separation of water of Span 83 is none which indicates that the emulsion prepared by using it as emulsifier is the most stable among three emulsifiers. As shown in the Figure 4.34, Cocamide DEA has the most water separation and the water start to separate of emulsion is the fastest unlike the in Section 4.3.2.1 which emulsion prepared by Triton X-100 is the fastest. The reason is almost the same as discussed in Section 4.3.2.1.

In **Figure 4.37**, there are no oil separation for emulsion prepared by and Cocamide DEA and Triton X-100. This indicates the emulsifiers dissolve in water rather to play no role to emulsifier the emulsion to produce o/w emulsion instead of w/o emulsion at room temperature as discussed in **Section 4.3.1.1** which show the emulsion is o/w at room temperature and inverse to w/o when certain temperature is reached. This is due to Triton X-100 and Cocamide DEA is nonionic surfactant and they are w/o type at high temperature but an o/w type at low temperature, and a phase inversion in the emulsion takes place at some medium temperature due to HLB changes with temperature (Shinoda and Friberg, 1986) as discussed in **Section 4.3.1.1**.

While for the emulsion prepared by Span 83, the oil is separated due to the amount of emulsifier is not enough to be well-distributed on the surface on the crude oil and hence some of the oil does not form emulsion with water droplets and it is separated but the amount separated is lower than previous **Section 4.3.2.1**. This is because the amount of emulsifier is higher than previous **Section 4.3.2.1** and it is able to trap more water droplets to form stable emulsion and less oil is separated.



4.3.2.3 Emulsion 50%-50% for Emulsifier 0.5v% RPM 1500

Figure 4.38:Percentage of Water Separation versus Time



Figure 4.39: Percentage of Oil Separation versus Time

From **Figure 4.38**, we can see that none of the water of emulsion prepared by Span 83 is separated .This indicates that the emulsion prepared by using it as emulsifier is the most stable among three emulsifiers. It is due to the concentration of the emulsifier is higher and this will ensure that the emulsifier will dissolve thoroughly on the surface of the crude oil and form enough and strong interfacial film which is strong enough to capture the water droplets and reduce the interfacial tension between oil and water which inhibit the stabilization of the emulsion. Based on Kokal and Aramco, 2006, the surfactants have a hydrophobic part that has an affinity for oil and a hydrophilic part that has an affinity for water. Because of this molecular structure, surfactants tend to concentrate at the oil/water interface, where they form interfacial films. This generally leads to a lowering of the interfacial tension (IFT) and promotes dispersion and emulsification of the droplets.

As shown in the **Figure 4.38**, Triton X-100 has the most water separation although the water start to separate of emulsion prepared by Cocamide DEA is the fastest. This is the total opposite compare with the **Section 4.3.2.1 and 4.3.2.2**. This is due to the at high concentration of emulsifier, the amount of emulsifier is well-distributed into the water instead of oil as Cocamide DEA and Triton X-100 is both water and oil soluble and water soluble respectively to form a interfacial film to encapsulating the oil instead. The former has the tendency to form interfacial film but weak while the latter dissolve in water to emulsifier the emulsion to produce o/w emulsion rather than w/o emulsion in ambient temperature. Therefore as shown in **Figure 4.39**, there are none of oil separated for emulsion prepared by Triton X-100 and Cocamide DEA respectively.

While for the emulsion prepared by Span 83, the oil is separated is among the least if compared with the **Section 4.3.2.1 and 4.3.2.2**. This is because the amount of emulsifier is enough to be well-distributed on the surface on the crude oil to form stable emulsion. The little amount of oil separated maybe due to the volume fraction dispersion as stated by Johnsen and Rønningse, 2003, the volume fraction of dispersed

phase, which is by far one of the main factors governing the viscosity which determine the stabilization of crude oil emulsions. Hence, the emulsion as 50%-50%, there is a possibility that water volume or oil volume is exceed than each other due to systematic problem like measuring device. This may cause the viscosity of emulsion to deviate and cause this situation as there is some unstable emulsion and cause the coalescence on either phase.



4.3.2.4 Emulsion 30%-70% for Emulsifier 0.1v% RPM 1500

Figure 4.40: Percentage of Water Separation versus Time



Figure 4.41: Percentage of Oil Separation versus Time

From **Figure 4.40**, we can see that none of the water of emulsions prepared by Span 83 and Cocamide DEA are separated .These indicate that the emulsion prepared by using these as emulsifiers are the very stable. For the Cocamide DEA, this is totally different from 50%-50%. As Johnsen and Rønningse, 2003 stated that the volume fraction of dispersed phase which determine the stabilization of crude oil emulsions. In this 30%-70% emulsion, the dispersed phase is lower and the Cocamide DEA is soluble in both oil and water. Crude oil is dominated and so it will soluble more into oil and form interfacial film to encapsulate the water droplet.

In addition, it is due to the concentration of the emulsifier is low and this will ensure that the emulsifier will dissolve almost thoroughly on the surface of the crude oil and form enough and strong interfacial film which is strong enough to capture the water droplets and reduce the interfacial tension between oil and water which inhibit the stabilization of the emulsion. Because of this, the continuous phase which is crude oil is separated more as shown in **Figure 4.41** because the interfacial film only enough to encapsulating the water and with same amount of oil and the rest will be settle as pure crude oil for both Span 83 and Cocamide DEA Only different is Span 83 has less oil
separated as it is purely oil soluble and can form strong interfacial film compare with Cocamide DEA.

Whereas for Triton X-100, the water and oil separated are almost equally as shown in **Figure 4.40** and **4.41**. This is due to the Triton X-100 is water soluble as discussed in **Section 4.3.2.1** till **4.3.2.3** and it will play no role as the concentration of emulsifier is very low and the interfacial tension of oil and water dominate than interfacial film which increases interfacial viscosity to stabilize the emulsion (Kokal and Aramco, 2006) and hence the oil and water separated without forming strong emulsion.



4.3.2.5 Emulsion 30%-70% for Emulsifier 0.3v% RPM 1500

Figure 4.42: Percentage of Water Separation versus Time



Figure 4.43: Percentage of Oil Separation versus Time

From **Figure 4.42**, we can see that none of the water of emulsions prepared by Span 83 and Cocamide DEA are separated .These indicate that the emulsion prepared by using these as emulsifiers are the very stable. The reason is the same as discussed in **Section 4.3.2.4**

On the other hand, the continuous phase which is crude oil is separated less for Cocamide DEA than Span 83 compare with previous **Section 4.3.2.4** as shown in **Figure 4.43** because the concentration of the emulsifier is higher and the interfacial film form is more and enough to encapsulating the more water and with same amount of oil and less will be settle as pure crude oil for Cocamide DEA. While for Span 83 the the oil separated is almost the same as previous **Section 4.3.2.4** only different it can hold longer the oil than previous **Section 4.3.2.4** due to strength of the interfacial film formed is stronger as higher concentration of the emulsifier.

Whereas for Triton X-100, the water and oil separated are almost equally or are almost fully separated as shown in **Figure 4.42** and **4.43**. This is due to the Triton X-100 is water soluble as discussed in **Section 4.3.2.1** till **4.3.2.3** and it will play no role or

dissolve into the water and due to water is dispersed or in droplets and if there is interfacial film, it is unable to capture the oil which is in continuous, non-droplets and high interfacial tension.



4.3.2.6 Emulsion 30%-70% for Emulsifier 0.5v% RPM 1500

Figure 4.44 Percentage of Water Separation versus Time



Figure 4.45: Percentage of Oil Separation versus Time

From **Figure 4.44**, we can see that none of the water of emulsion prepared by Span 83 is separated .These indicate that the emulsion prepared by using these as emulsifiers are the most stable among three emulsifiers in this concentration of emulsifier. It is due to the concentration of the emulsifier is high of the emulsion. Based on Kokal and Aramco, 2006, the surfactants have a hydrophobic part that has an affinity for oil and the Span 83 is oil soluble and hence the affinity to oil is higher than to water and this will ensure that it is dissolve on the surface of the crude oil and traps as much water droplets as possible. Therefore the oil separated takes longer time as shown **Figure 4.45** because the emulsion is strong and stable than others in **Section 4.3.2.4** and **4.3.2.5**.

On the other hand, Cocamide DEA has water separation in this concentration as shown in **Figure 4.44.** It is due to the concentration of the emulsifier, it is both soluble and the higher concentration of the emulsifier will encourage it to be dissolve in both phases and it increases the interfacial tension than increases the interfacial film strength as both form interfacial film on each other phase and this increases the competition in encapsulating each other and hence the water and oil separated as shown in Figure 4.44 and 4.45.

Whereas for Triton X-100, the water and oil separated are almost equally or are as shown in **Figure 4.44** and **4.45**. The reason is as discussed in **Section 4.3.2.4** and **4.3.2.5**.



4.3.2.7 Emulsion 50%-50% for Emulsifier 0.5v%

Figure 4.46: Percentage of Water Separation versus Agitation Speed after 2 days



Figure 4.47: Percentage of Oil Separation versus Agitation Speed after 2 days

From Figure 4.46 and 4.47, we can see that the agitation speed has influence on the water separation which is when the agitation speed increases, the water separation will be decreased and so as the oil separation. This is due to at higher agitation the dispersed phase can be break into smaller droplets and this will cause the emulsion to be stable and less water and oil separation. It is because stirring energy affects more the drop breaking mechanism than the coalescence rate. Thus, an increase in stirring energy is expected to widen the region where the decreasing tension produces smaller drops (Salager et. Al, 2001).

In addition, when the agitation increases, the higher the viscosity of the emulsion due to smaller droplets size which decreases the inter-distance between the droplets and the droplets move slowly and the rate of coalescence become slower and the water separation is slower and the emulsion is tighter and more stable. Next, the water cut is higher into emulsion, also enhances the droplets to coalesce because of elimination of protective rigid film (**Ilia Anisa and Abdurahman, 2010**) and increases tendency for the dispersed phase to meet each other to coalesce. Hence the 50%-50% has higher water separation than 30%-70% as shown in Section 4.3.2.8.

For the case that the increasing of agitation will increase the water separation, this is due to the optimum agitation for certain emulsion. Increasing in agitation has two roles to play, first is to break the dispersed phase into smaller droplets to enhance the stability while second is that increase in agitation will help the droplets to coalesce faster as the agitation will bring the droplets to meet each other faster and collide with each other and this enhance the collision frequency and increase the rate of coalescence and faster the water and oil are separated.



4.3.2.8 Emulsion 30%-70% for Emulsifier 0.5v%

Figure 4.48: Percentage of Water Separation versus Agitation Speed after 2 days



Figure 4.49: Percentage of Oil Separation versus Agitation Speed after 2 days

From **Figure 4.48** and **4.49**, we can see that the agitation speed has influence on the water separation which is when the agitation speed increases, the water separation will be decreased and so as the oil separation. This is due to at higher agitation the dispersed phase can be break into smaller droplets and this will cause the emulsion to be stable and less water and oil separation. The effect of differences in droplets size distribution is larger at high volume fractions of dispersed phase than at low volume fractions (Schramm,1992). Hence the water and oil separation for 30%-70% is uncertain and out of expectation.

Based on the present work and the previous study of Rønningsen, the relative viscosity of moderately concentrated water-in-crude-oil emulsions appears to be quite insensitive to oil type and conditions as long as the shear field produces droplets of reasonably small size. Therefore the oil separated for the emulsion prepared by the three emulsifiers is very high compare to 50%-50% emulsion. There is a very strong increase in viscosity for high water cuts **as discussed in previous Section 4.3.2.7**.

For the case that the increasing of agitation will increase the water separation, this is due to the optimum agitation for certain emulsion. Increasing in agitation will break the interfacial film on the interface of oil and water as too vigorous agitation will cause the resistance to form the interfacial film and instead increases the interfacial tension between oil and water besides of helping the droplets to coalesce faster as the agitation will bring the droplets to meet each other faster and collide with each other and this enhance the collision frequency and increase the rate of coalescence and faster the water and oil are separated.

4.3.3 Demulsification

4.3.3.1 Comparison of Percentage of Water Separation between Pure Chemical and Microwave-Assisted Chemical for 50%-50% Emulsion



Figure 4.50: Percentage of Water Separation versus Time with 0.1v% Pure Demulsifier



Figure 4.51: Percentage of Oil Separation versus Time with 0.1v% Pure Demulsifier



Figure 4.52: Percentage of Water Separation versus Time with 0.1v% Microwave Assisted Demulsifier



Figure 4.53: Percentage of Oil Separation versus Time with 0.1v% Microwave Assisted Demulsifier

For **Figure 4.50** and **4.51**, we can see that if only with pure chemical at low concentration is not enough to destabilize the water from the crude oil as the concentration of the demulsifier does not enough to reach the interface of oil and water to replace interfacial film that the emulsifier formed and since the separation does not occur even after two day and only oil is separated may due to the demulsifier has separated the oil but with low portion and the water coalesce at a very slow rate and the separation is not visible although the separation has occurred.

While for **Figure 4.52** and **4.53**, we can see that the water separation is low but at least the separation is visible. This is because the microwave heating manage to break certain interfacial film formed by the emulsifier and assist the demulsifier to rupture the film due to the reason stated at the previous paragraph above. The microwave manage to penetrate into the interface and try to enhance film drainage. This is due to the energy of the microwave is strong enough to pass through the emulsion and reach into the

interface that the low concentration of demulsifier fails to do so. The demulsifier will be hindered by the emulsion as the concentration is not strong enough to overcome the force of the emulsion and penetrate into it to reach the interface to break the bond.



Figure 4.54: Percentage of Water Separation versus Time with 0.3v% Pure Demulsifier



Figure 4.55: Percentage of Oil Separation versus Time with 0.3v% Pure Demulsifier



Figure 4.56: Percentage of Water Separation versus Time with 0.3v% Microwave Assisted Demulsifier



Figure 4.57: Percentage of Oil Separation versus Time with 0.3v% Microwave Assisted Demulsifier

For **Figure 4.54** and **4.55**, we can see that only with Cocoamine the separation of water from crude oil is occurred. This due to as Kokal stated that the demulsifiers which work for certain emulsion may not be work for another or not affect or ineffective for another. This is what happening as for the same emulsion, it is only Cocoamine can separate the water effectively compare to Hexylamine and PEG-600 although the agitation is at its optimum. In addition, in this case only Cocoamine can convert firm films to soft films that are fragile and can be ripped apart easily to improve coalescence (Kokal and Aramco, 2006).

While for **Figure 4.56** and **4.57**, we can see only Hexylamine has water separation while the other none. It is out of expectation that none of water separated by using Cocoamine. This may due to the microwave heating improve the penetration of Hexylamine while discouraging the other as the previous **Figure 4.52 and 4.53** also show the same result. In addition, the performance of the Hexylamine is better at higher



temperature even at low concentration while the other fails to perform well in high temperature and low concentration.

Figure 4.58: Percentage of Water Separation versus Time with 0.5v% Pure Demulsifier



Figure 4.59: Percentage of Oil Separation versus Time with 0.5v% Pure Demulsifier



Figure 4.60: Percentage of Water Separation versus Time with 0.5v% Microwave Assisted Demulsifier



Figure 4.61: Percentage of Oil Separation versus Time with 0.5v% Microwave Assisted Demulsifier

For **Figure 4.58** and **4.59**, we can see only Hexylamine at RPM 1000 has water separation, this might due to this is at its optimum condition while the other is out of optimum condition as based on Kokal, the demulsifier concentration should enough to diffuse to the oil/water interface but it should not be larger or exceeded the critical aggregate concentration which the demulsifier will no longer function well.

While for **Figure 4.60** and **4.61**, the water separation for Hexylamine and Cocoamine are quite good and this due to at higher temperature, the demulsifier molecules will have more significant surface activity than natural surfactants and, hence, they will replace the surfactants at the interface by adsorbing in the spaces left by the natural surfactants. This will cause the IFT gradient to be reversed, the film drainage is enhanced, while the interfacial viscosity is decreased and this promote more water droplet to be coalesce and the water separation occurs. (Krawczyk et. al., 1991 & Bhardwaj and Hartland, 1994)



Figure 4.62: Percentage of Water Separation versus Time with Pure Demulsifier at RPM 500



Figure 4.63: Percentage of Oil Separation versus Time with Pure Demulsifier at RPM 500



Figure 4.64: Percentage of Water Separation versus Time with Microwave Assisted Demulsifier at RPM 500



Figure 4.65: Percentage of Oil Separation versus Time with Microwave Assisted Demulsifier at RPM 500

For **Figure 4.62** and **4.63**, we can see that only for Cocoamine, 0.3v% has water separation, this is because the demulsifier has a the right concentration to diffuse to the interfacial film formed by the emulsifier and begin to destabilize it. If the concentration is too small or too large as Kokal stated the critical aggregate concentration, the demulsification will not happen as the only the right amount of demulsifier concentration can diffuse into the oil and water interface to disturb the film and enhance the film drainage by rupturing the bond.

While for **Figure 4.64** and **4.65**, only three samples have water separation, the separation occurs quite fast as the agitation for the demulsification is low which do not enhance re-emulsification and the microwave have enough penetration power into the emulsion and rupture the interface of the oil and water and promote for the drainage of the water. In addition, the Cocoamine, 0.3v% has no water separation, this may be due to the demulsifier is sensitive to temperature, it cannot function well as demulsifier when the temperature is high which may degrade its characteristics and fail to destabilize. This is because the Cocoamine is manufactured from coconut oil which is easily degrade at high temperature.



Figure 4.66: Percentage of Water Separation versus Time with Pure Demulsifier at RPM 1000



Figure 4.67: Percentage of Oil Separation versus Time with Pure Demulsifier at RPM 1000



Figure 4.68: Percentage of Water Separation versus Time with Microwave Assisted Demulsifier at RPM 1000



Figure 4.69: Percentage of Oil Separation versus Time with Microwave Assisted Demulsifier at RPM 1000

For **Figure 4.66** and **4.67**, we can see that there two samples have water separation, this may due to the agitation of the demulsification is at the optimum agitation for both demulsifier concentration as stated in before, the demulsification condition which work for certain emulsion may not be work for another or not affect or ineffective for another.

Whereas for **Figure 4.68** and **4.69**, there are only three samples have water separation which as before, the separation occurs very fast as the agitation for the demulsification is at its optimum which the demulsifiers can reach the interface to rupture the film and with the help of the of the microwave heating, which enhance the drainage of the film at the interface of the oil and water and promote for the separation of the water.



Figure 4.70: Percentage of Water Separation versus Time with Pure Demulsifier at RPM 1500



Figure 4.71: Percentage of Oil Separation versus Time with Pure Demulsifier at RPM 1500



Figure 4.72: Percentage of Water Separation versus Time with Microwave Assisted Demulsifier at RPM 1500



Figure 4.73: Percentage of Oil Separation versus Time with Microwave Assisted Demulsifier at RPM 1500

For **Figure 4.70** and **4.71**, there is only Hexylamine 0.3v% has separation at RPM 1500 while the others have no water separation. This may due to the agitation has enough turbulence and intensity to allow the Hexylamine to reach the interface of oil and water which the other cannot to promote water separation. In addition the dosage of the Hexylamine may match with the agitation and enhance the water separation unlike the other demulsifiers that the dosage may over or under the requirement.

Whereas for **Figure 4.72** and **4.73**, the water separation is less feasible than the previous at lower agitation, this due to the vigorous agitation of the demulsification may enhance the emulsion instead of breaking of the emulsion as the agitation may exceed the critical and the vigorous agitation may break the droplets into smaller size and decrease the coalescence of water droplets,



4.3.3.2 Comparison of Percentage of Water Separation between Pure Chemical and Microwave-Assisted Chemical for 30%-70% Emulsion

Figure 4.74: Percentage of Water Separation versus Time with 0.1v% Pure Demulsifier



Figure 4.75: Percentage of Oil Separation versus Time with 0.1v% Pure Demulsifier



Figure 4.76: Percentage of Water Separation versus Time with 0.1v% Microwave Assisted Demulsifier



Figure 4.77: Percentage of Oil Separation versus Time with 0.1v% Microwave Assisted Demulsifier

For **Figure 4.74** and **4.75**, there is no separation happen. The reason is same as stated in **Figure 4.50** and **4.51**, as the concentration of the demulsifier does not enough to reach the interface of oil and water and the separation is not feasible.

While for **Figure 4.76** and **4.77**, the separation is better if compare with in **Figure 4.52** and **4.53**, this is due to as stated in **Section 4.2.1 and 4.2.2**, the viscosity of the 30%-70% is lower than 50-50% which is inverse than the reality due to sample preparation, maybe the batch the pure crude oil for 50%-50% consists of many natural demulsifier and cause the viscosity to be higher and hence the separation is easily occur at high temperature for 30%-70% as the viscosity is easily to be decreased at higher temperature if compare to 50%-50%.



Figure 4.78: Percentage of Water Separation versus Time with 0.3v% Pure Demulsifier



Figure 4.79: Percentage of Oil Separation versus Time with 0.3v% Pure Demulsifier



Figure 4.80: Percentage of Water Separation versus Time with 0.3v% Microwave Assisted Demulsifier



Figure 4.81: Percentage of Oil Separation versus Time with 0.3v% Microwave Assisted Demulsifier

For **Figure 4.78** and **4.79**, there is no separation also. This is due to in fact the viscosity of 30%-70% is higher than 50%-50% and the coalesce of the water is hard to occur for 30%-70% as the viscosity of the 30%-70% is high and the frequency for the water droplet to meet and collide is lower if compare to 50%-50%. Hence, there is no separation occur and due to the concentration of the demulsifiers also cannot overcome the viscosity to reach the film to break the emulsion and the agitation whether is not enough to cause the demulsifier to reach the interface or too vigorous until promote emulsification rather than demulsification.

While for **Figure 4.80** and **4.81**, the water separation is quite good for most of the demulsifiers. It is because the microwave heating can increase the temperature to a certain high level in a short time and this give room for the demulsifier to reach inside the film as when the temperature increases the viscosity of the emulsion will decrease and the demulsifiers can diffuse easily into the emulsion to rupture and destroy the interfacial film form between oil and water to encourage water separation.



Figure 4.82: Percentage of Water Separation versus Time with 0.5v% Pure Demulsifier



Figure 4.83: Percentage of Oil Separation versus Time with 0.5v% Pure Demulsifier



Figure 4.84: Percentage of Water Separation versus Time with 0.5v% Microwave Assisted Demulsifier



Figure 4.85: Percentage of Oil Separation versus Time with 0.5v% Microwave Assisted Demulsifier

For **Figure 4.82** and **4.83**, there are water separations start to occur. This is because the concentration of the demulsifiers have reach the right amount and it is strong enough to diffuse or penetrate inside the emulsion which has high viscosity with the help of agitation that assist to make a way for the demulsifier to get through the emulsion barrier to get into the interface of oil and water to destabilize it.

Whereas for **Figure 4.84** and **4.85**, the water separation is significant occur for almost all the samples. This is because the microwave heating offers a quick, clean, low-cost, and convenient method of heating, which frequently results in higher yields with shorter reaction or heating times in higher temperature. (Roussy and Pearce, 1995)



Figure 4.86: Percentage of Water Separation versus Time with Pure Demulsifier at RPM 500



Figure 4.87: Percentage of Oil Separation versus Time with Pure Demulsifier at RPM 500



Figure 4.88:Percentage of Water Separation versus Time with Microwave Assisted Demulsifier at RPM 500



Figure 4.89: Percentage of Oil Separation versus Time with Microwave Assisted Demulsifier at RPM 500

For **Figure 4.86** and **4.87**, we can see that only Hexylamine 0.5v% has water separation at lower agitation. This means that only in this condition with Hexylamine 0.5v% at RPM 500, there is water separation. The agitation is not at the optimum condition for most of the demulsifier and its concentration. Hence there is no water separation. The agitation does not promote the demulsifier to diffuse to the oil and water interface and the demulsifier cannot rupture the film to enhance film drainage to encourage coalescence of water droplets.

While for **Figure 4.88** and **4.89**, there are water separation for most of the demulsifiers, this is because with low agitation which does not encourage reemulsification and the microwave heating has opened a room for the demulsifiers to reach the interface by penetrating inside the interface to weaken the film formed by emulsifier and lower the viscosity of the emulsion. Hence, the water separation occurs.



Figure 4.90: Percentage of Water Separation versus Time with Pure Demulsifier at RPM 1000



Figure 4.91: Percentage of Oil Separation versus Time with Pure Demulsifier at RPM 1000



Figure 4.92: Percentage of Water Separation versus Time with Microwave Assisted Demulsifier at RPM 1000


Figure 4.93: Percentage of Oil Separation versus Time with Microwave Assisted Demulsifier at RPM 1000

For **Figure 4.90** and **4.91**, we can see that only Hexylamine 0.5v% has water separation at moderate agitation which same as **Figure 4.86** and **4.87**. This means that only in this condition with Hexylamine 0.5v% at RPM 1000, there is water separation. The reason is same as stated above for **Figure 4.86** and **4.87** but at higher agitation, the emulsion may be stronger as the agitation may encourage the demulsification to be reverse as mild agitation is needed only to allow the demulsifier to diffuse inside the emulsion to water and oil interface and higher agitation may disrupt the role of agitation in demulsification.

While for **Figure 4.92** and **4.93**, there are water separations for most of the demulsifiers, but are less if compare to in **Figure 4.88** and **4.89**. This is because with higher agitation this may promote re-emulsification which the emulsion has stronger bond or film. Although the microwave heating has opened a room for the demulsifiers to reach the interface by penetrating inside the interface to weaken the film formed by

emulsifier and lower the viscosity of the emulsion, higher energy is need to break it to let the water separation occur. Hence the water separation is less if compare in **Figure 4.88** and **4.89**.



Figure 4.94: Percentage of Water Separation versus Time with Pure Demulsifier at RPM 1500



Figure 4.95: Percentage of Oil Separation versus Time with Pure Demulsifier at RPM 1500



Figure 4.96: Percentage of Water Separation versus Time with Microwave Assisted Demulsifier at RPM 1500



Figure 4.97: Percentage of Oil Separation versus Time with Microwave Assisted Demulsifier at RPM 1500

For Figure 4.94 and 4.95, we can see that only Hexylamine 0.5v% has very low water separation at higher agitation which same as Figure 4.86 and 4.87 and Figure 4.90 and 4.91. This means that only in this condition with Hexylamine 0.5v% at RPM 1500, there is water separation. The reason is same as stated above for Figure 4.86 and 4.87 and Figure 4.90 and 4.91 and at very high agitation, the emulsion can be very strong as the vigorous agitation will definitely promote emulsification instead of demulsification, the water droplets will be broken into even small droplets and the demulsifier role has no effect on the emulsion as the emulsifier role has overcame it and the demulsification does not occur easily.

While for **Figure 4.96** and **4.97**, there are water separation for most of the demulsifiers, but are the least if compare to in **Figure 4.88** and **4.89** and **Figure 4.92** and **4.93**. This is because with very high agitation demulsification will definitely hard to occur as the demulsifier fail to play its role and only microwave heating play its role to

penetrate inside the interface to weaken the film formed by emulsifier and lower the viscosity of the emulsion. Higher energy or higher concentration but before critical aggregate concentration are needed to break it if higher water separation is desired. Hence the water separation is less if compared in **Figure 4.88** and **4.89** and **Figure 4.92** and **4.93**.

4.3.4 Surface Tension and Interfacial Tension

From the **Table 4.35** till **4.38**, we can see that the surface tension and interfacial tension of the 30%-70% is higher than the 50%-50%. This is due to for a liquid exposed to a gas the attractive van der Waals forces between molecules are felt equally by all molecules except those in the interfacial region. This imbalance pulls the latter molecules towards the interior of the liquid. The contracting force at the surface is known as the surface tension. Since the surface has a tendency to contact spontaneously in order to minimize the surface area, droplets of the liquid and bubbles of gas tend to adopt a spherical shape: this reduces the total surface free energy. For two immiscible liquid a similar situation applies, except that it may not be so immediately obvious how the interfacial tension and the interface will adopt a configuration that minimizes the interfacial free energy. The higher volume of the upper phase liquid which is oil will press the bottom liquid (water) to become curvier as it is heavier for 30%-70% is higher than the 50%-50% and hence the interfacial tension and surface tension will be higher for 30%-70%.

4.4 SUMMARY

In Chapter 4, result is being discussed in detail and the data is being analysis thoroughly. In the next chapter which is Chapter 5 Conclusion and Recommendation, the conclusion of the research, the precaution steps, the improvement steps and the safety steps will be recommended or suggested in order to obtain a more quality experimental work and results to ensure the results obtain are acceptable and precise.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

5.1.1 Introduction

In the research, the objectives are first to investigate the emulsion stabilization and destabilization of w/o emulsions by microwave-assisted chemical method follow by to compare the performance of microwave-assisted chemical method with conventional method for w/o emulsion demulsification and to find environmentally friendly chemicals for crude oils emulsion breaking and finally is to investigate overall performance of microwave-assisted chemicals for w/o emulsions demulsification. By conducting the research, there are a lot of parameters affect not only in the emulsification but also the demulsification. In the emulsification, the viscosity is governed by a lot of factors which 4 main factors will be listed out with the detail explanations in the **Section 6.2**. Whereas, in demulsification, the performance of the combination of Chemical and Microwave Heating method will be compared to the conventional method with justification in **Section 6.3**. The research will be concluded in the **Section 6.4**.

5.1.2 Stabilization/Emulsification

In the emulsification, the viscosity stands as the most important properties that affect the stability of the emulsions. On the other hand, the viscosity is governed by the other factors which the main factors are temperature, agitation or mixing speed, volume fraction of dispersed phase (water) and emulsifier concentration.

The temperature increases the thermal energy of the droplets and the droplets of the emulsion will start to move which will increase the frequency of the droplets collision and based on Kokal, 2006, this will increase the rate of droplet coalescence. This will cause the interfacial viscosity reduces and the emulsion will be broken easily. In other words, the viscosity is inversely proportional with the temperature as stated in Stoke's Law. However, in the same time the temperature will cause the phase inversion which is change of phase from w/o to o/w and the properties of the emulsion will totally inversed. The viscosity of the emulsion will no longer affected by the Stoke's Law but Brownian motion and due to this, the viscosity will increase with temperature. Hence, the influence the emulsion stability with temperature, the optimum temperature should be considered in order to increase or decrease of the emulsion stability. In this research the optimum temperature to conduct the experiment is at room temperature which promote the best results of emulsion stability as most of the w/o emulsion by using different types of emulsifier, the phase inversion temperature is below 50°C.

Moreover, the viscosity of the emulsion is governed by the agitation or mixing speed. When the agitation increases, the droplets become smaller and the movement of the droplets becomes slower and the energy of the collision becomes less and the viscosity will increase. In the other words, the viscosity is directly proportional to the agitation speed. However, there is the possibility that the mixing speed can increase the rate of coalescence. This because the vigorous mixing speed can help droplets to flocculate easily as it increase the collision of the droplets and hence we need to obtain the optimum mixing speed in the order to produce a stable emulsion. The most

optimum range of mixing speed is from 1000rpm to 1500rpm which the emulsion produced in this range, the emulsion produced is quite stable.

Furthermore, the viscosity of the emulsion is affect by the volume fraction. In theory the higher the density of the dispersed phase, the lower the viscosity of the emulsion and vice versa. However, the results on 50%-50% emulsion obtained is in the reverse which the higher the density of the dispersed phase, the higher the viscosity of the emulsion, once again it is due to Brownian motion which the Brownian motion is influence by the droplet size below 1µm. Since the sample's average droplets size is below 1µm and hence this phenomenon happens. Therefore, in order to reduce this phenomenon to happen careful selection of agitation speed and temperature are required in order to precise the results.

Besides, emulsifier concentration is another factor influence the emulsion stability. This is because concentration of emulsifying agent will affect the oil and water interface. The higher emulsifier concentration, the more the interfacial film is affected and hence the viscosity will increase and vice versa. However, it depends on the type of the emulsifier used, we need to choose the oil soluble emulsifier as it dissolves totally in oil which is the continuous phase and promote the encapsulation of the water droplets as dispersed phase. In the research the best emulsifier used is Span 83 at 0.5v% which will produce the most stable emulsion and it is an oil soluble emulsifier compared to Cocamide DEA (oil and water soluble emulsifier) and Triton X-100 (water soluble emulsifier).

5.1.3 Destabilization/Demulsification

In the demulsification which is the Microwave assisted Chemical demulsification. The separation efficiency is increased with less chemical usage. With less chemical usage and short heating time, we can promote a greener technology and in the same time we can save up the usage of chemical, energy used, this will reduce the

cost of production with higher yield. These can help in meeting the high demand and in the same time increase the profit and save the environment.

The method use is environment and better than conventional method due to microwave heating will reduce energy usage as in term of time as conventional the heating is not uniform and it requires longer heating time to effectively heat up the whole sample while microwave can uniform heat the sample thoroughly and can easily reach high temperature which can decrease the viscosity of the emulsion and separation is easily done. In addition, microwave assisted method is recommended as it meet the environmental friendly requirement as microwave heating will use up the heat as energy source to disturb the emulsion instead of produce heat which can contribute greenhouse effect to the environment. In addition, it avoid combustion which produce carbon dioxide, carbon monoxide that cause air pollution but by using electromagnetic field to affect the polar field of water and rearrange arrangement of water so as coalescence is easily to happen.

Besides, the demulsifiers used in the research which promote high water separation are Hexylamine and Cocoamine which are the hazardous chemical and environmental friendly chemical respectively. This shows that with the usage of environmental friendly chemical with the assistance of microwave heating, the separation of water still can meet and even as good as the hazardous chemical. This means that the research has found a better way for destabilizing the emulsion with a more environmental friendly chemical and short uniform microwave heating if compare with conventional method.

5.1.4 Summary

In a nutshell, in the investigation of the emulsion stabilization and destabilization of w/o emulsions by microwave-assisted chemical method, it is found that the emulsion is affect by temperature ($<50^{\circ}$ C), agitation speed (1000rpm-1500rpm), volume fraction and emulsifier concentration (Span83, 0.5v%) while the

demulsification by microwave-assisted chemical method, the separation efficiency is higher and better.

In the search of environmentally friendly chemicals for crude oils emulsion breaking, it is found that Cocoamine which is produced from coconut oil as an environmental friendly chemical with as good separation as the hazardous chemical with less usage in the assistance of microwave heating.

Finally, it is to compare the performance of microwave-assisted chemical method with conventional method for w/o emulsion demulsification and to investigate overall performance of microwave-assisted chemicals for w/o emulsions demulsification. It is found that the overall performance of the demulsification with microwave-assisted chemicals method is better than the conventional method with higher yield, faster separation which is within 2 days and the higher separation efficiency. Hence this combination method of chemical and microwave heating is better than the conventional method

5.2 **RECOMMENDATIONS**

5.2.1 Introduction

In conducting the experimental works, there are a few out of expectation cases happen which will affect the result and cause the deviation of the results. In addition, there are also unpredicted results happen although precaution steps have been taken and this can manage by either controlling the parameters or by alter the parameters based on the situation of the cases.

Besides, there are necessary to change the condition or procedures of the experimental works if there are a large deviation or experiment fails to obtain any reasonable results. The latter is much more serious and reconstruct of methodology is necessary in order to make the experiment work.

Below are the recommendations recommended in order to improve the results and procedures so that the experimental works can be carried out smoother and easier.

5.2.2 Stabilization/Emulsification

In the research, there is necessary to obtain w/o emulsion. Hence, the selection of the emulsifier is very crucial. We need to take into consideration that the emulsifier physical properties and chemical properties and its behavior and nature to decide whether it is suitable to be used as the emulsifier. In addition, we can ensure the emulsifier nature by observing the HLB number which can determine the solubility of the emulsifier. Next, every emulsifier has its hydrophilic and lipophilic part which determines its behavior towards oil and water. This is very important as it will determine the interface it will be attached, select the right emulsifier will ensure the stability of the emulsifier.

Moreover, in order to obtain accurate physical properties of the emulsion, we must avoid aging of the emulsion. This means that we must conduct the viscometer measurement right after the sample preparation. This is because if the sample is left to settle too long, separation may be occurred as the settling velocity of certain emulsion is very fast, some are slow. For those are very fast, if the emulsion is left for a long time, aging occurs; the physical properties of the sample will totally altered or deviate. Hence the properties obtain is less accurate and incorrect. To avoid aging, well-planned of schedule is necessary so that the experimental work can be carry out smoothly.

Furthermore, microscope analysis should be done before viscometer measurement. This is because we have to ensure that the emulsion is w/o emulsion before we proceed. Although we have test tube method and filter paper method to ensure the phase, microscope is the best way to confirm the phase other that droplet size distribution. Microscope analysis can provide us the phase of the emulsion so that we can double confirm the emulsion phase and proceed our experiment. Besides, in microscope analysis, the droplet size analyzer software should have automatic mode to analyze the droplet size as manually analyze the droplet size will cause inaccuracy as biases or laziness of human being. We will choose to analyze the droplet which has visible size and droplet that easy to measure rather than to measure the tiny droplets. This can cause variation of the droplet size. Droplet size distribution plays an important role in determine the emulsion stability and therefore strict measurement on the droplet size should be implemented in order to obtain the behavior of the emulsion.

As for the Agitation or mixing speed, there is an optimum mixing speed that promotes the most stable emulsion. It is not necessary the higher the agitation the better or stable the emulsion. There is a critical or optimum point that needs to be achieved. If the mixing speed too low, the water cannot break into smaller droplet and this will increase the settling velocity as the droplet is big, the droplet can meet with each other quickly and flocculation and coalescence will happen and separation occur. Whereas, too high of mixing speed will have two possibilities; first is the droplet size can be broken into even smaller pieces. However there is the second possibility that the mixing speed will speed up the coalescence as the high mixing speed may promote the small droplet size to meet with each other as while mixing, it opens the route or it reduces the obstacle for the droplets to meet. Therefore, optimum mixing speed is preferred to obtain stable emulsion.

Temperature has a big influence on the phase inversion. This is due to the emulsifier behavior. Some of the emulsifier will change from oil soluble to water soluble when temperature change and this will inverse their characteristics as an emulsifier. Hence, to avoid phase inversion we have to avoid phase inversion temperature that cause the behavior of emulsifier to change. This can be accomplished by maintaining the temperature of the emulsion at room temperature during sample preparation and after sample preparation for settling. Leave the sample at constant temperature or can be said in the same place at same surrounding condition to avoid temperature changing that can affect the emulsion stability.

The volume fraction of dispersed phase (water), which is by far one of the main factors governing the viscosity which determine the stabilization of crude oil emulsions (Johnsen and Rønningse, 2003). The viscosity of the most stable sample of 50%-50% and 30%-70% emulsions is measured with Brookfield viscosity and average viscosity of both emulsions at ambient temperature are 105.21 cp and 15.98 cp respectively. In fact, the higher the water content, the lower the viscosity as the density of the water increases and it will produce high interfacial tension and it will produce less stable emulsion. However, the result is inversed with theoretical value. This is because both the most stable sample was at the same agitation speed, the mean droplets size produced is almost the same but the amount of water droplet for 50%-50% will be more than 30%-70%. Hence, the viscosity for 50%-50% is higher as the movement is limited due to higher amount of water droplets and it will have higher surface area too (Schramm, 2005) and the emulsifiers can be thoroughly dissolved into the concentrated emulsion which is low in continuous phase (crude oil) and form more interfacial film on the surface of the crude oil to encapsulate the water droplets and cause higher viscosity. The viscosity of w/o emulsion was strongly augmented by increasing volume of water which the dispersed phase (Ilia Anisa and Abdurahman, 2010).

To avoid this inverse theoretical example to occur, the droplet size play an important role on it. This is because this sample for 50%-50%, the droplet size is too small until it is not affected by Stoke's Law whereas it is affected by Brownian motion which the viscosity is not a function of density and temperature. This can be solved by avoiding the too vigorous agitation which will cause the water droplets to be less than $0.1\mu m$. The emulsion will be very stable but the motion of the water droplets are hard to predict. Hence, optimum agitation is still very important.

Besides, Emulsifier Concentration plays an important role also in affecting the stability of the emulsion. This is because the emulsifier concentration will determine the separation of the emulsion by affecting the interface bonding which in another word interfacial film. The higher the emulsifier concentration, the stable the emulsion as there is enough amount of emulsifier to hold the interface of water and oil from separating.

But to increase the stability, it is necessary to collaborating with the agitation also. This is because with the assistant of agitation, the emulsifier can easily reach the interface with less hindering. This will reduce the waste of emulsifier which can reduce the cost of operating and meet the requirement of environmental value.

5.2.3 Destabilization/Demulsification

There are a lot of demulsification methods that have been introduced to the world in destabilizing the emulsion but most of them are either high usage of chemical or high usage of energy used. However, it is recommend that by combining chemical with microwave heating assisted, it can reduce the usage of chemical and in the same time it can reduce the energy usage in term of time and save the environment in term of gas emission with higher separation efficiency. The usage can be reduced as with microwave heating can assist the demulsifier effectively reach into the interface of water and oil and disturb the interfacial film without wastage and obstacle. While microwave heating will reduce energy usage as in term of time as conventional the heating is not uniform and it requires longer heating time to effectively heat up the whole sample while microwave can uniform heat the sample thoroughly and can easily reach high temperature which can decrease the viscosity of the emulsion and separation is easily done. In addition, microwave assisted method is recommended as it meet the environmental friendly requirement as microwave heating will use up the heat as energy source to disturb the emulsion instead of produce heat which can contribute greenhouse effect to the environment. In addition, it avoid combustion which produce carbon dioxide, carbon monoxide that cause air pollution but by using electromagnetic field to affect the polar field of water and rearrange arrangement of water so as coalescence is easily to happen.

As for the Agitation or mixing speed, there is an optimum mixing speed that promotes the most efficient demulsification process. It is not necessary the higher the agitation the better emulsion separation. There is a critical or optimum point that needs to be achieved. Mixing speed in demulsification is a way to ensure or enable the demulsifier to penetrate and dissolve into the emulsion so that it can reach the interface of the emulsion and disturb the film. If the mixing speed too low, the demulsifier cannot penetrate and dissolve into the emulsion. Whereas, too high of mixing speed, the droplet size can be broken into even smaller pieces and demulsifier has lost its function to destabilize, instead of demulsifying, it become emulsifying. Therefore moderate agitation is required for mixing purpose.

Demulsifier Concentration plays an important role also in affecting the stability of the emulsion. This is because the demulsifier concentration will determine the separation of the emulsion by affecting the interface bonding which in another word interfacial film. The higher the demulsifier concentration, the more the separation of the emulsion as there is enough amount of demulsifier to rupture the interface of water and oil for separating. However there is the critical aggregate concentration which the demulsifier will no longer function well and therefore optimum of demulsifier concentration need to be taken into consideration for better separation. Moreover, in order to increase the separation, it is necessary to collaborating with the agitation also. This is because with the assistant of agitation, the demulsifier can easily reach the interface with less hindering. This will reduce the waste of demulsifier which can reduce the cost of operating and meet the requirement of environmental value.

To increase the efficient of microwave heating, it is suggested that the samples are covered at the top and bottom by the aluminium foil so that the heating is only horizontal and no vertical heating is affected. The heating can only in the horizontal and the heat can only in the horizontal direction without losing of heat to the other direction. This can increase the heating efficiency and the frequency of the microwave can easily penetrate deep enough to heat up the whole samples. Temperature has a big influence of the emulsion viscosity. The higher the temperature, the lower the viscosity. Hence with microwave heating, the temperature rise is immediate without time wasting. This can save energy by reducing heating time consumption. In addition, to increase the heating efficiency, the microwave is set so that it would not rotate while heating so that the frequency can constantly penetrate into the sample at fix location. This is because the container is small, fix location is require for better heating. Rotating will cause imbalance of microwave penetration and the wave cannot easily penetrate to the sample due to motion of sample.

For microwave heating, the covered samples should have place for the gas to be released to reduce the pressure inside the samples while heating. This is to reduce the burst and splash of the samples which can cause wastage and the more important it can cause explosion if there is no place for releasing the gas inside the samples and the pressure will increase and explosion may happen. Goggles and gloves are the basic personal safety equipments that must wear during the experiments are conducted.

Besides, we need to take into the consideration that the adsorption and displacement processes which the demulsifier effectiveness also depend on pH, salt content, and temperature. The best demulsifiers are those that readily displace preformed rigid films and leave mobile films (films that exhibit little resistance to coalescence) in their place (Kokal and Aramco, 2006). Hence, choosing of demulsifier is very important. If the demulsifier is temperature sensitive, it is better to conduct the demulsification at its optimum temperature so that the demulsifier can perform better. In addition, the demulsifier characteristic need to be considered as it determines that it is oil soluble or water soluble. In this research, the emulsion is w/o emulsion and water soluble demulsifier is required so that it is soluble in the water and dissolve in the continuous oil phase and diffuse to the oil/water interface to rupture it. Moreover, demulsifier with high rate of adsorption at the interface is very important to ensure coalescence happen. Demulsifier with partition coefficient close to unity into water phase is preferred so that demulsification can happen smoothly.

5.2.4 Summary

The recommendations above should have helped in improving in the process of obtaining the optimum results. With careful and detail analysis of the results and with the guidance of the recommendations, the results achieved should have less error. If there is deviation, but with clear justification, there should be acceptable as in the area of research there is no 100% correct answer, the justification is more important than the desired results as it shows how the researcher understand the situations and find new situation rather than discuss what is already done by other research.

REFERENCES

- Abdurahman, H. Nour, F.S. Mohammed, Rosli M. Yunus and A. Arman; 2009; Demulsification of Virgin Coconut Oil by Centrifugation Method: A Feasibility Study; *International Journal of Chemical Tehnology*; 1 (2), 59-64
- Abdurahman, H. Nour and Rosli M. Yunus; 2006; A Continuous Microwave Heating of Water-In-Oil Emulsions: An Experimental Study; *Journal of Applied Sciences*; 6 (8), 1868-1872
- Abdurahman, H. Nour and Rosli M. Yunus; 2006; Stability and Demulsification of Water-In-Crude Oil (w/o) Emulsions via Microwave Heating; *Journal of Applied Sciences*; 6(8), 1698-1702
- Abdurahman, H. Nour, Rosli M. Yunus and H. Anwaruddin; 2007; Water-in-Oil Emulsions: Its Stabilization and Demulsification; *Journal of Applied Sciences*; 7 (22), 3512-3517
- Abdurahman, H. Nour, Rosli M. Yunus and Zulkifly Jemaat; 2007; Chemical Demulsification of Water-in-Oil Emulsions; *Journal of Applied Sciences*; 7(2), 196-201
- Abdurahman, H. Nour, Sothilakshmi, R. and Azhary H. Nour; 2010; Microwave Heating and Separation of Water-In-Oil Emulsions: An Experimental Study; *Journal of Chemical Technology*; 2(1), 1-11
- Abdurahman H. Nour, Rosli M. Yunus, and Azhary. H. Nour; 2010; Demulsification of Water-in-Oil Emulsions by Microwave Heating Technology; *World Academy of Science*; Engineering and Technology; 62.
- Alexandre Goldszal and Maurice Bourrel; 2000; Demulsification of Crude Oil Emulsions: Correlation to Microemulsion Phase Behavior; *Ind. Eng. Chem.*; 39, 2746-2751
- Ali, M.F. and M.H. Algam; 2000; The Role of Asphaltenes, Resins and Other Solids In the Stabilization of Water in Oil Emulsions and Its Effect on Oil Production in Saudi Oil Fields; *Elsevier Science Ltd*.
- Antonio E. Bresciani, Candido F.X. Mendonca, Rita M. B. Alves, Claudio A.O. Nascimento; 2010; Modeling the kinetics of the coalescence of water droplets in crude oil emulsions subject to an electric field, with the cellular automata technique; *Computers & Chemical Engineering*; Page 2
- Ariany Zulkania; 2001; Characterization of Malaysian Crude Oil Emulsion-Formation and Stability Study; *MSc. Research Proposal*; Universiti Teknologi Malaysia
- Aske, N., Kallevik, H. and Sjöblom, J.; 2001; Determination of Saturate, Aromatic, Resin and Asphaltenic (SARA) Components in Crude Oils by Means of Infrared and Near-Infrared Spectroscopy; *Energy & Fuels*; 1304-1312.
- Atkins, P.W.; 1986; Physical Chemistry, 3rd ed., Freeman and Co. New York, NY.

- Auflem, I. H.; 2002; Influence of Asphaltene Aggregation and Pressure on Crude Oil Emulsion Stability; *Doctor Ingeniør Thesis*; Norwegian University of Science and Technology
- Becker, J. R.; 1997; *Crude Oil Waxes, Emulsions, and Asphaltenes*; PennWell Publishing Company; Oklahoma; 126-129.
- Bhardwaj, A. and Hartland, S.; 1994; Dynamics of Emulsification and Demulsification of Water-in-Crude Oil Emulsions; *Industrial and Engineering Chemistry Research*; 33, 1271.
- Bhattacharyya, B. R.; 1992; Water Soluble Polymer As Water-In-Oil Demulsifier; *United States Patent*; 5100582
- Bobra, M.; 1990; A Study of the Formation of Water-in-Oil Emulsions; *Proc., 1990 Arctic and Marine Oil Spill Program Technical Seminar*; Edmonton, Canada Broto, F., D. Clausse, *J. Phys.* C 9 (1976) 4251
- Clausse, D., F. Gomeza, C. Dalmazzone, C. Noik; 2005; A method for the characterization of emulsions, thermogranulometry: Application to water-incrude oil emulsion; *Journal of Colloid and Interface Science*; Volume 287, Issue 2, 15 July 2005, Pages 694-703
- Chih, C.C. and C.C. Yeong; 2002. Demulsification of W/O Emulsions by Microwave Radiation; *Marcel Dekker, Inc.*
- Chin-Hsing Kuoa and Chon-Lin Lee; 2010; Treatment of oil/water emulsions using seawater-assisted microwave irradiation; *Separation and Purification Technology*; Volume 74, Issue 3, 6 September 2010, Pages 288-293
- Collea, R.D., E. Longob and S.R. Fontes; 2007; Demulsification of water/sunflower oil emulsions by a tangential filtration process using chemically impregnated ceramic tubes; *Journal of Membrane Science*; Volume 289, Issues 1-2, 15 February 2007, Pages 58-66
- Daniel-David, D., Le Follotec, A., Pezron, I., Dalmazzone, C., Noïk, C., Barré, L. and Komunjer, L.; 2008; Destabilisation of Water-in-Crude Oil Emulsions by Silicone Copolymer Demulsifiers; Oil & Gas Science and Technology - Rev. IFP; Vol. 63; No. 1, pp. 165-173
- Davis, H. T.; 1994b; Factors determining emulsion type: Hydrophile-lipophile balance and beyond; *Colloids and Surfaces A: Physicochemical and Engineering Aspects*; 91, 9.
- Eliseeva, V.I.; 1980; Polymer Dispersions, Khimia, Moscow.
- Ese M.H., Sjoblom J., Djuve J., Pugh R.; 2000; An Atomic Force Microscopy Study of Asphaltenes on Mica Surfaces; *Influence of Added Resins and Demulsifiers; Colloid Polym. Sci.*; 278, 532-538.
- Fang, C.S. and Lai, P.M.C.; 1995; Microwave Heating and Separation of Water-In-Oil Emulsions; *Journal of Microwave Power and Electromagnetic Energy*; Vol.30; No.1.
- Fortuny, M., Cesar B. Z. Oliveira, Rosana L. F. V. Melo, Márcio Nele, Raquel C.
 C. Coutinho, and Alexandre F. Santos; 2007; Effect of Salinity, Temperature, Water Content, and pH on the Microwave Demulsification of Crude Oil Emulsions; *Energy Fuels*; 21 (3), pp 1358–1364

- Fournanty, S., Le Guer, Y., El Omari, K. and Dejean, J.P.; 2008; Laminar Flow Emulsification Process to Control the Viscosity Reduction of Heavy Crude Oils; *Journal of Dispersion Science and Technology*; 29:1355–1366
- Gafonova, O.V.; 2000; Role of Asphaltenes and Resins in the Stabilization of Watering-Hydrocarbon Emulsions; *MSc. Thesis*; The University of Calgary
- Gafanova O.V., Yarranton W.; 2001; The Stabilization of Water-in-Hydrocarbon Emulsions by Asphaltenes and Resins; *J. Colloid Interf. Sci.*; 241, 469-478.
- Gou, S., J. Da, Y. Zhang, P. Hang, J. Zhang; 2005; A method and apparatus for demulsifying an oil–water emulsion via ultrasonic effect; *Patent Number W/O*; 2005/030360.
- Hanapi Bin Mat, Professor Dr. Ariffin Samsuri, Professor Dr. Wan Aizan Wan Abdul Rahman and Mrs Siti Ilyani Rani; 2006; Study On Demulsifier Formulation For treating Malaysian Crude Oil Emulsion; VOT 74004
- Ilia Anisa, A.N. and Abdurahman, H.N.; 2010; Affect of Viscosity and Droplet Diameter on water-in-oil (w/o) Emulsions: An Experimental Study; *World Academy of Science, Engineering and Technology*; 62
- Johnsen, E. E. and Rønningse, H. P.; 2003; Viscosity of 'live' water-in-crude-oil emulsions: experimental work and validation of correlations; *Journal of Petroleum Science and Engineering*; 38, 23–36
- Jones, T.J., Neustadter, E.L., and Wittingham, K.P.: "Water-in-Crude Oil Emulsion Stability and Emulsion Destabilization by Chemical Demulsifiers," J. Cdn. Pet. Tech. (April–June 1978) 100.
- Karel Verschueren; 2009; Handbook of Environmental Data on Organic Chemicals, Fifth Edition; John Wiley & Sons, Inc; v.1,2,3&4
- Kessel, D., H.J. Neumann, I. Rahimian; 1993; Asphaltics in water influences in-crude oil emulsions; *First World Congress on Emulsions*; Paris
- Kim, Young-Ho; 1995; A Study Of Dynamic Interfacial Mechanisms For Demulsification Of Water-In-Oil Emulsions; *PhD Thesis*; Illinois Institute Of Technology
- Kim, B.Y., Jun Hyuk Moon, Tae-Hyun Sung, Seung-Man Yang, and Jong-Duk Kim; 2002; Demulsification of Water-In-Crude oil Emulsions By A Continuous Electrostatic Dehydrator; Separation Science And Technology; 37(6), 1307-1320
- Kokal, S.; 2005; SPE Prod. Facil., February, 5-13
- Kokal, S. and Al-Juraid, J.I.: "Reducing Emulsion Problems by Controlling Asphaltene Solubility and Precipitation," *paper SPE 48995 presented at the 1998 SPE Annual Technical Conference and Exhibition*, New Orleans, 27–30 September.
- Kokal, S. L. and Saudi Aramco; 2006; Chapter 12—Crude Oil Emulsions; *Petroleum Engineering Handbook*; Vol. I; 556-557
- Krawczyk, M.A., Wasan, D.J., and Shetty, C.S.; 1991; Chemical Demulsification of Petroleum Emulsion Using Oil Soluble Demulsifier; *Industrial and Engineering Chemistry Research*; 30, No. 2, 367.
- Kuo, C.H., Lee, C.L.; 2010; Treatment of oil/water emulsions using seawater-assisted microwave irradiation; *Separation and Purification Technology*; 74, 288–293
- Levine, S. and Sanford, E.; 1985; Stabilization of Emulsion Droplets by Fine Powders; *Canadian J. Chemical Engineering*; 62, 258.

- MacPherson, I., Kuhliman, R.E., Milo, M.J.; 2005; Emulsifier/Demulsifier System; US Patent No. US2005/0288380A1
- Maeda, Y., M. Vinatoru, C. Stavarach, K. Iwai, H. Oshige; 2005; Method for producing fatty acid alcohol ester; US Patent Number 6884900.
- Mc Clements, D.J.; 2005; Food Emulsions, Principles, Practices, and Techniques, Second Edition; *CRC Series in Contemporary Food Science*.
- Mc Lean J.D., Kilpatrick P.; 1997; Effects of Asphaltene Solvency on Stability of Water-In-Crude Oil Emulsions; J. Colloid Interf. Sci.; 189, 242-253.
- Menon, V.B., Nikolov, A.D., and Wasan, D.T.; 1988; Interfacial Effects of Solids-Stabilized Emulsions: Measurements of Film Tension and Particle Interaction Energy; J. of Colloid and Interface Science; 124, No. 1, 317.
- Mommer, B.; 2004; The Value Of Extra-Heavy Crude Oil From The Orinoco Belt; MEES 47:11
- Newman, S.P., Hahn, C., McClain, R.D.; 2009; Environmentally Friendly Demulsifiers For Crude Oil Emulsions; US Patent No. US 7566744B2
- NRT Science & Technology Committee; 1997; Emulsion Breakers and Inhibitors For Treating Oil Spills; *Fact Sheet*.
- Oetter, G., K. Oppenlaender, Aufbau, Stabilisierung und Spaltung von Roho⁻⁻lemulsionen; 1994; Teil 1: Mechanismus der Stabilisierung und Spaltung von Roho⁻⁻lemuslionen; *Tenside Surf. Det. 31*; 6.
- Oprea, C.V. and Bulacovschi, V.; 1986; Polymerization Processes; *Process Theory, Technical Publishing House, Bucharest.*
- Oprea, S. and Dodita, T.; 2001; Influence of agitation during emulsion polymerization of acrylic–styrene latexes on end product properties; *Progress in Organic Coatings*; 42; 194–201
- Pangu, G.D.; 2006; Ultrasonically Enhanced Phase Separation; Acoustically Aided Coalescence of Droplets In Aqueous Emulsions; Page 18-19
- Pangu, G.D., D.L. Feke; 2004; Acoustically aided separation of oil droplets from aqueous emulsions; *Chem. Eng. Sci.*; 59 3183–3193.
- Perreux, L.; Loupy, A.; 2002; In Microwaves in Organic Synthesis; Loupy, A., Ed.; *Wiley*: Weinheim, Germany; pp 61-114.
- Porter, M.R.; 1994; Use of Surfactant Theory; *Handbook of Surfactants*; Blackie Academic & Professional; United Kingdom; 26-93.
- Rønningsen, H.P., 1993. Prediction of viscosity and surface tension of North sea petroleum fluids by using the average molecular weight; *Energy Fuels*; 7, 565.
- Rønningsen, H.P.; 1995; Correlations for predicting viscosity of W/ O emulsions based on North Sea Crude oils; *Proc. SPE Int. Symp. Oil Field Chem.*; Houston, TX, USA; p. 28968.
- Roussy, G.; Pearce, J. A.; 1995; Foundations and Industrial Applications of Microwave and Radio Frequency Fields: *Physical and Chemical Processes*; John Wiley and Sons: Chichester, U.K.

Salager, J. L., Marquez, L., Mira, I., Perez, M., Ramirez, M., Tyrode, E., Zambrano, N. and Choplin, L.; 2001; Emulsification Efficiency Related To The Combination Of Mechanical Energy Input And System Formulation And Composition Variables; *International Symposium on Mixing in Industrial Processes – ISMIP4 -* 14 – 16 May 2001 – Toulouse (France)

- Schramm, L.L. (Ed.); 1992; Emulsions—fundamentals and applications in the petroleum industry; *Advances in Chemistry Series*; vol. 231; Am. Chem. Soc., Calgary.
- Schramm, L.L.; 1996; Suspensions: Basic principles; In Suspensions: Fundamentals and Applications in the Petroleum Industry, Schramm, L.L. (Ed); American Chemical Society, Washington; pp. 3-44
- Schramm, L.L.; 2005; Emulsions, Foams, and Suspensions: Fundamentals and Applications; WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
- Schorling, P.C., D. G. Kessel and I. Rahimian; 1999; Influence of the crude oil resin/asphaltene ratio on the stability of oil/ water emulsions; *Colloids and Surfaces A: Physicochemical and Engineering Aspects*; Volume 152, Issues 1-2, Pages 95-102
- Selvarajan Radhakrisnan, Ananthasubramaniam Sivakumar and Robert A. M.; 2001; Aqueous Dispersion of An Oil Soluble Demulsifier For Breaking Crude Oil Emulsions; US Patent No. 6,294,093
- Sherman, P.; 1950; J. Soe. Chem. Ind. Suppl; Issue No. 2, 69, 540
- Sherman, P.; 1959; The Influence of Emulsifying Agent Concentration on Emulsion Viscosity; *Physical Chemistry Laboratory*; Y. Wall & Sons Ltd. London (Great Britain)
- Shinoda, K. and Friberg, S.; 1986; Emulsion and Stability; Wiley
- Shinoda, K; 1967; J. Colloid Interface Sci; 24,4
- Shun Chia Industrial Company Limited; TRITON X-100 Nonionic Surfactant; 8th FL. No. 177 Fu-Hsing South Road Sec. 2 Taipei Taiwan R.O.C.
- Sjoblom J., Johnsen E.E., Westvik A., Ese M.H., Djuve J., Auflem I.H., Kallevik H.; 2001; Demulsifiers in the Oil Industry; *Encyclopaedic Handbook of Emulsion Technology*; Sjoblom J. (ed.), Marcel Dekker, New York
- Speight, J. G.; 1991; The Chemistry and Technology of Petroleum; *Marcel Dekker Inc.* New York.
- Speight, J.G. and Moschopedis, S.E.; 1981; On the Molecular Nature of Asphaltenes; *Advances in Chemistry Series*; J.W. Bunger and N.C. Li (eds.), American Chemical Society 195, 1–15.
- Stack, L., P. Carney, H. Malone, T. Wessels; 2005; Factors influencing the ultrasonic separation of oil-in-water emulsions; *Ultrason. Sonochem*; 12 153–160.
- Stoker, H. S.; 2010; General, Organic, and Biological Chemistry; Special Fourth Edition with Study Guide and Solutions
- Susumu, Shunsuke Kikumoto and Hideaki Tokuyama; 2009; Quantitative approach to ultrasonic emulsion separation; *Ultrasonics Sonochemistry*; Volume 16; Issue 1; January; Pages 145-149
- Tambe, D.E. and Sharma, M.M.; 1993; Factors Controlling the Stability of Colloid-Stabilized Emulsions; *J. of Colloid Interface Science*; 157, 244.
- Von Hippel, A.R.; 1954; Dielectric Materials and Apllications; MIT Press, Cambridge, MA
- Wolf, N.O.; 1986; Use of Microwave Radiation in Separating Emulsions and Dispersions of Hydrocarbons and Water, U.S. Patent 4582629
- Retrieved 8th October 2010 from <u>http://baervan.nmt.edu/Petrophysics/group/intro-2-</u>asphaltenes.pdf

Retrieved on 26th October 2010 from (Brookfield) <u>http://www.brookfieldengineering.com/products/viscometers/index.asp</u> Refer on 26th October 2010 from (GlobalSpec) <u>http://www.globalspec.com/LearnMore/Sensors_Transducers_Detectors/Tensio</u> <u>n_Sensing/Tensiometers</u> Retrieved 27th June 2011 from (Cocamide DEA) <u>http://truthinaging.com/ingredients/cocamide-dea</u> Retrieved 7th July 2011 from (Zenitech) <u>http://www.zenitech.com</u> Retrieved 11th July 2011 from (Scott Bader)

www.scottbader.com

APPENDIX

Gantt's Chart for PSM I

Task-to-be- perform	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14
PSM topics released.														
Select Topic														
Find Potential Supervisor														
PSM topics finalized.														
Overview of the topic with Supervisor														
Gathering Data														
Data Analyzing														

Interview with Supervisor							
Preparing Project Report							
Show the Report draft to Supervisor							
Summit Chapter Introduction to Supervisor							
Gathering Data for Preparation of Literature Review							
Meeting with Supervisor							
Summit Literature Review							
Gathering data and consult Supervisor for the Methodology							
Submission of listed chemical and do order of chemical needed							
Submission of the presentation Approval form to coordinator.							

Preparing Power Point							
Presentation							
Presentation							
Submission of Report							

Indicator:

Symbolize the work that have been done

Gantt's Chart for PSM II

TASK		W 02	W 03	W 04	W 05	W 06	W 07	W 08	W 09	W 10	W 11	W 12	W 13	W 14
Thesis seminar														
Literature review and preparation of thesis														
Conduct research														
Analysis experimental data														
Chapter 4: Results and Discussions														
Chapter 5: Conclusion and														
Recommendation														
Submission for Correction of Report														
Submission of Presentation material														
Preparation of presentation														
PSM presentation														
Submitting the full research report														
Preparation of Dissertation														
Submission of Dissertation and logbook (Hardbound and softcopy)														

Indicator:

Symbolized the work that have been done