FORMATION AND STABILITY STUDY OF
SOME MALAYSIAN CRUDE OIL EMULSIONS

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A thesis submitted in fulfilment of
the requirements for the award of the degree of
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Faculty of Chemical and Natural Resources Engineering
Universiti Teknologi Malaysia

MAY 2004
For my beloved mother, late-father, brother, sisters, sister in-law, 
nephew "Rizal", and mas Ranto.
ACKNOWLEDGMENT

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ABSTRACT

The formation of water in crude oil emulsions is often undesirable since it causes problems in petroleum recovery and processing. Hence, the objective of this study is to investigate the crude oil emulsion characteristics and its stability using some selected Malaysian crude oil emulsion samples in order to obtain a better understanding on problems. Some crude oil emulsion samples provided by ESSO Production (M) Inc. as well as model systems consisting of pure oil, synthetic oil (toluene/decane), and crude oil components were used in the study. Some important properties of crude oils and oilfield brines, and the effect of some physical conditions on the crude oil emulsion stability were investigated. In addition, the effect of crude oil components on emulsion formation and stability was also studied. The stability was assessed by measuring the percentage of water separation. Some physical and chemical properties of crude oils have a correlation with each other. Analysis of crude oil components showed that hydrogen/carbon (H/C) ratio of wax is higher than asphaltene. Besides, Fourier Transform Infra Red (FTIR) analysis showed that asphaltene, resin, and oil contained substantial functional groups as polar carrier and aromatic contents, which have important roles in emulsion formation and stability. This study indicated that crude oils, which have higher asphaltene content, lower resin/asphaltene (R/A) ratio, and higher wax contents, would have a stable emulsion. At 28 °C, the 0.5% (w/w) of asphaltene content in crude oil was sufficient to form a stable crude oil emulsion. Asphaltene has a significant role to enhance emulsion stability, while resin would decrease the stability. Wax and solid particles could contribute to the emulsion stability but they do not effective as much as asphaltene. Analysis of factor controlling emulsion stability using factorial design provides the mathematical model, which indicates the role of crude oil components and their interactions terms on the crude oil emulsion formation and stability.
ABSTRAK

# TABLE OF CONTENT

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TITLE PAGE</td>
<td>i</td>
</tr>
<tr>
<td></td>
<td>DECLARATION</td>
<td>ii</td>
</tr>
<tr>
<td></td>
<td>DEDICATION</td>
<td>iii</td>
</tr>
<tr>
<td></td>
<td>ACKNOWLEDGMENTS</td>
<td>iv</td>
</tr>
<tr>
<td></td>
<td>ABSTRACT</td>
<td>v</td>
</tr>
<tr>
<td></td>
<td>ABSTRAK</td>
<td>vi</td>
</tr>
<tr>
<td></td>
<td>TABLE OF CONTENT</td>
<td>vii</td>
</tr>
<tr>
<td></td>
<td>LIST OF TABLES</td>
<td>xi</td>
</tr>
<tr>
<td></td>
<td>LIST OF FIGURES</td>
<td>xiii</td>
</tr>
<tr>
<td></td>
<td>LIST OF ABBREVIATIONS</td>
<td>xviii</td>
</tr>
<tr>
<td></td>
<td>LIST OF NOMENCLATURE</td>
<td>xx</td>
</tr>
<tr>
<td></td>
<td>LIST OF APPENDICES</td>
<td>xxi</td>
</tr>
</tbody>
</table>

## CHAPTER I

**INTRODUCTION**

1.1 Background
1.2 Objectives and Scopes of Work
1.3 Thesis Outline
1.4 Summary
CHAPTER II  LITERATURE REVIEW

2.1 Introduction 7

2.2 Crude Oil Emulsion Properties 7
  2.2.1 Physical properties of crude oils 9
  2.2.2 Physical properties of oilfield brine 12
  2.2.3 Chemical properties of crude oils 13
  2.2.4 Chemical properties of oilfield brines 23

2.3 Crude Oil Emulsion Formation and Stability 27
  2.3.1 Fundamental aspect of emulsion 27
    2.3.1.1 Emulsion formation 30
    2.3.1.2 Emulsion stability 35
  2.3.2 Crude oil emulsion formation 40
    2.3.2.1 Factor affecting crude oil emulsion formation 40
    2.3.2.2 Asphaltene and resin as surface active fractions 49
  2.3.3 Crude oil emulsion stability 51
    2.3.3.1 Effect of crude oil properties on emulsion stability 51
    2.3.4.2 Effect of crude oil components on emulsion stability 55

2.4 Demulsification Aspect of Crude Oil Emulsion 57

2.5 Summary 59

CHAPTER III  MATERIALS AND METHODS 60

3.1 Materials 60

3.2 Experimental Procedures 61
  3.2.1 Separation of interfacial active fractions 61
  3.2.2 Separation of wax and oil 63
  3.2.3 Emulsion preparation 65
3.3 Analytical Procedures

3.3.1 Physical characterization

3.3.2 Chemical characterization

3.3.2.1 Crude oil

3.3.2.2 Oilfield brine

3.4 Data Analysis

CHAPTER IV RESULTS AND DISCUSSION

4.1 Characterization of Crude Oils and Oilfield Brines

4.1.1 Physical properties of crude oils

4.1.2 Physical properties of oilfield brine

4.1.3 Chemical properties of crude oils

4.1.4 Chemical properties of oilfield brines

4.1.5 Characterization of crude oil components

4.1.6 Classification of Malaysian crude oil

4.2 Crude Oil Emulsion Formation and Stability

4.2.1 Emulsion stability of real samples

4.2.2 Factor affecting crude oil emulsion formation and stability.

4.2.2.1 Stability of single component emulsion.

4.2.2.2 Analysis factors controlling emulsion stability

4.3 Comparison between Models and Real Crude Oil Emulsion.

4.4 Summary

CHAPTER V CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions
5.1.1 Characterization
5.1.2 Formation and stability of emulsion
5.2 Recommendations

REFERENCES
APPENDICES
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>UNITAR definition of oil and bitumens [Yarranton, 1997]</td>
<td>8</td>
</tr>
<tr>
<td>2.2</td>
<td>Boiling ranges and the uses of the petroleum cuts [Yarranton, 1997]</td>
<td>8</td>
</tr>
<tr>
<td>2.3</td>
<td>Some physical properties of crude oil from some oilfields [Johansen <em>et al.</em>, 1989]</td>
<td>9</td>
</tr>
<tr>
<td>2.4</td>
<td>Elemental composition of crude oil [Kinghorn, 1983]</td>
<td>14</td>
</tr>
<tr>
<td>2.5</td>
<td>Trace element content of some crude oils [Valcovic, 1978]</td>
<td>20</td>
</tr>
<tr>
<td>2.6</td>
<td>Comparison of cations of sea water, river, water, and oilfield water [Kinghorn, 1983]</td>
<td>24</td>
</tr>
<tr>
<td>2.7</td>
<td>Comparison of anions of sea water, river water, and oilfield brine [Kinghorn, 1983]</td>
<td>25</td>
</tr>
<tr>
<td>3.1</td>
<td>Experimental range and levels of independent variables.</td>
<td>66</td>
</tr>
<tr>
<td>3.2</td>
<td>Correction factors for surface tension measurements with the ring method according to Harkins and Jordan for different density [Kruss, 1994].</td>
<td>69</td>
</tr>
<tr>
<td>3.3</td>
<td>The salinity and conductivity of NaCl solution.</td>
<td>70</td>
</tr>
<tr>
<td>3.4</td>
<td>Assignment of absorption bands in the 1800-1550 and 1100-950 cm-1 regions of infra red spectra of the crude oil fractions [Midttun and Kvalheim, 2001]</td>
<td>73</td>
</tr>
<tr>
<td>3.5</td>
<td>Relations between alkalinity to phenolphthalein and alkalinity to methyl orange in presence of carbonate and bicarbonate [Kinghorn, 1983].</td>
<td>75</td>
</tr>
<tr>
<td>3.6</td>
<td>The matrix design for a $2^3$ factorial design.</td>
<td>77</td>
</tr>
<tr>
<td>3.7</td>
<td>Design matrix of $2^4$ with three center points designs</td>
<td>78</td>
</tr>
<tr>
<td>4.1</td>
<td>Physical properties of six Malaysian crude oils</td>
<td>80</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>4.2</td>
<td>Physical properties of oilfield brines</td>
<td>82</td>
</tr>
<tr>
<td>4.3</td>
<td>Composition of six crude oil emulsions from the East Coast of Malaysia by the modified Ese et al. separation method.</td>
<td>83</td>
</tr>
<tr>
<td>4.4</td>
<td>SARA fractionations by using chromatography method of six Malaysian crude oils</td>
<td>85</td>
</tr>
<tr>
<td>4.5</td>
<td>Oilfield brine analysis</td>
<td>90</td>
</tr>
<tr>
<td>4.6</td>
<td>Oilfield brine analysis in milliequivalent per liter</td>
<td>91</td>
</tr>
<tr>
<td>4.7</td>
<td>Components of Tabu asphaltene from EDAX analysis</td>
<td>94</td>
</tr>
<tr>
<td>4.8</td>
<td>Elemental analysis of asphaltene using CHN-O analyzer</td>
<td>95</td>
</tr>
<tr>
<td>4.9</td>
<td>Elemental components of wax from EDAX analysis</td>
<td>99</td>
</tr>
<tr>
<td>4.10</td>
<td>Elemental analysis of wax using CHN-O analyzer</td>
<td>100</td>
</tr>
<tr>
<td>4.11</td>
<td>Elemental components of solid particle from EDAX analysis</td>
<td>101</td>
</tr>
<tr>
<td>4.12</td>
<td>Characterization of crude oil based on carbon number [McMurray, 1984].</td>
<td>105</td>
</tr>
<tr>
<td>4.13</td>
<td>Use of carbon number and boiling points for characterization of crude oil samples.</td>
<td>105</td>
</tr>
<tr>
<td>4.14</td>
<td>Use of density (as API gravity) for the characterization of petroleum samples [Altgelt and Boduszynski, 1994].</td>
<td>106</td>
</tr>
<tr>
<td>4.15</td>
<td>The factorial design and emulsion stability</td>
<td>122</td>
</tr>
</tbody>
</table>
# List of Figures

<table>
<thead>
<tr>
<th>Figure No.</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Examples of hydrocarbon group in petroleum [Kingham, 1990; Neumann et al., 1981].</td>
<td>15</td>
</tr>
<tr>
<td>2.2</td>
<td>Examples of sulfur and oxygen group in petroleum [Kingham, 1990; Neumann et al., 1981].</td>
<td>18</td>
</tr>
<tr>
<td>2.3</td>
<td>Examples of nitrogen and metal groups in petroleum [Kingham, 1990; Neumann et al., 1981].</td>
<td>19</td>
</tr>
<tr>
<td>2.4</td>
<td>Composition representation on ternary diagram of 640 different crudes. Compositions are in weight% and represent the fraction boiling above 210 °C (450+ °F) [Musser, 1998].</td>
<td>21</td>
</tr>
<tr>
<td>2.5</td>
<td>Schematic of SARA-separation of crude oil [Gafanova, 2000].</td>
<td>22</td>
</tr>
<tr>
<td>2.6</td>
<td>Examples for common Stiff diagram/water pattern [McCain, 1990]</td>
<td>26</td>
</tr>
<tr>
<td>2.7</td>
<td>Schematic illustration of oil-in-water (O/W) and water-in-oil (W/O) macroemulsion [Sharman an Shah, 1985]</td>
<td>28</td>
</tr>
<tr>
<td>2.8</td>
<td>Schematic illustration of multiple W/O/W and O/W/O microemulsion [Sharman and Shah, 1985].</td>
<td>28</td>
</tr>
<tr>
<td>2.9</td>
<td>Some steps occur in the process of emulsification [Schubert and Armbruster, 1992]</td>
<td>30</td>
</tr>
<tr>
<td>2.10</td>
<td>Naphtoic acid in an oil/water mixture [Becker, 1997].</td>
<td>33</td>
</tr>
<tr>
<td>2.11</td>
<td>The association behavior of surfactant in solution, showing the critical micelle concentration (CMC) [Schramm, 1992].</td>
<td>34</td>
</tr>
</tbody>
</table>
2.12 Emulsion separations by flocculation, sedimentation, and coalescence.
2.13 Schematics of the emulsion stability [Davis and Smith, 1976]
2.14 Electric double layer [Sullivan, 2000].
2.15 Stearic repulsion [Sullivan, 2000].
2.16 Marangoni-Gibbs Effect [Sullivan, 2000].
2.17 Hypothetical representation of an average asphaltene molecules [Strauze et al., 1992].
2.18 Hypothetical representation of average resin molecules [Speight, 1980].
2.19 (a) Average structure of a paraffin wax molecule-Malu Isan; (b) Average structure of a microcrystalline wax-San Joaquin Valley [Musser, 1998].
2.20 Alkylated aromatic hydrocarbon in oils [Speight, 1980].
2.21 Proposed mechanism of interaction between resins and asphaltenes [McLean and Kilpatrick, 1997a].
2.22 Accumulation of asphaltene aggregates at the oil-water interface [Aske, 2002].
2.23 Solid particles stabilize an emulsion when they are adsorbed at the interface [Sharman and Shah, 1985].
3.1 The modified procedure for recovering interfacially active fractions [Es et al., 1997].
3.2 The modified procedure for recovering wax crystal and oil [Burger et al., 1981].
3.3 Correlation between concentration and salinity of NaCl solution.
3.4 Standard matrices for complete $2^k$ experimental designs; (a) $2^2$ design; and (b) $2^3$ design [Montgomery, 1997].
4.1 Correlation between °API and viscosity of six crude oil samples.
4.2 Correlation between waxes content and viscosity of crude oils.

4.3 Correlation between asphaltene+solid content and viscosity of crude oils.

4.4 Correlation between asphaltics (asphaltene+polar) content and API gravity of crude oils.

4.5 Correlation between paraffin content and API gravity of crude oils.

4.6 Chromatograms of crude oil samples obtained by using High Temperature Gas Chromatography (HTGC) (a) Semangkok crude oil; (b) Tabu crude oil; (c) Irong Barat crude oil; (d) Seligi crude oil; (e) Tapis crude oil; and (f) Guntung crude oil.

4.7 Water pattern/Stiff graph of oilfield brines in Malaysia (a) Tapis, (b) Seligi, (c) Tapis A1, (d) Tapis A2, (e) Seligi A, (f) Raya A, and (g) Larut A.

4.8 FTIR spectra for asphaltene fraction in (a) Semangkok, (b) Tabu, and (c) Tapis crude oils.

4.9 FTIR spectra for resin fraction in (a) Semangkok, (b) Tabu, and (c) Tapis crude oils.

4.10 FTIR spectra for solid particles fraction in (a) Semangkok, (b) Tabu, and (c) Tapis crude oils.

4.11 FTIR spectra for oil fraction in (a) Semangkok, (b) Tabu, and (c) Tapis crude oils.

4.12 Correlation between the weight of the heaviest cut and viscosity of crude oil samples.

4.13 Stability of six crude oil emulsions by visual analyzing of water separation (a) at room temperature (28 °C) and (b) at 70 °C.

4.14 The difference of emulsion stability of crude oil samples at two different temperatures.

4.15 The stability of crude oil emulsion based on asphaltene content of crude oil samples.
4.16 Effect of pH on the emulsion stability of three stable crude oil emulsions at room temperature.

4.17 Effect of salinity to emulsion stability (a) Tabu crude at 70 °C; (b) Irong Barat at 70 °C; and (c) Tapis crude oil at 40 °C.

4.18 Comparison of effect of salinity on emulsion stability for three crude oil emulsions after 30 days.

4.19 Emulsion stability of resins of some crude oil in pure n-decane at room temperature after 24 hours.

4.20 Dominant contributor to asphaltene solubility, state of aggregations, and the resulting impact on interfacial activity [McLean and Kilpatrick, 1997b].

4.21 Effect of single and mixed components on the model emulsion stability by using pure oil.

4.22 Effect of resin type on emulsion stability. Decan-toluene system and Tabu’s asphaltene (1.5%) were used in model oil. Experimental condition: resin: 20%; model 1: only asphaltene; model 2: using Tabu resin; model 3: using Semangkok resin; and model 4: using Tapis resin.

4.23 Comparison effect of resin types on emulsion stability after 30 days. Decan-toluene system and Tabu’s asphaltene (1.5%) were used in model oils. Experimental condition: resin: 20%; model 1: only asphaltene; model 2: using Tabu resin; model 3: using Semangkok resin; and model 4: using Tapis resin.

4.24 Effect of asphaltene to model emulsion stability in mixture system.

4.25 Effect of resin and ratio of resin/asphaltene in mixture system.

4.26 Effect of waxes to model emulsion stability in mixture system.
4.27  Effect of solid particles on model emulsion stability in mixture system.  

4.28  Correlation between observation and prediction  

4.29  Regression coefficient. The negative values tend to reduce the water separation, while the positive values increase the water separation.  

4.30  Correlation between asphaltene and resin concentration for constant waxes and solid concentration (waxes: 600 mg/l and solid: 35 mg/l).  

4.29  Correlation between asphaltene and waxes concentration for constant resin and solid concentration (resin: 750 mg/l and solid: 35 mg/l).  

4.32  Correlation between asphaltene and solid concentration for constant resin and waxes concentration (resin: 750 mg/l and waxes: 600 mg/l)  

4.33  Effect of single and mixed components on the model emulsion stability with synthetic oil (decane-toluene: 7/3).  

4.34  Comparison of emulsion stability after 30 days observation between two model emulsions by using pure oil and synthetic oil (decane-toluene: 7/3).  

4.35  Comparison of model emulsion with 1% of asphaltene content in various systems (A: single component in the real oil; A’: mixed with resin (15%), waxes (12%), and solid particles (0.7%) in the pure oil; A’’: single component in synthetic oil).  

4.36  Comparison between crude oil emulsions and model emulsion stability.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Asphaltene</td>
</tr>
<tr>
<td>A°</td>
<td>Amstrong</td>
</tr>
<tr>
<td>AAS</td>
<td>Atomic Absorption Spectrophotometry</td>
</tr>
<tr>
<td>API</td>
<td>American Petroleum Institute</td>
</tr>
<tr>
<td>b.s.w</td>
<td>Bottom, sediment, and water</td>
</tr>
<tr>
<td>C</td>
<td>Concentration, mg/l</td>
</tr>
<tr>
<td>°C</td>
<td>°Celcius</td>
</tr>
<tr>
<td>Cal</td>
<td>Calorie</td>
</tr>
<tr>
<td>CMC</td>
<td>Critical Micelle Concentration</td>
</tr>
<tr>
<td>cm</td>
<td>centimeter</td>
</tr>
<tr>
<td>Cn</td>
<td>Carbon number (n = 1,2,3,4,…… )</td>
</tr>
<tr>
<td>cP</td>
<td>Centi Poise</td>
</tr>
<tr>
<td>EDAX</td>
<td>Energy Dispersive X-Ray</td>
</tr>
<tr>
<td>°F</td>
<td>°Farenheit</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infra Red</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>ICPMS</td>
<td>Inductive Coupled Plasma-Mass Spectroscopy</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>Kg</td>
<td>Kilogram</td>
</tr>
<tr>
<td>m</td>
<td>Meter</td>
</tr>
<tr>
<td>meq/l</td>
<td>Milliequivalent per liter</td>
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<tr>
<td>mg</td>
<td>Milligram</td>
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<tr>
<td>mg/L</td>
<td>Milligram per liter</td>
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<tr>
<td>mmN/m</td>
<td>Milli-Newton per meter</td>
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<tr>
<td>ng</td>
<td>nanogram</td>
</tr>
<tr>
<td>O/W</td>
<td>Oil-in-water emulsion</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>O/W/O</td>
<td>Oil-in-water-in-oil emulsion</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>R</td>
<td>Resin</td>
</tr>
<tr>
<td>rpm</td>
<td>Rotation per minutes</td>
</tr>
<tr>
<td>RSM</td>
<td>Response Surface Methodology</td>
</tr>
<tr>
<td>S</td>
<td>Solid particles</td>
</tr>
<tr>
<td>SARA</td>
<td>Saturates Aromatic Resin Asphaltenes</td>
</tr>
<tr>
<td>UNITAR</td>
<td>United Nations Institute of Research</td>
</tr>
<tr>
<td>W</td>
<td>Wax</td>
</tr>
<tr>
<td>W</td>
<td>Weight</td>
</tr>
<tr>
<td>W/O</td>
<td>Water-in-oil emulsion</td>
</tr>
<tr>
<td>W/O/W</td>
<td>Water-in-oil-in-water emulsion</td>
</tr>
<tr>
<td>w/w</td>
<td>Weight per weight</td>
</tr>
<tr>
<td>WS p</td>
<td>Water separation</td>
</tr>
</tbody>
</table>
LIST OF NOMENCLATURE

$A$  
Interfacial surface area of droplet, m$^2$

$G$  
Intensive Gibbs Energy, kJ/mole

$n$  
Constant

$k$  
Richardson constant

$R$  
Radius of sphere, cm

$P_L$  
Laplace pressure, dyne

$T$  
Temperature, °C or K

$\Delta S$  
Change in entropy, cal/mole

Greek Symbols

$\phi$  
Dispersed phase volume fraction

$\gamma$  
Interfacial tension, mN/m

$\eta$  
Intrinsic viscosity, cP

$\pi$  
Interfacial pressure, mN/m

$\rho$  
Liquid density, kg/m$^3$
<table>
<thead>
<tr>
<th>APPENDIX</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Analysis of Differential Scanning Calorimetry (DSC)</td>
<td>150</td>
</tr>
<tr>
<td>B</td>
<td>Analysis of Energy Dispersive X-Ray (EDAX)</td>
<td>154</td>
</tr>
<tr>
<td>C</td>
<td>Results of CHN-O Analyzer</td>
<td>157</td>
</tr>
<tr>
<td>D</td>
<td>FTIR Complete Range Peak of 600-4000 cm(^{-1})</td>
<td>159</td>
</tr>
<tr>
<td>E</td>
<td>Results of Stability Analysis</td>
<td>160</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Background

Crude oil production in Malaysia has been stable in recent years, with monthly production rate from 1996 to the early of 2002, fluctuated between 650,000 to 730,000 barrels per day (bbl/d) [EIA, 2002]. Malaysia’s domestic oil productions produced primarily from the offshore of Peninsula Malaysia, while some are produced in the fields of East Malaysia such as Kinabalu field.

Most of Malaysia’s oil contains low sulphur and high quality crude with petroleum gravity in the range of 35 – 45 °API [Petronas, 2004]. However, the Malaysia petroleum industries are still having several emulsion problems in demulsifying the crude oil emulsion [Sim, 1999]. Particularly, the emulsion problems can be encountered at the early stages of the offshore production of crude oil. It raises two consequences; first, it leads to shut down of the oil wells to prevent the b.s.w (bottom, sediment, and water) level from going higher. Second, the crude oil has to be sold in the form of low price oil because of the difficulties and high cost of treating the emulsion [Sim, 1999].

Emulsions may be encountered in all stages in petroleum recovery and processing industry (drilling fluid, production, process plant, and transportation emulsions). Generally, the reservoir contains gas, oil, and water within a porous matrix and it is retained by a geological trap such as an impermeable anticline The
presence of water, which always be produced with crude oil, could be coming from
the original reservoir saturation or due to a variety of circumstance such as well
bored position, reservoir permeability, reservoir depleting or aging, injection of water
or steam beneath the crude oil zone as mean of secondary oil recovery. Initially,
water and oil phases present as independent phases. Shearing force in the well and
across control valves cause intense mixing of the fluids and forming water-in-crude
oil emulsion [McMahon, 1992]. The emulsion is undesirable since the volume of
dispersed water occupies space in the processing equipments and increases the
overall viscosity of the oil phase. Furthermore, because it is highly saline (in some
cases it might be approaching saturation, which salinity is over than 35,000 ppm
[Collins, 1975]), it variable leads to cause and extend corrosion problems. As was
reported by Taylor [1992], an equivalent volume of water accompanied the daily
productions of some 60 million barrels of crude oil. Presently, the numbers of crude
oil field co-producing water with crude oil in emulsion form is steadily increasing
[Taylor, 1992; Ooi et al., 1997].

Understanding of the chemistry involved in the stabilization of water-in-crude
oil emulsion is important for both economic and environmental reasons. In
economical aspect, the separation of the crude oil emulsion is necessary. The water
presence is unwanted since it has high concentration of chloride salt, which causes
some difficulties (i.e. refining difficulties) such as corrosion, coke deposition,
forming, and poisoning of downstream refinery catalyst and transportation
difficulties such as pipeline and tank corrosion, scaling, and fouling. Extra power
consumption and additional equipments are needed because the undesirable water
occupies space in the processing equipment, thus it causes increasing of viscosity of
the processing fluid, volume of involving equipments, and expense pumping [Clark
et al.; 1993, Li et al., 1992; McMahon, 1992]. Therefore, a premium is placed for
treated oil and then, increasing API-degree through elimination of water usually
causes a higher price for the oil.

The environmental aspect of the problems is emulsion formation during
oceanic oil spills. Mixing energies from the action of wind and wave induce
turbulence and lead to emulsification of the oil spill in the seas. When emulsions are
formed, the properties and characteristics of oil spills are changing significantly
[Fingas et al., 2002]. As for environmental reason, pollution after oil spillage could be reduced if effective clean-up technique was developed. Past incidents have shown that the water-in-oil emulsions are responsible to make the effective clean up of the oil spillage more difficult [Yan et al., 1996; Li et al., 1992].

Crude oil emulsion system under surfactant effect composes complicated associated phenomena that cannot be treated as a subsystem. Surfactant effects create impulsive colloid repulsion imposing an energy barrier, which delay the formation of flocks almost definitely, thereby leading to kinetic stability condition [Rosen, 1978, CPS, 2004]. On the other hand, this kinetically stable system due to the imposed effect from the surfactant is at unstable thermodynamic condition that is out of the role of surfactant. Entropy and internal energy in the system are in values, which cannot be assumed that this system is thermodynamically stable. Therefore, the emulsions are to be said thermodynamically unstable and are frequently kinetically stable. The emulsion will finally separate into two clear liquids if it is left for enough time. However, in some cases, emulsion break-up can take very long time (even years) [Schramm, 1992]. In these cases, the emulsion is called stable.

Stability is a desired property for some emulsions. In other case, stability is undesirable, for examples, emulsions of waste oil in wastewater, as well as, water in crude oil emulsions occurring during oil production. Thus, in crude oil production industry, demulsification or destabilization treatment is necessary to speed up the phase of separation process in order to obtain high purity of crude oil [Cavallo et al., 1990]. In fact, a lot of fundamental questions concerning stability mechanism and destabilization process still need further study. Many studies have been extensively undertaken to solve those two questions [Johansen et al., 1989; Clark and Pilehvari, 1993; Ese et al., 1997; Khadim and Sarbar, 1999; Ali and Alqam, 2000; Gafonova, 2000; Aske, 2002; Gu et al., 2002]. The previous studies have established that there are many factors that could affect formation of stable emulsion, such as salinity of formation water, concentration of paraffinic compound in the crude oil, wax of fine particle content, the effect of surface-active component (asphaltene and resin), the effect of solid particles, fine dispersed droplet size, and others. It was recognized that concentration of asphaltene of crude oil has very important role in emulsion stability. However, the exact reasons, which contribute mostly to the formation of
stable emulsion in those particular fields, are only fully understood. In order to solve the emulsion problems, the understanding of this emulsion system is important.

The formation and stability of emulsion have been an interesting study due to the emulsion problems encountered. Most previous study dealt with standard international of crude oils. Less attention has been paid to Malaysian crude oils and their characteristics involving emulsion. From this point of view, it is important to study Malaysian crude oil in order to have complete information on their properties and emulsion characteristics. Another important factor is the solid particles found in asphaltene. No literature of the authors has dealt with this issue lending to a lack of information regarding the effect of solid particles isolated from asphaltene on emulsion behaviour. This causes a delay in the progress of understanding of some aspects in crude oil emulsion. In addition, interaction between different components of crude oil holds a considerable role in understanding the emulsion mechanism. For engineering application, it is a matter of induce to deal with emulsion using mathematical models based on experimental data that can widen the usage and analysis of different systems. It is, however, required specifically for Malaysian crude oils since such mathematical representations are lack in literature. From those points, this study, therefore, tries to answer the following question: What are the characteristics of Malaysian crude oil emulsion that affect on emulsion formation and stability.

1.2 Objectives and Scopes of Works

The objectives of this research are:

a. To study the characteristics of some selected Malaysian crude oil emulsions in order to provide valuable information to solve the emulsion problems. This was achieving by analyzing some important properties of selected Malaysian crude oils and oilfield brines, such as °API, viscosity, pour point, wax appearance, chemical composition of crude oils, and chemical analysis
of crude oil components (functional groups and elemental analysis). These
will lead to predict the degree of stability of crude oil emulsion samples.
b. To study the formation and stability of Malaysian crude oil emulsion
samples, which includes to study:
   i. The effect of temperature, asphaltene content, pH, and salinity of
      aqueous phase on the formation and stability of crude oil
      emulsions;
   ii. The effect of crude oil components such as asphaltene, resin, wax,
       and solid particles on the formation and stability of water-in-oil
       emulsion as single component and mixed components;
   iii. Factors (fractions) controlling the emulsion stability using
        factorial design.

1.3 Thesis Outline

This thesis is organized into five chapters. Chapter 1 presents general
information regarding the background, objectives, and scopes of this research.

Chapter 2 discusses a general topic on the subject of water-in-crude oil
emulsion. The first section of this chapter deliberates about the basic emulsion
principles with a main focus on controlling factors of the stability of emulsion.
Then, it is followed by a section describing characterization of the asphaltenes,
resins, waxes and solid particles as components of crude oil, with the main focus on
the mechanism of their association and surface-active properties. The next section
provides a description of the conducted research in the area of crude oil emulsion.

Material and experimental procedures, which are used to achieve the
objectives of this research, are presented in Chapter 3. This includes separation of
crude oil components such as asphaltenes, resins, waxes and solid particles;
measurement of physical and chemical properties of crude oil, crude oil components
and oilfield brine; preparation of model emulsion; and finally, emulsion stability test.
The main findings of this research are presented in Chapter 4, which summarizes the results obtained from the characterization of crude oil, components of crude oil (asphalthenes, resin, waxes, and solid particles), and oilfield brine. The results from stability test for single component and mixture of varying concentration of asphalthenes, resins, waxes and solid particles are presented in this chapter. Comparative study of model emulsion and crude oil emulsion is presented as well. The effect of interaction between the components and the emulsion stability, which is analysed using Response Surface Methodology (RSM), is reported in this chapter.

Finally, Chapter 5 summarizes the findings of the study followed by recommendations for additional research required for further characterizing of stability mechanisms of water-in-crude oil emulsion.

1.4 Summary

Crude oil emulsions, which are encountered in the petroleum production industry, are undesirable as they cause several problems. Therefore, the study of factor(s), which affects the formation and stability crude oil emulsion and the effects of interfacially active fractions to the emulsion stability, serves as prerequisites results for solving the emulsion problems. After understanding the factors that cause certain oil fields have more stable emulsion compare to the other fields, specific designs or technique can be developed or selected to prevent or demulsify these stable crude oil emulsions. Furthermore, the data of physical and chemical properties of the reservoir can be used to develop correlation to predict the future of emulsion crude oil wells.
carbonyl and pyrrole, and aromaticity in crude oil and crude oil components, in order to give a clearer illustration of their effect on formation and stability of emulsion. In addition, analysis of acidic, basic and amphoteric contents of fractions is suggested to obtain a complete picture of crude oil components characterization.

ii. Molecular weight of crude oil and its components is recommended to be analyzed in sequence to obtain their correlation with the functional groups and aromaticity which then, can be used to study their effect on emulsion stability.

iii. Instead of using bottle test to assess the emulsion stability, more details study to include the water concentration profile (hold-up) and sedimenting and coalescing interface behaviour studies are suggested.

iv. To understand the role of each crude oil components on the emulsion formation and stability, it is proposed to measure the compositional of the interfacial film formed by the components (asphaltene, resin, wax and solid particles), followed by the determination of the surface active compounds per area of water-oil emulsion interface. These data may provide information in what form of asphaltene, resin, wax or solid particles adsorbed on the interface.

v. The comparison study of emulsion stability at different oil compositions is suggested since it is another good tool for understanding of each component role on emulsion stability.
REFERENCES


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