DEVELOPING NEW CHEMICAL-RHEOLOGICAL MODELS AND CHEMICAL-DURABILITY INDICES OF BITUMEN

MADI HERMADI
HF-080011

A thesis submitted in fulfilment of the requirement for the award of the Doctor of Philosophy

Faculty of Civil and Environmental Engineering
Universiti Tun Hussein Onn Malaysia

NOVEMBER, 2013
ABSTRACT

Significant correlation among chemical properties, rheological characteristics and durability of bitumen is very important in evaluating and modifying bitumen. However, a number of previous studies found inconsistent correlation. Therefore, a study on developing new chemical-rheological models and chemical-durability indices was carried out. Two bitumen fractionation method, Rostler and Corbett methods were used to extract each chemical fraction of bitumen. A number of experiments were conducted to evaluate the effect of each chemical fraction on bitumen rheology such as the effect of asphaltenes, polar aromatics, naphthene aromatics, nitrogen bases, first acidaffins, second acidaffins and paraffins on elastic modulus (G’), viscous modulus (G”) or fatigue factor (G*sin[δ]), and rutting factor (G*/sin[δ]). Two bitumen from different sources, namely Petronas petroleum bitumen and Buton rock asphalt (BRA) bitumen, were used. New chemical-rheological models were formulated to estimate the bitumen rheology in incorporating parameters which are G’, G” or (G*sin[δ]), and (G*/sin[δ]) based on the chemical properties. Furthermore, new chemical durability indices that may indicate the ageing rate of bitumen during short-term and long-term ageing were also formulated. Based on statistical analyses, the models and the indices, which were developed by using chemical properties according to Rostler method were found to be invalid because the real and the predicted rheology were significantly different. While according to Corbett method the models and the indices were valid because the differences is not significant since t-score of the models and the indices were maximum 2.679 and 2.119 or less than t-critical 2.797 and 2.861 respectively). The novelties of this study are the new models and the new indices can be used to predict the bitumen rheology and ageing rate based on the chemical composition. Furthermore, they are very important as guides in modifying a bitumen chemical composition to produce a bitumen mixture with the desired rheology and short-term or long-term ageing rate.
TABLE OF CONTENTS

TITLE  i
DECLARATION  ii
DEDICATION  iii
ACKNOWLEDGEMENTS  iv
ABSTRACT  v
ABSTRAK  vi
TABLE OF CONTENTS  vii
LIST OF TABLES  xiii
LIST OF FIGURES  xviii
LIST OF SYMBOLS AND ABBREVIATIONS  xxiii
LIST OF APPENDICES  xxvii

CHAPTER 1  INTRODUCTION  1
1.1 Background of study  1
1.2 Problem statement  6
1.3 Research aim and objectives  7
1.4 Research scopes  8
1.5 Thesis organization  9

CHAPTER 2  LITERATURE REVIEW  11
2.1 Introduction  11
2.2 Bitumen chemistry  13
   2.2.1 Bitumen chemical properties according  17
to Rostler precipitation method

   2.2.2 Bitumen chemical properties according  19
to Corbett chromatography method
CHAPTER 3  RESEARCH METHODOLOGY  76

3.1  Introduction  76

3.2  Experimental approach  76

3.2.1  Extracting the chemical fraction component of bitumen according to
3.2.2 Extracting the chemical fraction component of bitumen according to Corbett method (ASTM D 4124) 78
3.2.3 Rheological characteristics tests of bitumen by dynamic shear rheometer 80
3.2.4 Ageing conditioning of bitumen 80
3.2.5 Formulation of new chemical-rheological models and chemical durability indices of bitumen 81
3.2.6 Validation of chemical-rheological models and chemical durability indices 82
3.3 Materials selection 87
3.3.1 Description of BRA bitumen 87
3.3.2 Description of petroleum bitumen 89
3.3.3 Description of aggregates 90
3.4 Selection of the experimental variables and data analysis method 91
3.5 The differences of assessing technique between previous and this study 94
3.6 Chapter summary 95

CHAPTER 4 EFFECT OF BITUMEN CHEMICAL FRACTIONS BASED ON ROSTLER ON RHEOLOGICAL CHARACTERISTICS OF BITUMEN AND ITS CHEMICAL DURABILITY INDICES 96
4.1 Introduction 96
4.2 Factorial analysis of the effect of chemical fractions according to Rostler method on bitumen rheological characteristics 97
4.3 Regression analysis of the effect of chemical fractions according to Rostler method on
chapter 5 effect of bitumen chemical fractions based on corbett on rheological characteristics of bitumen and its chemical durability indices
CHAPTER 6  VALIDATION OF THE NEW CHEMICAL-RHEOLOGICAL MODELS AND CHEMICAL DURABILITY INDICES OF BITUMEN  

6.1   Introduction  
6.2   Chemical properties of the blended bitumen  
6.3   Rheological characteristics of the blended bitumen  
6.4   Validation of the new chemical-rheological models of bitumen  
   6.4.1  The new chemical-rheological models based on Rostler chemical properties
6.4.2 The new chemical-rheological models based on Corbett chemical properties 160

6.5 Validation of the new chemical durability indices of bitumen 165

6.5.1 The new chemical durability indices based on Rostler chemical properties 166

6.5.2 The new chemical durability indices based on Corbett chemical properties 167

6.6 Chapter summary 169

CHAPTER 7 PERFORMANCE OF BITUMEN AND ITS MIXTURE 171

7.1 Introduction 171

7.2 The optimum composition and volumetric of the mixtures 172

7.3 Indirect tensile stiffness modulus 174

7.4 Dynamic creep stiffness 176

7.5 Fatigue test of long term aged mixture 178

7.6 Chapter summary 183

CHAPTER 8 CONCLUSION AND RECOMMENDATION 184

8.1 Conclusion 184

8.2 Recommendations 187

PUBLICATIONS DURING STUDY 189

REFERENCES 191
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Structures and dipole moment values of some organic molecules</td>
<td>16</td>
</tr>
<tr>
<td>2.2</td>
<td>Viscosity of bitumen fractions at same average molecular weight (Petersen, 1982)</td>
<td>24</td>
</tr>
<tr>
<td>2.3</td>
<td>Performance Grade (PG) Specification of bitumen (ASTM D6373 - 2007)</td>
<td>45</td>
</tr>
<tr>
<td>2.4</td>
<td>RDR value criteria for bitumen binder (Rostler, 1985)</td>
<td>48</td>
</tr>
<tr>
<td>2.5</td>
<td>Fractional composition of the original and aged Cold Lake and Ural Bitumen in % (Michalica et al., 2008b)</td>
<td>53</td>
</tr>
<tr>
<td>2.6</td>
<td>Estimation of natural asphalt deposit in the world (Deputy Minister of Energy and Mineral Resources, 1999)</td>
<td>65</td>
</tr>
<tr>
<td>2.7</td>
<td>Estimation of Lawele B.R.A. deposit (Ministry of Public Work, 2006)</td>
<td>66</td>
</tr>
<tr>
<td>2.8</td>
<td>Requirement of Processed Lawele BRA (Directorate General of Highway, 2009)</td>
<td>70</td>
</tr>
<tr>
<td>2.9</td>
<td>Requirement of Lawele BRA bitumen (Directorate General of Highway, 2009)</td>
<td>70</td>
</tr>
<tr>
<td>3.1</td>
<td>Gradation limits for asphaltic concrete</td>
<td>83</td>
</tr>
<tr>
<td>3.2</td>
<td>Characteristics of BRA raw material</td>
<td>88</td>
</tr>
<tr>
<td>3.3</td>
<td>Characteristics of pre-processed BRA</td>
<td>89</td>
</tr>
<tr>
<td>3.4</td>
<td>Characteristics of BRA bitumen</td>
<td>89</td>
</tr>
<tr>
<td>3.5</td>
<td>Characteristics of the petroleum bitumen penetration grade 80-100 (Petronas, Malaysia)</td>
<td>90</td>
</tr>
<tr>
<td>3.6</td>
<td>Characteristics of the fine and coarse aggregates</td>
<td>90</td>
</tr>
<tr>
<td>3.7</td>
<td>Factor and level of factor based on Rostler chemical fractions</td>
<td>92</td>
</tr>
<tr>
<td>3.8</td>
<td>Factor and level of factor based on Corbett chemical</td>
<td></td>
</tr>
</tbody>
</table>
fractions

3.9 Variants

3.10 The differences of assessment technique between previous and this study

4.1 Factor and level factor in the factorial strip plot design analysis of the effect of Rostler chemical properties on bitumen rheology

4.2 The factorial analysis results of the effect of the bitumen chemical fraction based on Rostler method on complex modulus (G*)

4.3 The factorial analysis results of the effect of the bitumen chemical fraction based on Rostler on phase angle (δ)

4.4 Linearity analysis of the relationship between bitumen chemical fractions based on Rostler with rheology characteristics of non-aged bitumen

4.5 Linearity analysis of the relationship between bitumen chemical fractions based on Rostler with rheology characteristics of RTFOT-aged bitumen

4.6 Linearity analysis of the relationship between bitumen chemical fractions based on Rostler with rheology characteristics of PAV-aged bitumen

4.7 The coefficients in regression of the effect of bitumen chemical fractions based on Rostler on rheological characteristics of the non-aged bitumen

4.8 The coefficients in regression of the effect of bitumen chemical fractions based on Rostler on rheological characteristics of the RTFOT-aged bitumen

4.9 The coefficients in regression of the effect of bitumen chemical fractions based on Rostler on rheological characteristics of the PAV-aged bitumen

4.10 The average molecular weight number (M_n) of Cold Lake bitumen and Ural bitumen using a vapour pressure osmometer (VPO) (Michalica et al., 2008b)
4.11 Carbonyl and sulfoxide index of the asphaltenes of Cold Lake and Ural bitumen (Michalica et al., 2008b)

4.12 Elemental composition of the original and aged Cold Lake and Ural bitumen (Michalica et al., 2008b)

4.13 The contribution of the Rostler chemical fractions of the bitumen RTFOT Ageing Indices

4.14 The contribution of the Rostler chemical fractions of the bitumen PAV Ageing Indexes

5.1 Factor and level factor in the factorial strip plot design analysis of the effect of Corbett chemical properties on bitumen rheology

5.2 The Analysis of variants results of the effect of the Corbett chemical fractions on natural logarithmic of complex modulus (ln G*)

5.3 The Analysis of variants results of the effect of the Corbett chemical fraction on phase angle (δ)

5.4 Linearity of relationship between Corbett chemicals with rheology of non-aged bitumen

5.5 Linearity of regression between Corbett chemicals with rheology of RTFOT aged bitumen

5.6 Linearity of regression between Corbett chemicals with rheology of PAV bitumen

5.7 The coefficients in regression of the effect of Corbett chemicals on rheological characteristics of the non-aged bitumen

5.8 The coefficients in regression of the effect of Corbett chemicals on rheological characteristics the bitumen after RTFOT

5.9 The coefficients in regression of the effect of Corbett chemicals on rheological characteristics the bitumen after PAV

5.10 The contribution of the Corbett chemical fractions on Chemical Durability Indices of RTFOT-aged bitumen
5.11 The contribution of the Corbett chemical fractions of the bitumen PAV Ageing Indices

6.1 Percentage of Rostler chemical fractions of the blended bitumen

6.2 Percentage of Corbett chemical fractions of the blended bitumen

6.3 Elastic modulus of the blended bitumen at non-aged condition

6.4 Viscous modulus of the blended bitumen at non-aged condition

6.5 Rutting factor of the blended bitumen at non-aged condition

6.6 Elastic modulus of the blended bitumen at RTFOT-aged condition

6.7 Viscous modulus of the blended bitumen at RTFOT-aged condition

6.8 Rutting factor of the blended bitumen at RTFOT-aged condition

6.9 Elastic modulus of the blended bitumen at PAV-aged condition

6.10 Viscous modulus or fatigue factor of the blended bitumen at PAV-aged condition

6.11 Comparison of rheological characteristics of the blended bitumen at non-aged condition between actual and predicted based on Rostler chemical properties

6.12 Comparison of rheological characteristics of the blended bitumen at RTFOT-aged condition between actual and predicted based on Rostler chemical properties

6.13 Comparison of rheological characteristics of the blended bitumen at PAV-aged condition between actual and predicted based on Rostler chemical properties

6.14 Rheological characteristics of the blended bitumen based on actual tests and predicted using Rostler.
chemical properties

6.15 Comparison of rheological characteristics of the blended bitumen at non-aged condition between actual and predicted based on Corbett chemical properties

6.16 Comparison of rheological characteristics of the blended bitumen at RTFOT-aged condition between actual and predicted based on Corbett chemical properties

6.17 Comparison of rheological characteristics of the blended bitumen at PAV-aged condition between actual and predicted based on Corbett chemical properties

6.18 Rheological characteristics of the blended bitumen based on actual tests and predicted using Corbett chemical properties

6.19 Durability indices of the blended bitumen based on actual tests and predicted by using Rostler chemical properties

6.20 Durability indices of the blended bitumen based on actual tests and predicted by using Corbett chemical properties

7.1 The mixture volumetric at optimum compensations and the requirement

7.2 Dynamic creep stiffness and bitumen rutting factor estimated at 40°C

7.3 Ageing and fatigue characteristics of bitumen and mixture
LIST OF FIGURES

2.1 The broad structures of aliphatics hydrocarbon in bitumen 13
2.2 The broad structures of cyclics hydrocarbon in bitumen 14
2.3 The broad structures of aromatics hydrocarbon in bitumen 14
2.4 The combining structures of hydrocarbon in bitumen 14
2.5 Heteroatom structure of hydrocarbon in bitumen 15
2.6 Bitumen chemical precipitation test according to Rostler method (ASTM D2006-1965) 18
2.7 Bitumen chemical separation test according to Corbett method (ASTM D4124-2001) 20
2.8 Glassy, elastic and viscous behaviour of bitumen (Breen & Stephens, 1967) 27
2.9 Viscous, elastic and viscoelastic behaviour 28
2.10 Stress-strain response between the two extremes bitumen (U.S. National Highway Institute, 2009) 29
2.11 Stress-strain response of viscoelastic bitumen (U.S. National Highway Institute, 2009) 30
2.12 Viscous and elastic behaviour comparison of two typical bitumen samples 30
2.13 Rheological characteristic tests at each ageing bitumen condition (U.S. National Highway Institute, 2009) 31
2.14 Rotational Viscometer (U.S. National Highway Institute, 2009) 32
2.15 Temperature – viscosity relationship (The Asphalt Institute, 1996) 33
2.16 Oscillation at dynamic shear rheometer (U.S. National
2.17 Used dimension in stress and strain calculations (U.S. National Highway Institute, 2009) 35
2.18 Vertical and Horizontal Components of Complex Modulus, (Hrdlicka, 2007) 36
2.19 Loading and Unloading of Asphalt Binder for the First Three Cycles (Hrdlicka, 2007) 37
2.20 Schematic of bending beam rheometer (BBR) (National Highway Institute, 2009) 38
2.21 The two evaluated parameters in BBR (U.S. National Highway Institute, 2009) 39
2.22 DTT measurement principle (U.S. National Highway Institute, 2009) 40
2.23 Typical changes in chemical composition of bitumen (Brownridge, 2010) 50
2.24 The effect of ageing on chemical composition of binder recovered from porous asphalt (Isacsso & Zeng, 1997) 54
2.25 Change composition of Ural and Cold lake bitumen during ageing (Michalica et al., 2008) 54
2.26 SARA fractions for Ras Tanura and Riyadh bitumens before and after 85 min and 340 min RTFOT ageing (Lesueur, 2009) 55
2.27 SARA fractions for Kuwait and Bahrain bitumens before and after 85 min and 340 min RTFOT ageing (Lesueur, 2009) 55
2.28 Location and map of Buton Island (Ministry of Public Work, 2006) 65
2.29 Kabungka BRA deposit of Sarana Karya 66
2.30 Lawele BRA deposit of Sarana Karya 67
2.31 Lawele BRA deposit of Buton Asphalt Indonesia 67
2.32 The effect of BRA percent on stiffness modulus of hot mix asphalt mixture (Directorate General of Highway, 2006) 68
3.1 Flow Chart of Research Activity 77
3.2 Chemical precipitation method according to Rostler 78
3.3 Chemical chromatography method according to Corbett 79
3.4 Chromatographic column for separation of bitumen by elution-absorption 79
3.5 Correlation between loss on heating of BRA with penetration of BRA-bitumen 88
4.1 The treatment-effect-coefficient of asphaltenes in the regression equations based on Rostler composition 104
4.2 The treatment-effect-coefficient of nitrogen bases in the regression equations based on Rostler composition 107
4.3 The treatment-effect-coefficient of first acidaffins in the regression equations based on Rostler composition 108
4.4 The treatment-effect-coefficient of second acidaffins in the regression equations based on Rostler composition 109
4.5 The treatment-effect-coefficient of paraffins in the regression equations based on Rostler composition 110
4.6 The treatment-effect-coefficient of temperatures in the regression equations based on Rostler composition 112
4.7 The non-treatment-effect-coefficient in the regression equations based on Rostler composition 113
5.1 Comparison of the treatment effect coefficient between Rostler and Corbett asphaltenes in the regression equations 129
5.2 The treatment effect coefficient of polar aromatics in the regression equations based on Corbett composition 130
5.3 The treatment effect coefficient of naphthene aromatics in the regression equations based on Corbett composition 131
5.4 The treatment-effect-coefficient of saturates in the regression equations based on Corbett composition 132
5.5 Comparison of the treatment-effect-coefficient of temperatures on the bitumen rheological characteristics
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.6</td>
<td>Comparison of the non-treatment effect coefficient in the Rostler and Corbett regression equations</td>
</tr>
<tr>
<td>6.1</td>
<td>The effect of percentage of BRA bitumen on Rostler chemical properties of the blended bitumen</td>
</tr>
<tr>
<td>6.2</td>
<td>The effect of percentage of BRA bitumen on Corbett chemical properties of the blended bitumen</td>
</tr>
<tr>
<td>6.3</td>
<td>Elastic modulus of the blended bitumen at non-aged condition</td>
</tr>
<tr>
<td>6.4</td>
<td>Viscous modulus of the blended bitumen at non-aged condition</td>
</tr>
<tr>
<td>6.5</td>
<td>Rutting factor of the blended bitumen at non-aged condition</td>
</tr>
<tr>
<td>6.6</td>
<td>Elastic modulus of the blended bitumen at RTFOT-aged condition</td>
</tr>
<tr>
<td>6.7</td>
<td>Viscous modulus of the blended bitumen at RTFOT-aged condition</td>
</tr>
<tr>
<td>6.8</td>
<td>Rutting factor of the blended bitumen at RTFOT-aged condition</td>
</tr>
<tr>
<td>6.9</td>
<td>The effect of percentage of BRA bitumen on temperature at which the Superpave requirement for G*/sin[δ] is fulfilled</td>
</tr>
<tr>
<td>6.10</td>
<td>Elastic modulus of the blended bitumen at PAV-aged condition</td>
</tr>
<tr>
<td>6.11</td>
<td>Viscous modulus of the blended bitumen at PAV-aged condition</td>
</tr>
<tr>
<td>6.12</td>
<td>Actual and predicted (based on Rostler chemical composition) of the blended bitumen temperature at G*/sin[δ] is fulfilled requirement</td>
</tr>
<tr>
<td>6.13</td>
<td>Actual and predicted (based on Corbett chemical composition) of the blended bitumen temperature at G*/sin[δ] is fulfilled requirement</td>
</tr>
<tr>
<td>7.1</td>
<td>The aggregate gradation of the mixtures</td>
</tr>
</tbody>
</table>
7.2 Mixing and compaction temperatures of petroleum and BRA bitumen
7.3 Indirect tensile stiffness modulus of the mixtures with different binders
7.4 Creep strain slope of the mixtures at 40 °C
7.5 Creep strain slope of the mixtures and G* / sin[δ] of the bitumen at 40 °C
7.6 The correlation between G*sin[δ] of bitumen and fatigue life of mixture at 40°C
7.7 The correlation between percentage of BRA bitumen and chemical durability indices of short-term age at 40°C
7.8 The correlation between percentage of BRA bitumen and chemical durability indices of long-term age at 40°C
7.9 The effect of percentage of BRA bitumen on fatigue life (Nf) at 40°C of the asphalt mixture
7.10 The effect of the chemical durability index of short-term ageing bitumen on fatigue life (Nf) of the asphalt mixture at 40°C
7.11 The effect of the chemical durability index of long-term ageing bitumen on fatigue life (Nf) of the asphalt mixture at 40°C
### LIST OF SYMBOLS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Asphaltenes</td>
</tr>
<tr>
<td>A&lt;sub&gt;1&lt;/sub&gt;</td>
<td>First acidaffins</td>
</tr>
<tr>
<td>A&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Second acidaffins</td>
</tr>
<tr>
<td>AI</td>
<td>Ageing Index</td>
</tr>
<tr>
<td>BBR</td>
<td>Bending Beam Rheometer</td>
</tr>
<tr>
<td>BRA</td>
<td>Buton Rock Asphalt, that natural rock asphalt from Buton Island</td>
</tr>
<tr>
<td>CDI</td>
<td>Chemical Durability Index</td>
</tr>
<tr>
<td>CDI-I</td>
<td>Chemical Durability Index based on Rostler fractionation method</td>
</tr>
<tr>
<td>CDI-II</td>
<td>Chemical Durability Index based on Corbett fractionation method</td>
</tr>
<tr>
<td>cP</td>
<td>Centi Poises</td>
</tr>
<tr>
<td>CSS</td>
<td>Creep Strain Slope</td>
</tr>
<tr>
<td>DSR</td>
<td>Dynamic Shear Rheometer</td>
</tr>
<tr>
<td>DTT</td>
<td>Direct Tension Test</td>
</tr>
<tr>
<td>ESALs</td>
<td>Equivalent single axle loads</td>
</tr>
<tr>
<td>δ</td>
<td>Phase angle</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionization Detection</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transforms Infrared Spectroscopy</td>
</tr>
<tr>
<td>G’</td>
<td>Elastic modulus</td>
</tr>
<tr>
<td>G’’</td>
<td>Viscous modulus</td>
</tr>
<tr>
<td>G’*</td>
<td>Complex shear modulus</td>
</tr>
<tr>
<td>G’*/sin[δ]</td>
<td>Rutting factor to indicate rutting susceptibility</td>
</tr>
<tr>
<td>G’*sin[δ]</td>
<td>Fatigue factor to indicate fatigue susceptibility</td>
</tr>
<tr>
<td>G&lt;sub&gt;mm&lt;/sub&gt;</td>
<td>Maximum specific gravity</td>
</tr>
<tr>
<td>GR</td>
<td>Gotolski Ratio</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Sulfuric acid</td>
</tr>
<tr>
<td>85% H₂SO₄</td>
<td>Glover sulfuric acid</td>
</tr>
<tr>
<td>98% H₂SO₄</td>
<td>Concentrated sulfuric acid</td>
</tr>
<tr>
<td>H₂SO₄+SO₃</td>
<td>Fuming sulfuric acid</td>
</tr>
<tr>
<td>H₂S₂O₇</td>
<td>Fuming sulfuric acid</td>
</tr>
<tr>
<td>HP-GPC</td>
<td>High Performance Gel Permeation Chromatography</td>
</tr>
<tr>
<td>HMA</td>
<td>Hot mix asphalt</td>
</tr>
<tr>
<td>HMAC</td>
<td>Hot mix asphalt concrete</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>I.E.C.</td>
<td>Ion Exchange Chromatography</td>
</tr>
<tr>
<td>Iₐ</td>
<td>Asphalten Index</td>
</tr>
<tr>
<td>I₉</td>
<td>Gastel Index</td>
</tr>
<tr>
<td>Iₐ</td>
<td>Colloidal Index</td>
</tr>
<tr>
<td>IDT</td>
<td>Indirect tension</td>
</tr>
<tr>
<td>ITFT</td>
<td>Indirect Tensile Fatigue Test</td>
</tr>
<tr>
<td>ITSM</td>
<td>Indirect tensile stiffness modulus</td>
</tr>
<tr>
<td>Kabungka BRA</td>
<td>Buton Rock Asphalt from Kabungka region</td>
</tr>
<tr>
<td>kPa</td>
<td>Kilo Pascals</td>
</tr>
<tr>
<td>Lawele BRA</td>
<td>Buton Rock Asphalt from Lawele region</td>
</tr>
<tr>
<td>Long-term ageing</td>
<td>Ageing of bitumen during asphalt pavement construction and in service</td>
</tr>
<tr>
<td>MP</td>
<td>Melting point</td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen bases</td>
</tr>
<tr>
<td>Nᵢ</td>
<td>Gyration numbers at initial compaction</td>
</tr>
<tr>
<td>Nᵈ</td>
<td>Gyration numbers at design compaction</td>
</tr>
<tr>
<td>Nₘₐₓ</td>
<td>Gyration numbers at maximum compaction</td>
</tr>
<tr>
<td>OBC</td>
<td>Optimum bitumen content</td>
</tr>
<tr>
<td>P</td>
<td>Paraffins</td>
</tr>
<tr>
<td>PaS</td>
<td>Pascal Second</td>
</tr>
<tr>
<td>PAV</td>
<td>Pressure Ageing Vessel that used to simulate long-term ageing condition of bitumen</td>
</tr>
<tr>
<td>PAV-aged</td>
<td>After long-term ageing that simulated by PAV</td>
</tr>
<tr>
<td>PG</td>
<td>Performance Grade</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>POBC</td>
<td>Predicted optimum bitumen content</td>
</tr>
<tr>
<td>RDR</td>
<td>Rostler Durability Ratio</td>
</tr>
<tr>
<td>RTFOT</td>
<td>Rolling Thin Film Oven Test that used to simulate short-term ageing condition of bitumen</td>
</tr>
<tr>
<td>RTFOT-aged</td>
<td>After short-term ageing that simulated by RTFOT</td>
</tr>
<tr>
<td>RV</td>
<td>Rotational Viscometer</td>
</tr>
<tr>
<td>SARA</td>
<td>Saturates, Aromatics, Resin and Asphaltene</td>
</tr>
<tr>
<td>SGC</td>
<td>Superpave Gyratory Compactor</td>
</tr>
<tr>
<td>Short-term ageing</td>
<td>Ageing of bitumen during construction of asphalt pavement</td>
</tr>
<tr>
<td>SHRP</td>
<td>Strategic Highway Research Program</td>
</tr>
<tr>
<td>T</td>
<td>Maximum applied torque,</td>
</tr>
<tr>
<td>TFOT</td>
<td>Thin Film Oven Test that used to simulate short-term ageing condition of bitumen</td>
</tr>
<tr>
<td>Tg</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin Layer Chromatography</td>
</tr>
<tr>
<td>TSR</td>
<td>Tensile strength ratio</td>
</tr>
<tr>
<td>UTM</td>
<td>Universal Testing Machine</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet rays or electromagnetic radiation with a wavelength shorter than that of visible light, but longer than X-rays</td>
</tr>
<tr>
<td>VMA</td>
<td>Voids in Mineral Aggregate</td>
</tr>
<tr>
<td>W_c</td>
<td>Work dissipated per load cycle,</td>
</tr>
<tr>
<td>τ</td>
<td>shear stress</td>
</tr>
<tr>
<td>γ</td>
<td>shear strain response</td>
</tr>
<tr>
<td>τ_max</td>
<td>Maximum applied shear stress</td>
</tr>
<tr>
<td>γ_max</td>
<td>Maximum response shear strain</td>
</tr>
<tr>
<td>σ_o</td>
<td>Applied stress</td>
</tr>
<tr>
<td>ε_0</td>
<td>Strain</td>
</tr>
<tr>
<td>R</td>
<td>Radius of specimen</td>
</tr>
<tr>
<td>θ</td>
<td>Deflection (rotation) angle</td>
</tr>
<tr>
<td>H</td>
<td>Height of specimen</td>
</tr>
<tr>
<td>S(t)</td>
<td>Creep stiffness at the time</td>
</tr>
</tbody>
</table>
L  Applied constant load or peak value of the applied vertical load
B  beam width
l  Distance or length between beam supports
Δ(t)  Deflection at time
σ_f  Failure stress
Sm  Indirect tensile stiffness modulus (MPa)
D  Amplitude of the horizontal deformation
H  Thickness of the test specimen
ν  Poisson's ratio which for bituminous mixtures is normally assumed to be 0.35
D(t)  the creep compliance at time t (1/kPa),
GL  Gage length (meters),
ΔH  Horizontal deformation (meters),
D  Diameter of specimen (meters),
C_{compl}  nondimensional creep compliance factor that is calculated as 0.6354(X/Y)^{-1}-0.332,
X/Y  the ratio of horizontal to vertical deformation.
ε_{x,max}  Maximum tensile horizontal strain at the centre of the specimen in micro-strain (µε)
σ_{x,max}  Maximum tensile stress at the centre of the specimen in kPa,
N_f  Fatigue life (number of cycles to failure)
ε_0  Initial tensile (microstrain),
σ  Stress (Newton per square meter)
ε_{3600}  strain at 3600th cycle
ε_{1200}  strain at 1200th cycle
## LIST OF APPENDICES

<table>
<thead>
<tr>
<th>APPENDIX</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>The data of the effect of chemical properties based on reactivity to sulfuric acid (Rostler method) on rheological characteristics of bitumen</td>
<td>201</td>
</tr>
<tr>
<td>B</td>
<td>Regression analysis of the effect of chemical properties based on reactivity to sulfuric acid (Rostler method) on rheological characteristics of bitumen</td>
<td>256</td>
</tr>
<tr>
<td>C</td>
<td>The data of the effect of chemical properties based on polarity (Corbett method) on rheological characteristics of bitumen</td>
<td>266</td>
</tr>
<tr>
<td>D</td>
<td>Regression analysis of the effect of chemical properties based on polarity (Corbett method) on rheological characteristics of bitumen</td>
<td>292</td>
</tr>
<tr>
<td>E</td>
<td>Rostler chemical composition, predicted and actual rheological characteristics of the blended bitumen</td>
<td>302</td>
</tr>
<tr>
<td>F</td>
<td>Corbett chemical composition, predicted and actual rheological characteristics of the blended bitumen</td>
<td>318</td>
</tr>
<tr>
<td>G</td>
<td>Statistical analysis of validation of chemicals-rheological models and chemical-durability indices based on Rostler and Corbett methods</td>
<td>334</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Background of study

The worldwide need of petroleum bitumen is continuously increasing but the supply is limited and the price tends to increase continuously. On the other hand, there is a potential deposit of natural rock asphalt in Buton Island, Indonesia. It is called Buton Rock Asphalt (BRA) that consists of around 30% bitumen (Affandi, 2012). Currently, BRA is not fully utilized because the bitumen should first be modified to ensure that its characteristics could meet the current bitumen specification. A proper modification method requires knowledge about the chemical composition and its relation with the rheological characteristics of bitumen.

A significant relationship among chemicals, rheology and durability of bitumen can be used as guidance in modifying bitumen, including BRA bitumen; however, previous studies have indicated that they were not significantly related (Lu, 2002; Hermadi & Sjahdanulirwan, 2005; Michalica, Daucik & Zanzotto, 2008b) thus, there is a need to study and find a new approach, as claimed in this study.

1.1.1 The needs and sources of bitumen

Bituminous mixture or asphalt is a commonly used pavement material around the world. It plays a vital role in global transportation infrastructure, drives economic growth and social well-being in developed as well as developing countries (Mangum, 2006). In addition to the construction and maintenance of roads and
highways, bitumen is also used extensively for airport runways and taxiways, private roads, parking areas, bridge decks, footways, cycle paths, and sports and play areas.

Asphalt covered more than 90% of the four million kilometres of roads and highways and about 85% of airport runways in North America. A similar percentage of 5.2 million kilometres of roads and highways in Europe are also covered with asphalt whilst in Asia, about four million kilometres of roads are surfaced with asphalt (EAPA and NAPA, 2011).

About 1,600 million metric tonnes of asphalt were produced during the year of 2007 alone (EAPA & NAPA, 2011). With bitumen content within the range of five to six% of total weight of asphalt mix and bitumen for other applications such as chip seal, prime and tack coats, it is estimated that the current world use of bitumen is approximately 102 million metrical tonnes per annum. The vast majority of bitumen (85%) is used in asphalt pavement. Around 10% are used in roofing application and the remainder for a variety of other purposes (The Asphalt Institute & Eurobitum, 2011). Global consumption of bitumen is forecasted to advance 4.1% annually from a very weak 2010 base to 119.5 million metric tons in 2015, which is equivalent to 725 million barrels of primary bitumen (The Freedonia Group, 2012).

The main source of bitumen that the world relies on is petroleum where the availability and price of bitumen are depending on the reserve, production and price of crude oil. It is well recognised that, for crude oil supply, the world depended very much on the Middle East and the North African region. Proven crude oil reserve of this region is about 727.5 billion barrel which accounted for almost 70% of the global oil reserve and contributed about 30% of the world crude oil production (Okogu, 2003). However, instability of geopolitical conditions in the Middle East constantly provokes the crude oil price escalation and world anxiety of supply shortage of petroleum.

In the last decade, the increase of crude oil price has significantly increased the price of bitumen. The bitumen price increment as high as 250% during the period of 2005 to 2008 were reported (Portland Cement Association, 2009). It is estimated that the bitumen supplies will likely become more expensive and unreliable in future.

Besides the political situation in the middle-east and economic distress in many countries, there are two other reasons for the price increment. Firstly, as non-
renewable material, crude oil prices increased continuously and as a result, the bitumen prices also increased. Secondly, the changes in oil refining practices have led to a reduction in heavy crude production. This production shift was made possible by supplementing existing refining processes with equipment called cokers. Refineries with installed cokers produce fewer lower-margin residual products such as bitumen (Portland Cement Association, 2009). Therefore, it is realistic to look for other alternatives of refined bitumen such as Portland cement, recycling asphalt mixture, and exploring natural bitumen reserve. Natural bitumen is reported in 586 deposits in 22 countries. It occurs in clastic and carbonate reservoir rocks and commonly in small deposits at, or near, the earth’s surface. One of them is Buton Island deposit in Indonesia (Attanasi & Meyer, 2007). The current production levels of natural extra-heavy oil and natural bitumen in the world is just under 2% of world crude oil production (Attanasi & Meyer, 2007).

1.1.2 Potential of Buton Rock Asphalt

The use of Buton Rock Asphalt (BRA) as an alternative to petroleum bitumen has been explored with total estimated deposit of above 700 million tons (Ministry of Public Work, 2006). It is probably the largest source of rock asphalt in the world. However, the utilization of BRA in the past was limited mainly because, as a naturally occurring material, BRA has a number of disadvantages compared to conventional bitumen such as:

(i) Bitumen of BRA is impregnated inside the rock;
(ii) Bitumen content of BRA is low and widely varies (in range 10% to 30%);
(iii) Wide variation of bitumen consistency (i.e. from very hard to very soft);
(iv) High water content,

The disadvantages of BRA are expected to cause difficulties during the construction process as well as low quality of the final product (asphalt mixes). The low bitumen content makes the transportation cost of BRA high because only a small proportion of the transported material is bitumen while the rest is rock which, in case of conventional bitumen, should be available locally at project sites.

In order to overcome the above problems, ideally, bitumen of BRA should be
extracted to produce bitumen identical to conventional petroleum bitumen. According to Affandi (2012), especially for BRA from Lawele region, pure BRA bitumen can be categorized as PG 70 or better than petroleum bitumen penetration grade 60/70 that is mostly categorized as PG 58.

Refinery of rock asphalt would be expensive because unlike refinery of crude oil; it required a large quantity of additional solvent, which may not be 100% recoverable, and it only produces a single end product which is bitumen. In the past, this option would not be economically competitive enough; however, as the source of petroleum bitumen has declined and the price of crude oil increased, it is believed that the refinery of BRA is becoming profitably feasible thus; the extracted bitumen can be utilized as ordinary bitumen.

1.1.3 The importance of chemical properties of bitumen

As a binder, bitumen should have the physical properties desired to produce stable asphalt in terms of its ability to carry the traffic and its durability or ability to maintain its performance during the expected service life. The performance of bitumen includes all phases of its life from spraying, mixing, laying, compaction, and its service life. In the latter, resistance to plastic deformation and fatigue cracking is especially important.

As thermoplastic and viscoelastic material, bitumen characteristic is affected by temperature, loading and duration of loading, its behaviour under applied force or stress can better describe its rheological properties.

Superpave uses dynamic shear rheometer (DSR) to characterize the elastic (G’) and viscous (G”) behaviour of bitumen (ASTM D7175) at the high and intermediate pavement service temperature. The DSR measures the complex shear modulus (G*) and phase angle (δ). Superpave uses G*/sin[δ] to address rutting susceptibility, and G*sin[δ] to indicate fatigue cracking resistance.

It is widely known that characteristic and performance of bitumen are strongly affected by its chemical properties. Theoretically, it should be possible to correlate the change of bitumen behaviour under different temperature and duration
of loading with its chemical composition. The knowledge on this matter can be utilized to evaluate and modify or improve conventional bitumen.

However, bitumen consists of thousands of different hydrocarbon molecules with different and complex chemical structure. As a result, the effect of chemical properties on performance of bitumen is complicated and difficult to identify. Moreover, publications related to this subject were also quite limited.

Lu & Isakson (2002) found that chemical and rheological changes were generally inconsistent. Michalica et al. (2008a) concluded that there is definite relationship between the chemical and rheological (physical) properties of bitumen however it is very complex due to the concurrent actions of various material properties. Chiu & Chiu (2008) stated that the composition test based in fractional separation is not consistent with field performance.

Most of the research used advanced instrumentation to analyse and determine the chemical composition of bitumen. The work involved a number of bitumen from different sources with different chemical composition. Rheology of each bitumen was then determined, and the correlation between the chemical composition and rheology of bitumen was developed. It is postulated that the inclusiveness of the reported results appeared because of the effect of each fraction cannot be distinguished or identified. To address this problem, a new technique to identify the contribution of each chemical fraction on rheology is necessary.

The current practice to identify durability of bitumen is either by (i) comparing the amount of the more reactive to the less reactive to the environment with hydrocarbon molecules of the bitumen, or (ii) comparing the physical or rheology of bitumen before and after short-term and long-term ageing (Demirebs, 2002; Kumar et al., 2009; Michalica et al., 2008b). The earlier is known as the durability ratios while the latter is the ageing indices.

Two durability ratios have been introduced in the past. They are Rostler Durability Ratios (RDR) and Gotolski Ratios (GR). Both are based on the ratio of the reaction amount of hydrocarbon molecules to sulphuric acid. Both ratios can be illustrated as Equation (1.1) and Equation (1.2).

\[
RDR = \frac{N_b + A_1}{A_2 + P}
\]  

(1.1)
where:

\[ GR = \frac{N_b + A_1 + A_2}{A + P} \]  

where:

\( Nb \) = nitrogen bases
\( A_1 \) = first acidaffins
\( A_2 \) = second acidaffins
\( P \) = paraffins
\( A \) = asphaltenes

It can be seen from the above formulations that Rostler and Gotolski have different opinion regarding the reactivity of the second acidaffins and asphaltenes. These two formulas had been subjected to a number of critics and being rejected by scientists and practitioners thus both indices were never being used in any bitumen specification.

Expression of the durability of bitumen by comparing the physical or rheology of bitumen before and after ageing has been adopted worldwide. For examples, penetration before and after Thin Film Oven Test (TFOT) was adopted in ASTM D946 *Standard Specification for Penetration-Graded Asphalt Cement for Use in Pavement Construction*. Viscosity before and after TFOT was adopted in ASTM D3381 *Standard Specification for Viscosity-Graded Asphalt Cement for Use in Pavement Construction*. Rheology before and after short-term ageing by Rolling Thin Film Oven Test (RTFOT) and long-term ageing by Pressure Ageing Vessel (PAV) aged was adopted by Strategic Highway Research Program (SHRP) specification, which later also adopted by ASTM D 6373 *Standard Specification for Performance Graded Asphalt Binder*. Nevertheless, the usefulness of these indices are limited because they do not provide any information on why and how the ageing of bitumen different from each other.

1.2 Problem statement

From the preceding discussion, it may be concluded that the need for petroleum bitumen worldwide is increasing but the supply is limited and the price tends to
increase continuously due to political instability of the Middle East and world anxiety of petroleum supply shortage. In another hand, there is a large deposit of BRA in Buton Island that is a potential to substitute petroleum bitumen but currently has not been fully explored. Some BRA consists of bitumen that does not meet the requirement of asphalt binder. Improvement of the quality of bitumen (either petroleum or natural bitumen) can be implemented effectively if a solid knowledge on chemical-rheological relationship of bitumen was available however; previous study found that the correlation is not significant (Lu, 2002; Hermadi & Sjahdanulirwan, 2005; Michalica, Daucik & Zanzotto, 2008b) hence, in order to develop the knowledge of the correlation between chemical properties and rheological characteristics of bitumen to use in improving the performance of bitumen, some problems were identified and stated as follows:

(i) Chemical properties of bitumen and how they affect the performance of bitumen, in terms of rheology and durability is not fully understood.

(ii) Although it is acknowledged that a strong relationship between the chemical properties and performance of bitumen exist, most researchers tried to develop a structured relationship which leads to inconclusive results.

(iii) Guidance on how to utilize the knowledge of chemical-rheological bitumen to improve the performance of bitumen is presently not available.

1.3 Research aim and objectives

The above stated problem provided a justification for the aim of the experiment described in this thesis, which directed toward the development of new chemical-rheological models and chemical durability indices of bitumen. A different approach in assessing the effect of chemical fractions on the rheology of bitumen is required. The approach should be simple yet able to distinguish the effect of individual chemical fractions.

From the arguments presented above, the specific objectives of the study are as follows:
(i) To develop a new technique for the assessment on the effect of chemical fractions on rheology and durability of bitumen.

(ii) To develop new models of chemical-rheological characteristics and chemical durability indices of bitumen.

(iii) To verify the models and indices by experimentally studying the relationship between chemical and rheological characteristics of bitumen of different sources.

1.4 Research scopes

The scopes of this research are as follows:

(i) The two sources of bitumen were used in this study that is the BRA bitumen from Lawele region in Indonesia and petroleum bitumen penetration grade 80-100 dmm from Kemaman Malaysia.

(ii) The coarse and fine aggregates used in this experiment were from Hanson quarry in Batu Pahat, Malaysia.

(iii) In reviewing the physical characteristics of the bitumen, the specifications used were penetration grade specification (ASTM D 946) and performance grade specification (ASTM D 6373).

(iv) Ageing bitumen was conducted artificially in the laboratory. The standard test methods used were RTFOT (ASTM D2872) for short-term ageing and PAV (ASTM D 6521) for long-term ageing.

(v) In this study, two standard test methods to evaluate the chemical properties of the bitumen were used. These were ASTM D 2006 “Method of Test for Characteristic groups in Rubber Extender and Processing Oils by the Precipitation Method” and ASTM D 4124 “Standard Test Methods for Separation of Asphalt into Four Fractions”. ASTM D 2006 separated the
bitumen into five fractions based on their reactivity to sulphuric acid and ASTM D 4124 separated the bitumen into four fractions based on their polarity. The other test methods, such as Thin Layer Chromatography (TLC), Size Exclusion High Performance Gel Permeation Chromatography (HP-GPC), Ion Exchange Chromatography (IEC), and Fourier transforms infrared spectroscopy (FTIR) were not used because those methods cannot physically isolate and extract the chemical fractions of bitumen. The extracted fractions were very important in the experiment to evaluate each fraction’s effect on the bitumen rheological characteristics.

(vi) The test method that was used to evaluate the bitumen rheological characteristic was ASTM D 7175 Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer. By this method, the viscous modulus, the elastic modulus, deformation susceptibility at high temperature and crack susceptibility at medium range temperatures (which addressed fatigue cracking) could be evaluated. The other test methods, such as Bending Beam Rheometer (BBR) and Direct Tension Test (DTT) which addressed cracking at a low temperature were not covered in this study.

(vii) Mixture performance test on the bituminous mixture of BRA and petroleum bitumen were based on Superpave guide line. The tests covered testing and evaluated the mechanistic properties of bituminous mixtures using Universal Test Machine to test Creep stiffness, Indirect Tensile Stiffness Modulus, and Indirect Tensile Fatigue.

1.5 Thesis organization

This thesis is organized into eight chapters. The background and purposes of the research program are presented in this first chapter. The scope of the research program along with the objectives is discussed.

Chapter Two provides a review on chemical and rheological of bitumen, asphalt mixture performance and Buton Rock Asphalt including chemical and rheological of bitumen, characterizations and correlation of both. Asphalt mixture
performance was discussed covering Superpave volumetric mix design, permanent deformation, fatigue cracking, low temperature cracking, moisture damage, and ravelling effort. Furthermore, Chapter Two also describes location, deposit and current utilization technology of BRA as asphalt binder.

Methodology of this study is described in Chapter Three which includes experimental design, preparation of samples, chemical properties tests, rheological characteristics tests, and ageing conditioning of bitumen. Performance tests of asphalt mixture and data analysis are also covered within this chapter.

Chapter Four and Five present the results and discussion on the effect of chemical properties on rheological characteristics of bitumen. Chapter Four based on Rostler chemical properties, while Chapter Five based on Corbett's chemical properties. Development of new chemical-rheological models and chemical durability indices are discussed in both chapters. Furthermore, validation of the models and the durability indices are described in Chapter Six and Seven. The validation based on bitumen rheological characteristics is in Chapter Six and based on mixture performance is in Chapter Seven.

Finally, the conclusion and recommendation that made through the study are presented in Chapter Eight.
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter elaborates the chemical properties and rheological characteristics of bitumen, their methods of measurement, relationship with asphalt mixture performance, and Superpave performance grade (PG) specification of bitumen that was developed through the Strategic Highway Research Programme (SHRP). Furthermore, this chapter also discusses about Buton Rock Asphalt (BRA), covering its history, potential deposit, and current utilization technology as a binder of asphalt pavement.

Theoretically, bitumen characteristics are formed by each chemical component characteristic. Therefore, the chemical composition of bitumen is useful for evaluating and modifying a bitumen composition to produce bitumen with better physical and rheological characteristics however; bitumen consists of thousand types of hydrocarbon molecules, which make it practically impossible to analyse the bitumen based on its individual molecule type thus the chemical composition of bitumen is usually analysed by chemical fractionation.

In fractionation, the molecules which have the same characteristics were grouped in one fraction. According to Rostler method (ASTM D2006), bitumen is fractionated to five fractions according to their reactivity to sulphuric acid. The fractions are asphaltenes, nitrogen bases, first acidaffins, second acidaffins, and paraffins. Corbett (1969) suggested a method to analyse bitumen chemical composition based on their polarity. The fractions are asphaltenes, polar aromatics, naphthene aromatics, and saturates. This method was standardized as ASTM D4126.
The other methods of fractionation are based on similarity of molecule weight, acidity-alkalinity and functional groups. These methods are also discussed throughout this chapter.

Rheological characteristic of bitumen is important because it influences the performance of asphalt mixtures from the construction stage up to the in-service lifetime.

Bitumen is a viscoelastic material which exhibits both viscous and elastic characteristics when undergoing deformation (Kamboozia & Arabani, 2012; Meyer & Chawla, 2009). The rheological characteristics depend on temperature and the level of ageing. At high temperatures, such as during mixing and compaction of asphalt, bitumen dominantly exhibits viscous behaviour, while at very low-in-service temperature bitumen exhibits more as elastic material. In between these two extremes, it exhibits as viscoelastic material.

Bitumen of hot mix asphalt is subjected to non-ageing or fresh, short-term ageing, and long-term ageing conditions. These conditions are related with before construction, after construction or early in-service and after long-term in-service condition stages of asphalt respectively. Performance of asphalt in terms of its resistance to permanent deformation and fatigue can be explained based on the rheological characteristics of its bitumen at relevant age condition.

Understanding the relationship of chemical properties with rheological characteristic of the bitumen is very useful in investigating and modifying the bitumen. Most chemical separation is based on the reactivity or polarity of the various molecular types thus bitumen molecules can be conveniently separated or grouped into molecular types or fractions with a narrower range of properties based on their chemical functionality. The separation and classification of molecular types have been useful in providing chemically definitive component fractions for further characterization, thus aiding in determining how different molecular types affect the physical or rheological and chemical properties of the whole bitumen and how the bitumen mixer differs chemically from one another (Petersen, 2009).
2.2 Bitumen chemistry

Bitumen is a complex mixture of organic molecules which varies widely in its composition, molecular weight, and compound types with hydrocarbon as dominant molecules (Petersen, 2009). It also consists of heterocyclic and functional groups containing oxygen, sulphur and nitrogen, even in a minor amount. Metals, such as iron, nickel, magnesium calcium, vanadium, etc., may also be found in bitumen in traced quantities (Airey, 1997; Meyer & Witt, 1990). All chemical molecules have a contribution on bitumen characteristics such as chemical, physical, rheological and ageing. However, the composition of bitumen is very complex. The number of molecules with different chemical structure is extremely large hence it is impossible to separate and identify every different molecule. Currently, the chemical composition of bitumen is characterized by separating different groups or fractions based on chemical reactivity, precipitation or solubility, chromatography, molecular size and spectroscopic (Bell, 1989; Youtcheff & Jones, 1994).

There are three broad group structures of hydrocarbon molecules in bitumen, namely aliphatic, cyclics and aromatics (Robertson, 1991; Berkers, 2005; Polacco et al., 2008; Jones, 1992; Lesueur, 2009). The structures are shown in Figures 2.1, 2.2 and 2.3. The other molecules are a combination of them as shown in Figure 2.4. While the major mass of bitumen is hydrocarbons, large proportion of molecules also contained one or more heteroatoms such as nitrogen, sulphur, oxygen and metals as shown in Figure 2.5. As a single structure, the molecules are non-polar but if the structure is combined with each other or contained heteroatoms, the molecules became polar. The polarity of molecules that indicated by Dipole moment value at various molecule structures are shown in Table 2.1.

![Figure 2.1: The broad structures of aliphatic hydrocarbon in bitumen](image)

<table>
<thead>
<tr>
<th>Saturate</th>
<th>un-saturate</th>
</tr>
</thead>
</table>

Figure 2.1: The broad structures of aliphatic hydrocarbon in bitumen
Figure 2.2: The broad structures of cyclics hydrocarbon in bitumen

Figure 2.3: The broad structures of aromatics hydrocarbon in bitumen

Figure 2.4: The combining structures of hydrocarbon in bitumen
Figure 2.5: Heteroatom structures of hydrocarbon in bitumen
Table 2.1: Structures and dipole moment values of some organic molecules

<table>
<thead>
<tr>
<th>Names</th>
<th>Structures</th>
<th>Dipole Moment</th>
<th>Polarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td><img src="image" alt="Hexane" /></td>
<td>0.00 D</td>
<td>Less-Polar</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td><img src="image" alt="Cyclohexane" /></td>
<td>0.00 D</td>
<td>Less-Polar</td>
</tr>
<tr>
<td>Benzene</td>
<td><img src="image" alt="Benzene" /></td>
<td>0.00 D</td>
<td>Less-Polar</td>
</tr>
<tr>
<td>Toluene</td>
<td><img src="image" alt="Toluene" /></td>
<td>0.36 D</td>
<td></td>
</tr>
<tr>
<td>0-xylene</td>
<td><img src="image" alt="0-xylene" /></td>
<td>0.45 D</td>
<td></td>
</tr>
<tr>
<td>Chlorobenzen</td>
<td><img src="image" alt="Chlorobenzen" /></td>
<td>1.57 D</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td><img src="image" alt="Water" /></td>
<td>1.87 D</td>
<td>More Polar</td>
</tr>
<tr>
<td>Pyridine</td>
<td><img src="image" alt="Pyridine" /></td>
<td>2.37 D</td>
<td>More Polar</td>
</tr>
</tbody>
</table>
2.2.1 Bitumen chemical properties according to Rostler precipitation method

The test method based on solubility and chemical reactivity was developed by Rostler-Stenberg and had been standardized in ASTM D2006-1965 *Method of Test for Characteristic Groups in Rubber Extender and Processing Oils by the Precipitation Method* which was discontinued in 1976. Nevertheless, the standard is still being used in evaluating, modifying or rejuvenating bitumen. Boyer (2000), Siswosoebrotho *et al.*, (2005), Houston *et al.*, (2005), Shen *et al.*, (2007), and Brownridge, (2010) used the test standard in evaluating bitumen.

Basically, the test separates bitumen into five fractions, namely asphaltenes (A), nitrogen bases (N), first acidaffins (A₁), second acidaffins (A₂) and paraffins (P). The percentage of asphaltenes is the amount of bitumen that is insoluble in low molecular weight of normal paraffins such as n-pentane, n-hexane and n-heptane. Nitrogen base percentage is the amount of bitumen parts that is soluble in low molecular weight of normal paraffins but become insoluble after being treated by glover sulphuric acid (85% sulphuric acid, H₂SO₄). The percentage of the first acidaffins is determined by calculating the amount of the bitumen fractions that is soluble in low molecular weight of normal paraffins and still soluble after being treated with glover sulphuric acid, however, the fraction becomes insoluble after being treated by concentrated sulphuric acid (98% sulphuric acid). The percentage of second acidaffins is the amount of the bitumen fractions that is soluble in low molecular weight of normal paraffins and still soluble after being treated with glover and concentrated sulphuric acid. The second acidaffins becomes insoluble after being treated by fuming sulphuric acid (H₂SO₄+30%SO₃ or H₂S₂O₇). The last fraction is paraffins percentage of bitumen fractions that is soluble in low molecular weight of normal paraffins and after being treated by glover, concentrated and fuming sulphuric acids. The test method is showed in Figure 2.6.

Asphaltenes are large, discrete solid inclusions of bitumen. They are responsible for the presence of structure in asphalts and for their non-Newtonian rheological behaviour. They are the most highly polar molecules, insoluble in non-polar solvent such as low molecular weight normal paraffins. The function of asphaltenes in bitumen is as the thickening, structuring or bodying agent and impart strength, stiffness and colloidal structure (Boyer, 2000; Oyekunle, 2005).
Asphaltenes are most complex molecules presented in bitumen containing aliphatic hydrocarbon side chains, aromatics core system, heteroatoms and metals (Siddiqui, 2003). Oyekunle (2006) described asphaltenes as a black or brown coloured, hard, non-plastic, non-malleable high molecular weight compound ranging between 1,200 and 200,000 g/mol. They contain predominantly carbon and hydrogen with sulphur, oxygen, nitrogen and other heteroatoms. Hardee (2005) found asphaltenes as a brittle amorphous solid, which are highly condensed aromatic compounds with molecular weight 2,000-5,000 g/mol and constitute to 5-25% of the total weight of asphalts.

Deasphaltene bitumen or parts of bitumen which is soluble in low molecular weight of normal paraffins, such as n-pentane, n-hexane and n-heptane are called petrolenes or maltenes (Lesueur, 2009). According to Rostler method (ASTM D2006), maltenes is defined as parts of bitumen, which is soluble in n-pentane. It consists of nitrogen bases, first aciddaffins, second aciddaffins and paraffins.

Nitrogen bases are polar compounds. It is a bitumen fraction of highly reactive resins, which acts as a peptizer for the asphaltenes (Boyer, 2000; Petersen, 2009). Nitrogen bases mostly consist of hydrocarbon containing nitrogen molecules,
however, it also contains all molecule bases and heteroatoms that can react and precipitated with glover sulphuric acid.

First acidaffins are resinous hydrocarbon components, which functions as a solvent for the peptized asphaltenes (Boyer, 2000). The molecules are mostly consisted of aromatics.

Second acidaffins are components of slightly unsaturated hydrocarbon that also serve as a solvent for the peptized asphaltenes (Boyer, 2000).

Paraffins are saturated hydrocarbon, functioning as bonding agent for the asphalt components (Boyer, 2000). The molecules consist of saturated, aliphatic and cyclic which cannot react with fuming sulphuric acid.

2.2.2 Bitumen chemical properties according to Corbett chromatography method

The test method was introduced by Corbett & Swarbrick (1969) based on absorption-desorption chromatography and has been standardized in ASTM D 4124-2001 Standard Test Methods for Separation of Asphalt into Four Fractions. As shown in Figure 2.7, the test separates the bitumen based on solubility and polarity grade into four components which are asphaltenes, saturates, naphthene aromatics, and polar aromatics. Asphaltenes is the insoluble part of bitumen in n-heptane solvent. Saturates or saturated oil components is the soluble part of bitumen in n-heptane solvent and cannot be absorbed by alumina absorbent. Naphthen aromatics or aromatics oil component is the soluble part of bitumen that can be absorbed by alumina absorbent and can be eluted by toluene solvent. Polar aromatics or resin component is the soluble part of bitumen that can be absorbed by alumina absorbent and can be eluted by trichloroethylene solvent or mix of methanol and toluene in 1:1 proportion.

Asphaltenes based on Corbett method and Rostler test is basically identical as an insoluble part of bitumen in low molecular weight normal paraffins.

Saturates fraction of bitumen is a mixture of pure aliphatics, aliphatics with side chains, cycloaliphatics, and cycloaliphatics with side chains. The average molecular weight of the oil is in the C_{40}-C_{50} range, and it is colourless liquid. The
The average molecular weight is around 600 g/mol with very few polar atoms or aromatic ring content (Lesueur, 2009). Saturates are viscous liquids or solids ranging from straw to clear in colour, consisting mainly of a long chain saturated hydrocarbons with some branched chain compounds, alkyl aromatics with long side chains and cyclic paraffins (naphthenes), with molecular weights of 500-1,000 g/mol. It constitutes 5-20% of the total weight of the asphalt (Hardee, 2005).

![Bitumen chemical separation test](image)

Figure 2.7: Bitumen chemical separation test according to Corbett method (ASTM D 4124-2001)

Naphthene aromatics or aromatics are the most abundant constituents of bitumen binder together with polar aromatics or resins, since they contain about 30 - 45% of the total bitumen. They consist of several aryl groups connected by aliphatic chains and appear as yellowish to red liquid at room temperature. They are somewhat more viscous than saturates at the same temperature because of a higher glass transition temperature around -20°C. The average number of molecular weight is around 800 g/mol (Lesueur, 2009). According to Hardee (2004), naphthen aromatics are viscous dark-brown liquids containing mainly carbon, hydrogen and sulphur with minor amount of oxygen and nitrogen, with a molecular weight of 500-900 g/mol, which constitutes to 45-60% of the total weight of bitumen.

Polar aromatics that are also called resins consist of aliphatics, naphthenes
and aromatics in multi ring structure along with sulphur, oxygen and nitrogen compounds. It is black semi-solid materials with average number of molecular weight around 11,800 g/mol. It is polar and sometimes can be more polar than asphaltenes and functions as a stabilizer for the asphaltenes (Lesueur, 2009). Polar aromatics are brown-black, adhesive, shiny solids or semi-solid which comprised heterogeneous polar aromatics compounds with a small amount of oxygen, nitrogen and sulphur with molecular weights of 800-2,000 g/mol and constitutes to 15-25% of the total weight of bitumen (Hardee, 2005).

### 2.2.3 Bitumen chemical properties according to other methods

Separation and other characterization methods in analysing chemical properties of bitumen may also be performed using other methods such as:

(i) Thin layer chromatography (TLC-FID),

(ii) Size exclusion (High Performance Gel Permeation Chromatography/HP-GPC),

(iii) Ion Exchange Chromatography (IEC),

(iv) Characterization of Bitumen Chemical Properties According to Fourier transforms infrared (FTIR) spectroscopy.

Comparing with Rostler and Corbett methods, these methods are faster and more accurate however; the methods were not designed to extract the chemical components of bitumen.

Even though Rostler and Corbett methods are classical, the two methods are able to isolate and extract the chemical components. This feature enables the investigation of the effect of individual chemical fraction on the characteristics of bitumen.

#### 2.2.3.1 Characterization of bitumen chemical properties based on thin-layer chromatography with flame ionization detection (TLC-FID)

The TLC-FID is a method to analyse and separate bitumen into four fractions: saturates, aromatics, resins, and asphaltenes. In the TLC-FID, 2% (w/v) solutions of
bitumen were prepared in dichloromethane, and 1 µl sample solution spotted on Chromatography rods using a spotter. Bitumen is then separated into four generic fractions (saturates, aromatics, resins and asphaltenes) by a three-stage development using \( n \)-heptane, toluene and dichloromethane/methanol (95/5 by volume), respectively. The fractions were determined by an Iatroscan MK-5 analyser (Lu & Isacsson, 2002; Guern et al., 2010).

TLC-FID test are faster and more accurate than the conventional tests (Corbett and Rostler tests) in determining a chemical fraction composition of bitumen however; the procedure cannot be used to extract and recover the chemical fractions hence the chemical fraction cannot be analysed individually in identifying its effect on the bitumen rheological characteristics. A research on the effect of chemical properties on rheological characteristics can only be done by correlating or regressing chemical composition or its change with rheological characteristics. Percentage ratio of each chemical fraction in bitumen has strong correlation with percentage ratio of another chemical fraction. It causes one or more chemical fraction to become excluded variables. If percentage of one chemical fraction decreased or increased, then percentage of the other fractions will increased or decreased accordingly. As a consequence, it is not clear which fraction will affect the rheological characteristics of the bitumen.

Lu & Issacsson (2002) conducted a chemical characteristic study on bitumen and compared test results from TCL-FID and rheology. According to their study, ageing of bitumen decreases aromatics and increases the content of resins and asphaltenes at the same time. The content of saturates changes slightly due to their inert nature to oxygen. However, as a result of the chemical changes, the mechanical properties of aged bitumen become more solid-like, as indicated by increased complex modulus and decreased phase angle. They also found the chemical and rheological changes generally inconsistent.

Montepara & Giulani (2001) evaluated the chemical properties of bitumen using TLC-FID of fresh, short-term ageing process by RTFOT and after long-term ageing by PAV. They concluded that saturates remain substantially unchanged in bitumen during short-term and long-term ageing process. On the other hand, the reactivity of aromatics and resins to air induced the formation of polar groups, and increased their concentration in bitumen significantly.
The other study was reported by Guern et al. (2010). They used TLC–FID Iatroscan to determine the colloidal instability index or Gaestel index ($I_c$). The index is a ratio of asphaltenes and saturates percentage to aromatics and resin percentage. It is typically used to characterize the colloidal stability of bitumen. It was compared to the agglomerate content value determined by HS-SEC. The result showed a significant evolution in agglomerate content hence the concept of stability provided by the colloidal index did not appear to be systemically correlated with agglomerate content.

### 2.2.3.2 Characterization of bitumen chemical properties based on high performance gel permeation chromatography (HP-GPC)

HP-GPC involves the separation of bituminous materials into their components according to molecular size. Size exclusion chromatography (HP-GPC) separates components of the bitumen based on the apparent size (hydrodynamic volume) of molecules and molecular aggregations or associations in dilute solution. The chromatogram describes the molecular size profile of bitumen. For the purpose of HP-GPC determination, the bitumen sample is introduced into a solvent (typically tetrahydrofuran or toluene) flowing at high pressure through a column packed with a highly porous, solid material. The liquid transports the asphalt through and around the porous packing material in the column and as a result smaller size molecules in the asphalt can enter freely into all the pores of the column packing while larger molecules can enter none of those pores (Yapp et al., 1991).

Molecules of intermediate size have access to varying amounts of available pore volume thus the larger molecules move through the column faster than the smaller ones. The Large Molecular Size portion of the bitumen leaves the column first, followed by the medium-size and then the small size components. A detector measures the amount of each component. The resultant chromatogram represents the relative amount of material appearing at a given elution time (Yapp et al., 1991).

Furthermore, Yapp et al. (1991) investigated the relationship between HP-GPC parameters and performance of bituminous concrete pavements however; the relationships are inconsistent and likely to be confounded by test method, methods
of interpretation of the HP-GPC test data, and relationship to different types of pavement distress (i.e., transverse cracking, fatigue cracking, rutting or tender mixes).

Even though the molecule size generally can affect the bitumen consistency, it could be fuzzy if the molecule polarity or molecule structure is different. Polarity and molecule structure that cannot be detected by HP-GPC can also affect the bitumen consistency as shown in Table 2.2. Since the relationships between HP-GPC parameters and bituminous consistency were not consistent, as a consequence, the relationships of the parameters on rutting of bituminous pavement become inconsistent as well.

On the other hand, molecules size of bitumen fractions cannot indicate bitumen elasticity, brittleness and ageing reactivity hence it cannot indicate cracking performance of the bituminous pavement.

Table 2.2: Viscosity of bitumen fractions at same average molecular weight
(Petersen, 1982)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Polarity</th>
<th>Apparent molecular wt.</th>
<th>Viscosity Pa.S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturates</td>
<td>Less polar</td>
<td>500</td>
<td>10</td>
</tr>
<tr>
<td>Aromatics</td>
<td></td>
<td>500</td>
<td>1,000</td>
</tr>
<tr>
<td>Resins</td>
<td>More polar</td>
<td>500</td>
<td>100,00</td>
</tr>
</tbody>
</table>

2.2.3.3 Characterization of bitumen chemical properties based on Ion Exchange Chromatography (IEC)

Ion exchange chromatography (IEC) is a technique used to separate bitumen into distinct chemical fractions based on chemical functionality without the need for initial asphaltene precipitation. IEC accomplishes this fractionation by pumping solution of bitumen, dissolved in selected solvents, into columns filled with activated cation or anion resins. Bitumen components containing acidic functional group absorbed on anion resins, from which they can be desorbed. Bitumen component having basic functional groups are absorbed in cation resins. Component containing
REFERENCES


Airey, G. D., Mohammed, M. H., (2008), *Rheological properties of polyacrylates used as synthetic road binders*, Springer.


Demirabs, A., (2002), Asphaltene yields from five types of fuels via different methods, Energy Conversion and Management 43 1091–1097


Hamzah, M. O., Shahadan, Z., (2011), Effects of Aging on the Physical, Rheological


Hermadi, M., Syahdanulirwan, M., (2005), Correlation of Durability Index with Durability of Bitumen, Road and Bridge Journal Vol.22 N0. 3, 2005” Ministry of Public Work, Bandung.


Montepara, A., Giuliani, F., (2001), *Variation in Chemical and Rheological Properties of Bitumen Due to Aging Action*, Departement of Civil Engineering, University of Parma, Italy.


Portland Cement Association, (2009), The Monitor Flash Report of Paving, the New Realities, USA.

Petersen, J. C., (1982), *Relationships between Asphalt Chemical Composition and Performance-Related Properties,* Larami Energy Technology Center, U.S.
Department of Energy, Las Vegas.


Transportation Department Research Program Division of Highways, Resource Center, Idaho State University.


