TRIBOPOLYMERIZATION AS AN APPROACH TO TWO-STROKE ENGINE LUBRICATION

by

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Thesis submitted to the Faculty of
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE
in
Mechanical Engineering

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November 1995
Blacksburg, Virginia
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(ABSTRACT)

A literature review was performed to investigate the current status of two-cycle gasoline engines from the standpoint of design, performance, benefits, lubrication and emissions. The two-stroke engine offers several significant advantages over its four-stroke counterpart, which include: simple design, low production cost, higher power to weight ratio, smaller size, lower peak operating temperatures, and lower NO\textsubscript{x} emissions. The main drawbacks of two-stroke engines are the high unburned hydrocarbon and particulate exhaust emissions which are attributed to the lubricating oil and the scavenge process. Technologies to reduce exhaust emissions from two-stroke engines are strongly contingent on the ability to develop improved, environmentally friendly, lubricants which can be used at high fuel:oil ratios.

An experimental study of lubrication of an air-cooled, two-stroke, gasoline engine by tribopolymerization is presented. Tribopolymerization is defined as the planned or intentional formation of protective polymeric films directly and continuously on rubbing surfaces to reduce damage and wear by the use of minor concentrations of selected compounds capable of forming polymeric films

ABSTRACT
in situ [12]. Two monomers were investigated as potential anti-wear compounds, namely (a) $C_{36}$ dimer acid/ethylene glycol monoester, a condensation monomer, and (b) diallyl phthalate, an addition monomer.

The condensation monomer was found to provide sufficient wear protection under a range of unloaded test conditions. Under loaded test conditions, however, piston scuffing occurred well before the planned test period of 20 hours had expired with all of the lubricants tested. Photomacrograph and SEM photographs reveal rather thick deposits on the monoester lubricated piston using a mass concentration of 0.5% monoester in gasoline. The heavy deposits were not noted using a mass concentration of 0.5% diallyl phthalate or with a 0.1% mass concentration of the monoester in bis (2-ethylhexyl) sebacate, a synthetic base oil.

As a secondary topic which parallels this study, other existing and rising fuel lubricity problems have been investigated. The poor friction and wear characteristics of diesel, jet, and alcohol fuels have led to tribological problems in various engine fuel system components. The outstanding anti-wear performance of monomer additives in several similar tribological systems in the past shows good potential for the solution to a variety of current fuel lubricity problems.

**ABSTRACT**
ACKNOWLEDGMENTS

I would like to express my appreciation to everyone who has assisted me with completing this work. Special thanks goes to my advisor, Dr. Michael J. Furey for his guidance, enthusiasm, insight and very helpful suggestions throughout this work. Thanks to my committee members, Dr. Norman Eiss and Dr. Alan Kornhauser for their many contributions throughout various phases of this project. I am extremely grateful for the number of times Dr. Kornhauser went out of his way to assist me with the design and construction of the engine test apparatus.

I attribute much of what I have learned about the chemistry of fuel constituents, tribopolymerization, and engine oils to the guidance provided to me by Dr. Czeslaw Kajdas and Dr. Roman Kempinski.

The support that I received from the machine shop and the electrical shop was an essential part of the completion of this research.

I received a notable amount of support from Dr. Jose Lopez-Domiguez with the set-up of the data acquisition equipment used in the study.

I would also like to thank graduate students Mr. Eric Swanson, Mr. Matthew Schroeder, Mr. Rich Lomenzo, Mr. Jeffrey Kozak, Ms. Susan Larkin, and Mr. Michael DeLorenzo for sharing their experiences and friendship over the past two years.

I give thanks to the Triad Investment Corporation for my support along with the funding necessary to purchase the equipment required to conduct the experimentation in this work.

Finally, I would like to thank God, my mother and my father, my three sisters and their families, and my friends for their love, encouragement and support over the past two years.
# TABLE OF CONTENTS

ABSTRACT. ................................................................. ii

ACKNOWLEDGMENTS. ................................................. iv

TABLE OF CONTENTS. ................................................ v

LIST OF TABLES. ....................................................... ix

LIST OF FIGURES. ...................................................... x

1. INTRODUCTION. .................................................. 1

1.1 Project Significance and Rationale. ............................. 1

1.1.1 Fuel Lubricity Problems. ...................................... 3

1.1.2 The Two-Stroke Engine and its Lubrication Problems. ...... 5

1.2 Tribopolymerization: A Novel Two-Cycle Engine Lubrication Approach. ...................................................... 7

1.3 Objectives of this Research. .................................... 10

2. LITERATURE REVIEW. ............................................ 13

2.1 Tribopolymerization. ............................................. 13

2.1.1 Ryder Gear Tests. .............................................. 15

2.1.2 Radioactive Valve Lifter Wear Study. ....................... 18

2.1.3 Effect of Pre-Polymerization. .............................. 20

2.1.4 Steel Pin-on-Disk Experiments. ............................ 21

2.1.5 Ceramic Lubrication. ......................................... 22
2.1.5.1 Vapor-Phase Ceramic Lubrication. ........ 22
2.1.5.2 Pin-on-Disk Tests. .................... 25

2.2 Existing and Emerging Fuel Lubricity Problems. ........ 28
2.2.1 Diesel Fueled Engines. .................... 29
2.2.2 Alcohol Fuels. ............................ 31
2.2.3 Aviation Fuel Lubricity. .................. 33
2.2.4 Fuel Lubricity Assessment Techniques. .......... 34

2.3 The Two-Stroke, Spark-Ignition, Internal Combustion
Gasoline Engine. .................................. 41
2.3.1 Advantages and Applications of the
Two-Cycle Gasoline Engine. ...................... 41
2.3.2 Scavenging. ................................. 43
2.3.3 Lubrication. ................................. 48
2.3.3.1 Lubricating Systems. ..................... 49
2.3.3.2 Lubricant Requirements. ................. 53
2.3.3.3 Conventional Lubricants. ................. 56

2.4 Two-Cycle Engine Lubricant Testing Techniques .......... 60

3. ENGINE BENCH TESTING ............................ 76
### TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Equipment</td>
<td>76</td>
</tr>
<tr>
<td>3.1.1</td>
<td>The Tecumseh TVXL840 Two-Stroke Engine</td>
<td>77</td>
</tr>
<tr>
<td>3.1.2</td>
<td>Test Apparatus</td>
<td>78</td>
</tr>
<tr>
<td>3.2</td>
<td>Development of a Test Procedure</td>
<td>81</td>
</tr>
<tr>
<td>3.2.1</td>
<td>New Engine Disassembly and Inspection</td>
<td>81</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Engine Re-Assembly</td>
<td>82</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Installation of the Engine Into the Test Apparatus</td>
<td>85</td>
</tr>
<tr>
<td>3.2.4</td>
<td>Experimental Test Procedure</td>
<td>87</td>
</tr>
<tr>
<td>3.2.5</td>
<td>Post-Test Disassembly and Part Inspection</td>
<td>90</td>
</tr>
<tr>
<td>3.3</td>
<td>The Monomers</td>
<td>91</td>
</tr>
<tr>
<td>4.</td>
<td>EXPERIMENTAL RESULTS</td>
<td>94</td>
</tr>
<tr>
<td>4.1</td>
<td>Overview of the Engine Analysis and Some Terminology</td>
<td>94</td>
</tr>
<tr>
<td>4.2</td>
<td>Pre-Test Inspection of the Engine Parts</td>
<td>96</td>
</tr>
<tr>
<td>4.3</td>
<td>Diallyl Phthalate Test Results</td>
<td>99</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Diallyl Phthalate: 0.5% Concentration</td>
<td>100</td>
</tr>
<tr>
<td>4.4</td>
<td>C36 Dimer Acid/Ethylene Glycol Monoester</td>
<td>106</td>
</tr>
<tr>
<td>4.4.1</td>
<td>Monoester: 0.5% Concentration</td>
<td>107</td>
</tr>
<tr>
<td>4.4.2</td>
<td>0.5% Monoester With 0.5% Sebacate Base Oil</td>
<td>114</td>
</tr>
<tr>
<td>4.4.3</td>
<td>0.1% Monoester With 0.9% Sebacate</td>
<td>121</td>
</tr>
<tr>
<td>4.4.3.1</td>
<td>90 Minute Run-in at 2400 rpm</td>
<td>122</td>
</tr>
<tr>
<td>4.4.3.2</td>
<td>90 Minute Run-in at 3000 rpm</td>
<td>125</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>4.4.3.3</td>
<td>Loaded Test at the Minimum Throttle Setting</td>
<td>127</td>
</tr>
<tr>
<td>4.5</td>
<td>Conventional Lubricant Reference Test</td>
<td>130</td>
</tr>
<tr>
<td>4.6</td>
<td>Scanning Electron Microscope (SEM) Photographs</td>
<td>136</td>
</tr>
<tr>
<td>5.0</td>
<td>DISCUSSION</td>
<td>154</td>
</tr>
<tr>
<td>5.1</td>
<td>Overview</td>
<td>154</td>
</tr>
<tr>
<td>5.2</td>
<td>Photomacrophotograph Observations</td>
<td>164</td>
</tr>
<tr>
<td>5.3</td>
<td>SEM Observations</td>
<td>165</td>
</tr>
<tr>
<td>5.4</td>
<td>Important Factors That Play a Role under Boundary Lubrication Conditions</td>
<td>167</td>
</tr>
<tr>
<td>5.5</td>
<td>Summary</td>
<td>174</td>
</tr>
<tr>
<td>6.0</td>
<td>CONCLUSIONS</td>
<td>178</td>
</tr>
<tr>
<td>7.0</td>
<td>RECOMMENDATIONS</td>
<td>182</td>
</tr>
<tr>
<td>7.1</td>
<td>Two-Stroke Engine Lubrication</td>
<td>182</td>
</tr>
<tr>
<td>7.2</td>
<td>Fuel Lubricity</td>
<td>187</td>
</tr>
<tr>
<td>REFERENCES</td>
<td></td>
<td>189</td>
</tr>
<tr>
<td>APPENDIX A</td>
<td>Test Summary and Current Engine Status</td>
<td>197</td>
</tr>
<tr>
<td>APPENDIX B</td>
<td>Documentation of Test Apparatus</td>
<td>203</td>
</tr>
<tr>
<td>APPENDIX C</td>
<td>Theoretical Piston Loads and Speeds</td>
<td>210</td>
</tr>
<tr>
<td>VITA</td>
<td></td>
<td>218</td>
</tr>
</tbody>
</table>

TABLE OF CONTENTS
LIST OF TABLES

Table 1.1 California Emission Standards for Utility and Lawn and Garden Equipment Engines, g/hp-hr. .......................... 3

Table 2.1 Results of Ryder Gear Scuff Test of Jet Fuel Additives [12]. ........ 16

Table 2.2 Relative Additive Wear Protection Using a Radioactive Valve Train Test [12]. .................................................. 20

Table 2.3 Advantages of the Simple Two-Stroke Gasoline Engine .............. 42

Table 2.4 Common Applications of the Two-Stroke Engine ....................... 43

Table 2.5 Important Considerations in the Development of a Two-Stroke Lubricant .................................................. 54

Table 2.6 Emission Reduction Studies With Two-Stroke Engines ............... 72

Table 3.1 TVXL840 Engine Specifications ...................................... 77

Table 3.2 Test Conditions For Engine Bench Testing ............................ 87

Table 3.3 Start-up Procedure During 20-Hour Test .............................. 89

Table 5.1 Summary of Test Results .............................................. 156

Table 5.1 Possible Mechanisms of Failure of Monomers to Provide Adequate Wear Protection .......................... 175

Table A1 Status of Engine #1 .................................................. 198

Table A2 Status of Engine #2 .................................................. 199

Table A3 Status of Engine #3 .................................................. 200

Table A4 Status of Engine #4 .................................................. 201

Table A5 Status of Engine #5 .................................................. 202

Table A6 Status of Engine #6 .................................................. 203
LIST OF FIGURES

Fig. 1.1  Tribopolymerization as a Mechanism of Boundary Lubrication . . . 8

Fig. 2.1  Anti-Scuff Rating for a Variety of Fluids With and Without the Addition of the C_{96} Dimer Acid/Ethylene Glycol Monoester [12] . . 17

Fig. 2.2  Results Obtained Using the Standard BOCLE Lubricity Test on Several Fuels[37] ......................................................... 37

Fig. 2.3  Wear Maps for a a) Poor Lubricity Fuel and b) Good Lubricity Fuel [39]. ................................................................. 39

Fig. 2.4  Two-Cycle Engine Stages of Operation [41]. ...................... 46

Fig. 2.5  Oil Film Formation in Two-Cycle Engine Lubrication. ............ 50

Fig. 2.6  Lubrication Problems of 2-Cycle Engines. ........................ 55

Fig. 2.7  J1088 Small Engine Hydrocarbon Emissions[69]. ................. 67

Fig. 2.8  J1088 Small Engine Carbon Monoxide Emissions [69]. .......... 68

Fig. 2.9  J1088 Small Engine Nitrogen Oxides Emissions [69]. .......... 68

Fig. 2.10 J1088 Small Engine Particulate Emissions [69]. .................. 69

Fig. 3.1  Experimental Set-up. .................................................. 80

Fig. 3.2  Block Diagram of the Engine Assembly Procedure. ............... 83

Fig. 3.3  Chemical Structures of the Monomers Tested. ..................... 92

Fig. 4.1  Photograph of a Replacement Piston (Left) with one Removed from a New Engine (Right) which Shows Signs of Mild Run-in. . . 98

Fig. 4.2  Photomacrograph of the Edge of a Plastically Deformed Portion of a Piston Removed From a New Engine (31.25X Magnification). ................................. 99

Fig. 4.3  Engine Cylinder Wall Temperature History While Using 0.5% Diallyl Phthalate as a Lubricant ................................. 100
Fig. 4.4 Photograph of the Top, Major Thrust Side of the Piston Using 0.5% Diallyl Phthalate as a Lubricant ......................... 102
Fig. 4.5 Photograph of the Major Thrust Wear Scar of the Cylinder Using 0.5% Diallyl Phthalate. .............................. 103
Fig. 4.6 Photomacrograph of a Piston Wear Scar Using 0.5% Diallyl Phthalate (31.25X Magnification). ................ 105
Fig. 4.7 Photomacrograph of a Piston Wear Scar Using 0.5% Diallyl Phthalate as a Lubricant (31.25X Magnification). ........ 106
Fig. 4.8 Temperature History Using 0.5% Monoester as a Lubricant .... 108
Fig. 4.9 Photograph of the Scuffed Piston Using 0.5% Monoester as a Lubricant ........................................ 109
Fig. 4.10 Photograph of the Wear Scar in the Engine Cylinder Using 0.5% Monoester as a Lubricant. ....................... 111
Fig. 4.11 Photomacrograph of the Piston Wear Scar Using 0.5% Monoester as a Lubricant (31.25X Magnification). .......... 112
Fig. 4.12 Photomacrograph of the Lower Piston Ring Using 0.5% Monoester as a Lubricant (15X Magnification). ........ 114
Fig. 4.13 Engine Temperature History Using 0.5% Monoester Plus 0.5% Sebacate. ................................................. 116
Fig. 4.14 Photomacrograph of the Piston Surface After 36 Minutes of Operation Using 0.5% Sebacate and 0.5% Monoester as a Lubricant (31.25X Magnification). ...................... 117
Fig. 4.15 Photomacrograph of the Liquid Build-up on the Outer Edge of the Upper Piston Ring Using 0.5% Monoester and 0.5% Sebacate as a Lubricant (31.25X Magnification). .... 119
Fig. 4.16 Photograph of the Engine Cylinder After Piston Scuffing Had Occurred Using 0.5% Sebacate and 0.5% Monoester as a Lubricant ................................. 120
Fig. 4.17 Photomacrograph of the Lower Edge of the Piston After Using 0.5% Monoester and 0.5% Sebacate as a Lubricant (31.25X Magnification). ....................................................... 121

Fig. 4.18 Engine Cylinder Temperature History Using 0.1% Monoester and 0.9% Sebacate at a Speed of 2400 rpm after Warm-up ................................................................. 123

Fig. 4.19 Engine Cylinder Temperature History With 0.1% Monoester and 0.9% Sebacate at 3000 rpm ................................................................. 125

Fig. 4.20 Temperature History for the Loaded Test Using 0.1% Monoester and 0.9% Sebacate ................................................................. 127

Fig. 4.21 Photomacrograph of a Piston Wear Scar After Using 0.1% Monoester and 0.9% Sebacate (31.25X Magnification) ....................................................... 129

Fig. 4.22 Photograph of the Engine Cylinder After Operating With 0.1% Monoester and 0.9% Sebacate After 220 Minutes of Operation .......................................................... 130

Fig. 4.23 Temperature History for the Test Conducted Using 2.0% of the Conventional, Two-Cycle Oil ................................................................. 132

Fig. 4.24 Photograph of a Scuffed Piston Obtained Using Conventional Lubricant at a Concentration of 2.0% ................................................................. 133

Fig. 4.25 Photograph of the Undamaged but Well Run-in Side of the Piston After 345 Minutes of Operation with Conventional Lubricant at a Concentration of 2.0% .......................................................... 134

Fig. 4.26 Photomacrograph of the Piston Wear Scar using Conventional Two-Stroke Lubricant (31.25X Magnification) ....................................................... 135

Fig. 4.27 Photomacrograph of a Well Run-in Surface of the Piston After Loaded Testing With Conventional Two-Cycle Lubricant (31.25X Magnification) .......................................................... 136

Fig. 4.28 SEM Photograph of an Undamaged Portion of the Piston Surface After 27 Min. of Operation With 0.5% Diallyl Phthalate (430X Magnification) ....................................................... 138
Fig. 4.29 SEM Photograph of a Scuffed Region of the Piston After 27 Minutes of Operation with 0.5% Diallyl Phthalate (120X Magnification). .................................................. 139

Fig. 4.30 SEM Photograph of a Scuffed Region of the Piston After 27 Minutes of Operation with 0.5% Diallyl Phthalate (430X Magnification). .................................................. 140

Fig. 4.31 SEM Photograph of a Scuffed Region of the Piston After 27 Minutes of Operation with 0.5% Diallyl Phthalate (430X Magnification). .................................................. 141

Fig. 4.32 SEM Photograph of a Very Smooth Region of the Piston Surface After Operation for 27 Minutes Using 0.5% Diallyl Phthalate (430X Magnification). .................................................. 142

Fig. 4.33 SEM Photograph of a Well-Run in Portion of the Piston Surface After 27 Minutes of Operation Using 0.5% Diallyl Phthalate (1000X Magnification). .................................................. 143

Fig. 4.34 SEM Photograph of the Edge of the Lower Piston Ring after 27 Minutes of Operation Using 0.5% Diallyl Phthalate (120X Magnification). .................................................. 144

Fig. 4.35 SEM Photograph of the Piston Ring Groove After 27 Minutes of Operation With 0.5% Diallyl Phthalate (430X Magnification). .................................................. 145

Fig. 4.36 SEM Photograph of Typical Deposits Found on the Piston Surface After 35 Minutes of Operation Using 0.5% Monoester (440X Magnification). .................................................. 146

Fig. 4.37 SEM Photograph of the Edge of a Damaged Portion of the Piston Using 0.5% Monoester as a Lubricant (120X Magnification). .................................................. 147

Fig. 4.38 SEM Photograph of Typical Surface Features Observed Near the Center of the Wear Scars of the Piston from the 0.5% Monoester Test (120X Magnification). .................................................. 148

Fig. 4.39 SEM Photograph of the Damaged Piston Surface Using 0.5% Monoester as a Lubricant (440X Magnification). .................................................. 149

Fig. 4.40 SEM Photograph of the Damaged Piston Surface Using 0.5% Monoester as a Lubricant (430X Magnification). .................................................. 150

LIST OF FIGURES
Fig. 4.41 SEM Photograph of the Outer Edge of the Lower Piston Ring From the Engine Test Using 0.5% Monoester (440X Magnification) ........................................... 151

Fig. 4.42 SEM Photograph of Typical Deposits found on the Surface of the Piston Rings Using 0.5% Monoester (120X Magnification) .................................. 152

Fig. 4.43 SEM Photograph of Typical Deposits found on the Surface of the Piston Rings Using 0.5% Monoester (430X Magnification) .................................. 153

Fig. 5.1 Piston Ring Sliding Speed as a Function of Crank Angle at Various Engine Speeds ............................................. 169

Fig. B1 Thermocouple Holder ............................................. 204

Fig. B2 Engine Flywheel ............................................. 205

Fig. B3 Flywheel Bushing ............................................. 206

Fig. B4 Exhaust Block ............................................. 207

Fig. B5 Engine Mounting Plate ............................................. 208

Fig. B6 Shaft Support Plate ............................................. 209

Fig. C1 Simplified Piston Cylinder Geometry ............................................. 211

Fig. C2 Measured Pressure-Volume Relationship for a Single-Cylinder, 400 cc, Two-Stroke Engine [84] ............................................. 213

Fig. C3 Pressure-Volume Relationship for the TVXL840 Operating at 3000 rpm (Estimated) ............................................. 214

Fig. C4 Estimated Piston Thrust Forces Produced During the Two-Cycle Engine Combustion Process at 3000 rpm ............................................. 215

Fig. C5 Calculated Piston Speed/Thrust Load Relationship ............................................. 216
CHAPTER 1

INTRODUCTION

1.1 PROJECT SIGNIFICANCE AND RATIONALE

According to a study by Cayot [1], the population of internal combustion engines is expected to increase by a factor of 5 in the next 50 years, expanding the world motor vehicle fleet from 550 million to over 2.5 billion. The widespread use of internal combustion engines has drawn attention to the harmful exhaust emissions which pollute the environment and are dangerous to the human species. For example, carbon monoxide is toxic to humans and animals. Nitrogen oxides contribute to the increased amount of acid rain, and are said to contribute to the depletion of the ozone layer. Nitrogen oxides and unburned hydrocarbons produce a visible smog, particularly in sunlight and are harmful to the lungs and eyes. In addition, the accumulation of carbon dioxide and hydrocarbon gases in the atmosphere increases the threat of the "greenhouse effect" changing the climate of the earth [2].

The increased global concern over air quality has triggered many governments to impose emission limits on the main sources of air pollution. Powerplants, large manufacturing facilities, and the transportation industry have been among the first areas to have legislative action, in regard to hazardous air pollution emission limits, imposed upon them. Because of the extremely large
number of smaller internal combustion engines being used in utility, recreation and transportation applications, the contribution of these devices to the overall air pollution problem has become significant. As a result, state and federal governments have been working to pass legislation that limits exhaust emissions from these types of hazardous air pollution sources.

The California Air Resources Board (CARB) has already imposed strict exhaust emission limits for 1994 in several small engine categories, and has developed much more stringent regulations starting in 1999 [3,4]. CARB limits for small internal combustion engines are summarized in Table 1.1. It is believed that many local and federal governments world-wide will adopt similar regulations in the near future. In most cases, the 1994 emission standards have been or can be met with simple engine adjustments or by applying current emission reduction technologies. Existing technologies that have been employed to reduce exhaust emissions include: leaner air/fuel ratios, air injection in the exhaust, exhaust gas recirculation, catalytic oxidation with and without supplemental air, and ignition timing changes [5]. These and similar emission reduction technologies have been effective in meeting regulations to this point, but new technologies which include more efficient engine designs, improvements in materials, advances in tribology and cleaner burning fuels will need to be developed if more stringent future air quality standards are to be met and maintained.

INTRODUCTION
Table 1.1: California Emission Standards for Utility and Lawn and Garden Equipment Engines, g/hp-hr.

<table>
<thead>
<tr>
<th>NON HAND-HELD EQUIPMENT ENGINES</th>
<th>THC + NOₓ</th>
<th>CO</th>
<th>PARTICULATE MATTER</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 225 cm³ displ.</td>
<td>12.0</td>
<td>3.2</td>
<td>300</td>
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<tr>
<td>≥ 225 cm³ displ.</td>
<td>10.0</td>
<td>3.2</td>
<td>300</td>
</tr>
</tbody>
</table>

* Six-mode SAE J1088 test procedure

1.1.1 FUEL LUBRICITY PROBLEMS

Because the world population is growing at such an alarming rate and the population of internal combustion engines is growing even faster, it has become evident that cleaner burning fuels will be required if local and federal air quality standards are to be met and maintained. Oil companies have been working to develop new and modify existing fuels which produce lower amounts of undesirable exhaust emissions. In many cases, cleaner burning fuels have poor lubricity characteristics and contribute to fuel pump sticking and premature fuel system wear, scuffing, and failure.
Diesel engine manufacturers have been directing their efforts to design engines with reduced emissions in order to comply with the changing environmental regulations. To help meet some of these regulations, the federal government imposed limits on the allowable sulfur and aromatics content that highway diesel fuels are allowed to contain, effective October 1993 [6]. Since this time, there has been a dramatic increase in the occurrence of diesel fuel system failures.

It has been well documented that alcohol fuels have very poor lubricity characteristics compared with gasoline. Engine wear when fueled with methanol is generally seven to eight times greater than with gasoline, despite recent efforts to formulate lubricants that work with alcohol fuels [7]. This problem exists mainly because methanol tends to condense on engine parts and displace lubricant films, particularly during cold operating conditions due to the low volatility of methanol. The combustion of alcohol fuels also produces some very aggressive acids which attack metal surfaces after having the protective film “washed” by the condensed fuel. Improvements in lubricants, metallurgy and engine designs must be made before alcohol fuels will ever be considered a viable substitute for gasoline.

Fuel lubricity problems in aviation fuels such as Jet A-1 have been studied since the early 1960’s. Refinery hydrotreating processes dictate the resulting fuel lubricity characteristics. The Ball on Cylinder Lubricity Evaluator

INTRODUCTION
(BOCLE), first pioneered by Furey [8], has been adopted by the U.S. Air Force to evaluate fuel lubricity and is the most widely accepted test device for this purpose. Recently, the United States Army has implemented the use of Jet A-1 in all ground military vehicles in an effort to adopt a single battlefield fuel. The use of Jet A-1 has resulted in a dramatic increase in the frequency of fuel system failures, and can be attributed mainly to the lower viscosity and poorer lubricity characteristics of Jet A-1 in comparison with gasoline and diesel fuels.

1.1.2 THE TWO-STROKE ENGINE AND ITS LUBRICATION PROBLEMS

Rather unique problems exist with the lubrication of the two-stroke, spark-ignited, gasoline engine.

The two-stroke engine offers several advantages over its four-stroke counterpart, which include its light-weight design with only three (main) moving parts, its simple maintenance and its low production cost. Crankcase scavenged two-stroke engines offer the advantage of being operated in any orientation. The two-stroke engine is the most common type of engine used in outboard motors, snowmobiles, chainsaws, golf-carts, and string trimmers in the U. S. today. Although the market never materialized in the U. S., there are millions of mopeds, motorcycles and motor-scooters employed for everyday transportation in Europe and Asia that employ the two-stroke design. In Taiwan alone, there
are 8 million registered motorcycles, of which 70% are the two-stroke cycle type [9].

This engine design employs a “total loss, once through” lubrication system whereby lubricant is either pre-mixed with the fuel, or it is metered directly to the critical areas of lubrication and then sucked out of the crankcase into the combustion chamber and subjected to the combustion of the fuel. Due to the very low amount of lubricant present on the engine parts at any time, this method of lubrication places very severe demands on the engine lubricant.

The two-stroke gasoline engine has been criticized for its unpleasant odor, high HC, smoke, and particulate exhaust emissions. Conventional, high molecular weight, two-cycle lubricants are the main source of the unpleasant odor, smoke, and particulate emissions for which two-cycle engines are criticized [10]. Conventional lubricants also contribute to the overall amount of HC emissions, although the main source of HC emissions from most current engine designs can be attributed to unburned gasoline that gets short-circuited during the scavenge process of the two-stroke cycle.

Although the simple two-stroke engine has high HC emissions compared with its four-stroke counterpart, it emits very low amounts of NOx due to the lower operating temperatures and pressures of the two-stroke combustion process. Conventional two-stroke lubricants hinder the adaptation of many of the common four-stroke emission reduction technologies to the two-cycle engine. For

INTRODUCTION
example, exhaust after-treatment is difficult to adapt due to the large amount of unburned lubricant that is discharged through the exhaust which would poison most catalysts. Very few lubricants have been formulated that can provide adequate wear protection at concentrations of less that 2% by volume in the fuel. Those that have been found to provide adequate protection in concentrations of less than 2% are usually limited to a particular engine design and specific engine operating conditions [11].

1.2 TRIBOPOLYMERIZATION: A NOVEL TWO-CYCLE LUBRICATION APPROACH

The concept of tribopolymerization is that certain monomers, which are chemically capable of polymerization, will polymerize on highly stressed surface regions under loaded contact in relative motion. Past work with a variety of addition and condensation monomers has shown that monomers can react and form very thin, but extremely effective, protective polymeric films which reduce friction and wear [12-19]. The idea behind the use of these monomers as anti-wear additives is that they will only form a polymeric film on surfaces where there are high surface stresses and the presence of the film will reduce surface contact and thereby reduce the rate of film formation. A substantial amount of work has been conducted with monomers at very low concentrations in hydrocarbon carrier fluids which have produced very impressive reductions in
friction and wear. An oversimplified schematic representation of the tribopolymerization concept is shown in Figure 1.1.

Because these monomers are ashless and they have been found to form extremely durable films in concentrations of well below 1% in a carrier fluid, they appear to be very good candidates for an entirely new class of anti-wear and possibly anti-friction fuel additives. The wide variety of systems and carrier fluids in which they have been found to provide exceptional anti-wear characteristics exhibit their excellent potential to the various fuel lubricity problems explored in this study.

---

**FIGURE 1.1:** Tribopolymerization as a Mechanism of Boundary Lubrication.
The focus of the experimentation conducted in this study is to apply the concept of tribopolymerization in a crankcase scavenged, spark ignited, air cooled, two-cycle gasoline engine which employs a pre-mixed lubrication system. This novel approach to two-cycle engine lubrication exhibits several significant potential advantages over conventional lubricants which include:

1. These ashless monomers are not expected to contribute to the emission of smoke and particulates.
2. Unlike conventional lubricants which are rarely found to provide acceptable wear and scuffing protection in concentrations below 2% by volume in the fuel, past work with these monomers show good potential of providing superior wear protection at concentrations well below 1% in the fuel.
3. These monomers have been found to provide suitable wear protection in a large range of applications and in a large variety of carrier fluids, making them reasonable candidates for a universal two-cycle lubricant. Conventional lubricants that perform well in one two-stroke design, commonly exhibit little, no, or sometimes adverse performance in a different engine design, e.g. a developed air-cooled lubricant in a water-cooled engine.
4. High molecular weight conventional lubricants contribute to excessive deposits inside two-stroke engines, causing exhaust port blockage, combustion chamber deposits, and poisoning of exhaust after-treatment catalysts. These monomers are expected to have no excessive deposit forming attributes, particularly at the low concentrations in which they are expected to perform. Prior use in jet aircraft fuels exhibits the cleanliness of these additives.

5. The use of conventional lubricants in outboard boat motors is known to leave deposits of high molecular weight lubricant on the surface of the water, destroying marine life. The monomers used in this study are expected to have no negative environmental effects.

6. If these monomers do form very durable, protective surface films during engine operation as expected, they may provide adequate rust and corrosion protection during off season storage.

1.3 OBJECTIVES OF THIS RESEARCH

The main focus of this research is to demonstrate the anti-wear and anti-scuffing performance of two monomer additives in an actual two-stroke engine. The motivation behind the assessment of these novel fuel additives is the belief that these ashless monomers will provide adequate wear protection at very low
concentrations (well below 1% in the fuel) resulting in a new class of effective, environmentally friendly, anti-wear additives for two-stroke engines.

A secondary topic of this research is to investigate other fuel lubricity problems where the tribopolymerization concept exhibits good potential. Existing test methods to evaluate fuel lubricity will be explored and recommendations will be generated for future test equipment and procedures.

In summary, the objectives of this study include:

1. To study existing two-stroke lubricant testing techniques and develop a relatively short term, inexpensive test procedure that can be employed with the greatest potential of reasonable correlation with field performance.

2. To design an engine bench test apparatus which can be used to evaluate the wear behavior of the different monomer additives.

3. To build an experimental set-up for the evaluation of different anti-wear additives.

4. To evaluate the anti-wear and anti-scuffing performance of two candidate monomers in an air-cooled, crankcase-scavenged, spark-ignited, two-stroke cycle gasoline engine that employs a pre-mixed lubrication system, through a series of engine bench tests.
5. To employ different surface analysis techniques to study the behavior of the monomers at the rubbing interfaces.

6. To investigate the potential merit of applying the concept of tribopolymerization to other existing and emerging fuel lubricity problems.

7. To generate recommendations for a test procedure and test apparatus for which the concept of tribopolymerization can be applied to other fuel lubricity problems.

It is anticipated that the research and experimentation conducted in this study will promote enthusiasm for further studies where the tribopolymerization concept is a strong candidate for the solution to a wide range of fuel lubricity problems.
CHAPTER 2
LITERATURE REVIEW

An appreciable amount of work has been conducted in a wide variety of tribological systems that demonstrate that the concept of tribopolymerization is a remarkable mechanism of boundary lubrication. A substantial amount of literature has been reviewed in the areas of tribopolymerization, fuel lubricity problems, lubrication and emission problems associated with the two-stroke cycle gasoline engine and testing techniques for evaluating two-stroke lubricants and exhaust emissions. Material most relevant to this project is summarized in this chapter.

2.1 TRIBOPOLYMERIZATION

The concept of tribopolymerization was first conceived by Furey [12] and later refined by Furey and Kajdas [13-17]. Tribopolymerization is defined as the planned or intentional formation of protective polymeric films directly and continuously on rubbing surfaces to reduce damage and wear by the use of minor concentrations of selected compounds capable of forming polymeric films in situ [12]. According to this concept, potential polymer-forming compounds or monomers are dissolved or mixed at low concentrations in a carrier fluid and
used as the lubricant. The deposited films function primarily because they form in the contact region and offer greater resistance to deformation and penetration than the carrier fluid.

The tribopolymerization process is believed to be influenced by high surface temperatures, exoelectron emission [13], and possibly other effects such as high contact pressures that occur at very localized, highly loaded contact regions. The formation of a protective film reduces contact between the substrates, thereby lowering surface temperatures and reducing the rate of film formation. In a dynamic system, the films are continuously being formed and worn away. The system therefore has built-in control: as the film wears away, surface contact and temperatures rise, causing the rate of film formation to increase and reduce surface contact.

The outstanding past performance of very low concentrations of certain monomer compounds when mixed in hydrocarbon carrier fluids make them very attractive candidates as a solution to the lubrication problems associated with poor fuel lubricity. This approach would be an ideal solution to the problems of lubricating the two-cycle gasoline engine. Experimental tests that have been conducted that most closely relate to the mechanisms of lubrication required by a two-stroke engine system will be discussed in this section. Although the lubrication of metallic substrates most closely relates to fuel systems which require anti-wear additives, recent work that demonstrates the striking anti-wear
performance of monomers on ceramic substrates has also been reviewed. Recent work with ceramic substrates clearly supports and further demonstrates the *in situ* polymerization concept. In addition, recent engine manufacturer interests in using ceramic materials for engine components brings attention to this work.

2.1.1 RYDER GEAR TESTS

The first demonstration of the *in situ* polymer concept was demonstrated by Furey [12] using a Ryder gear test machine. The Ryder gear test machine is a high load test device that is used to rate a lubricant's ability to prevent scuffing. This test device was developed to evaluate the wear performance of different aviation fuels and fuel additives. In the Ryder test, the lubricant is held in a heated reservoir and sprayed through a jet onto rotating gear surfaces. The interaction between the gear teeth is quite complex and involves both sliding and rolling motion. Load is applied between the two gears at 10 minute intervals, after which the test is halted and all 28 gear teeth are inspected under a microscope for percentage of scuffed area per inch of gear tooth width. Plots of percentage of scuffed area versus load are generated, and lubricant ratings are given by the load necessary to produce 22.5% scuff area.

An inexpensive compound was developed by partially reacting oil-soluble C_{36} dimer acid with an inexpensive glycol, ethylene glycol. The resultant
compound is essentially a monoester, capable of undergoing further polymerization as follows:

\[
\text{nHOOC - R - COO - C}_2\text{H}_4\text{OH} \quad \rightarrow \quad \text{HO[OC - R - COO - C}_2\text{H}_4\text{O]}_n\text{H} + \text{nH}_2\text{O}^\uparrow
\]

This "tailor made" condensation monomer was the first additive to meet the Ryder gear test requirement for a particular jet fuel application, in fact it exceeded the requirement of 1000 lb./in. by 50% with a concentration in the jet fuel of one-tenth of one percent. A summary of the Ryder gear test results is presented in Table 2.1.

**Table 2.1:** Results of Ryder Gear Scuff Test of Jet Fuel Additives [12].

<table>
<thead>
<tr>
<th>Additive in Jet Fuel</th>
<th>Ryder Gear Scuff Rating (N/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>700</td>
</tr>
<tr>
<td>0.1% C_{36} Dimer Acid/Ethylene Glycol Monoester</td>
<td>2600</td>
</tr>
<tr>
<td>0.1% C_{36} Dimer Acid</td>
<td>840</td>
</tr>
</tbody>
</table>

The Ryder gear test device was also employed to evaluate the effectiveness of the monoester in different types of carrier fluids. The results,
first presented by Furey [12], are summarized in Fig 2.1. The remarkable performance of the monomer in a variety of very different hydrocarbon carrier fluids demonstrates its potential in a wide variety of tribological applications. The monomer almost doubled the load carrying capacity of all the carrier fluids, and increased it by over an order of magnitude in JP-4. In fact, the addition of only 0.1% monoester to JP-4 increased the scuff rating above mineral oil and synthetic base aviation lubricants.

![Graph showing scuff rating for various fluids with and without 0.1% monoester addition.]

**Figure 2.1:** Anti-Scuff Rating for a Variety of Fluids With and Without the Addition of the C_{36} Dimer Acid/Ethylene Glycol Monoester [12].
2.1.2 RADIOACTIVE VALVE LIFTER WEAR STUDY

Another early application of the tribo-polymerization concept was conducted by Furey [19] using a four-stroke, V-8, automotive engine with radioactive valve lifters. This engine was equipped with 16 radioactive valve lifters to study valve train wear in the cam/lifter system under normal operating conditions. During engine operating conditions of no load at constant speed, radioactive valve lifter wear debris would accumulate in the engine crankcase oil. Periodic oil samples were taken during engine operation, and by using scintillation radioactive counting techniques, the amount of radioactive wear debris was calculated and the sample was returned to the engine. Several advantages to this testing technique include: (1) rapid and inexpensive wear data could be obtained without the problems of test interruption and engine teardown, (2) very accurate measurements of wear data were obtained from the beginning of the test, where minor part wear would be difficult to detect and quantify through dimensional measurements of the engine components, (3) testing under normal (non-accelerated) operating conditions yield the most consistent results with field performance, (4) accurate wear data can be studied as a function of time and can be easily compared with other additives over the same duration of time. (5) several tests could be conducted with the same engine parts after flushing the engine with a non-additive base oil. This
eliminates the uncertainties associated with accurate re-assembly and metallurgical variations in different engine components.

Data obtained from this test are summarized in Table 2.2. A 1% equimolar mixture of C\textsubscript{36} dimer acid and C\textsubscript{16} glycol reduced the valve lifter wear rate by about 90% over a non-additive paraffinic mineral base oil, with pronounced carry over effects up to 6 hours (360,000 rev) in a non-additive base oil afterwards. This carryover effect demonstrates the formation of (a) very durable protective film(s) that had formed on the contact region between the valve lifters and the cam. The 1% dimer acid and glycol mixtures alone in the base oil (which, by themselves are not capable of polymerization) had wear rates 3-4 times greater than the combination of the two additives in the base oil. The dimer acid/glycol mixture performed about as well as the same concentration of zinc dialkyldithiophosphate (ZDDP), which is a commonly used additive in controlling valve train wear. No carryover effects were found with the use of the ZDDP additive.
Table 2.2: Relative Additive Wear Protection Using a Radioactive Valve Train Wear Test [12]

<table>
<thead>
<tr>
<th>Compound in Paraffinic Mineral Oil</th>
<th>Relative Valve Lifter Wear Rate</th>
<th>Beneficial Carryover Effect?</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>100</td>
<td>----</td>
</tr>
<tr>
<td>1% Equimolar mixture of C_{36} dimer acid and C_{16} glycol</td>
<td>12</td>
<td>Yes (3-6 h)</td>
</tr>
<tr>
<td>1% C_{36} dimer acid</td>
<td>42</td>
<td>No</td>
</tr>
<tr>
<td>1% C_{16} glycol</td>
<td>30</td>
<td>No</td>
</tr>
<tr>
<td>1% Zinc di (C_6) alkyl dithiophosphate</td>
<td>10</td>
<td>No</td>
</tr>
</tbody>
</table>

2.1.3 EFFECT OF PRE-POLYMERIZATION

Furey also demonstrated the effect of pre-polymerization on the effectiveness of the monomer. A more polymerized tetraester reduced valve train wear by only 15%, while the C_{36} dimer acid/glycol monoester reduced the valve train wear rate by over 90% over the same 28-hour test. This result is extremely important from a mechanism standpoint, and is consistent with the idea that the additive performs by forming a polymer in the contact region of the material(s) where relative motion occurs and is relatively ineffective when pre-polymerized in the carrier fluid.
Subsequent testing was conducted to investigate the behavior of other possible polymer formers. A ball on cylinder device which was developed by Furey [8,12] was used to study the behavior of several condensation and addition type monomers. The results of these tests support the in situ polymerization concept although some of the monomer additives provided only moderate wear protection and some performed exceptionally well only after adding a polymerization catalyst.

2.1.4 STEEL PIN-ON-DISK EXPERIMENTS

To further understand tribopolymerization as a mechanism of boundary lubrication, a pin-on-disk apparatus was employed which featured a 1/8 in. diam. AISI 5210 steel ball sliding against a polished 1045 steel disk [15]. A series of tests were conducted at applied loads which ranged from 10 to 30 N for periods of 10, 30, and 60 min. Disk wear was measured using photomicrography and stylus profilometry. In hexadecane, the monoester was found to reduce disk wear by 95% over hexadecane alone at a load of 10 N. Significant wear reductions were observed at higher loads although they could not be quantified as a percentage due to the excessive scuffing using hexadecane alone.

Analysis of the disk wear track clearly supported the tribopolymerization concept. Fourier Transform Infra Red Microscopy (FTIRM) was employed to inspect the disk samples. The specifics of the findings can be found in the

LITERATURE REVIEW
literature, but evidence of polymerization (and other possible chemical reactions) was clear in the wear track and was not found on the surface of the specimens away from the wear track. In addition, the quantity of organic material in the wear track was at least 25 times greater with the monoester than those found using dimer acid alone or a more polymerized diester.

2.1.5 CERAMIC LUBRICATION

Several relatively recent experiments have been conducted to study the effects of tribopolymerization on ceramic substrates [16-20]. Ceramics have many advantages over metals due to their high hardness, low density, high strength, chemical inertness and very good thermal stability. A major problem associated with the use of ceramic materials in many applications is the inability to develop adequate lubricants and/or lubricating techniques. Many lubricants provide wear protection in the boundary lubrication regime by reacting with the surface of the substrate. The fact that ceramics do not react with most substances severely limits the range of effective ceramic lubricants, particularly under boundary lubrication conditions. The idea that the tribopolymerization concept works by forming a protective layer on the surface, without necessarily reacting with the surface, makes it an attractive candidate for ceramic substrates.
2.1.5.1 VAPOR PHASE CERAMIC LUBRICATION

Although the study of ceramic lubrication may appear very distant from the lubrication problems associated with the two-cycle gasoline engine, a recent study by Smith et al. [18] regarding the vapor phase lubrication of alumina (Al₃O₃) by monomers carries considerable interest here. The two-cycle gasoline engine relies on the fuel to carry lubricant to the critical areas of the engine after the fuel has been mostly vaporized through the carburetor and into the crankcase. Therefore, a vapor/liquid mist of fuel enters the crankcase, carrying with it, the lubricant. The upper cylinder liner area of the engine requires a lubricant that can survive the combustion process and form a protective film on the cylinder wall surface. Undoubtedly, some of the monomer additive will be consumed during the combustion process, but as the following discussion of Smith's results indicate only minor concentrations of the monomer may be needed to reach the cylinder wall and protect the surface.

In the study by Smith, monomer additives were heated, vaporized, and delivered to an enclosed ball-on-disk type geometry under sliding contact conditions. The load imposed between the ball and disk was 5 N and the sliding speed was .25 m/s. Nitrogen gas was used to purge the enclosure before each test, and was also the carrier fluid for each compound tested. Dry nitrogen was chosen due to its inertness with respect to each of the monomers and the alumina. Three addition type monomers were tested: lauryl methacrylate, diallyl
phthalate and vinyl octadecyl ether. All three of these monomers had previously been tested under a similar geometry and sliding conditions in a hydrocarbon carrier fluid.

Wear was evaluated by physically measuring the wear scars on the ball and the disk. Dramatic reductions in wear was observed for all three of the monomer additives when compared with reference tests of dry sliding with nitrogen gas only. Bulk temperatures of the system were controlled at set temperatures between 120 °C and 165 °C with the lowest wear in two cases at the highest temperature. Vinyl octadecyl ether appeared to provide relatively consistent wear protection over the entire temperature range, with a slight peak around 145 °C.

Ball wear reduction was extraordinary at the elevated temperatures -- ranging from 94 to 99% for the three compounds tested. This trend is of particular interest to the two-stroke application because typical cylinder wall temperatures under normal operating conditions are usually in the range of 180-270 °C for a typical air cooled two-cycle engine [22]. The coefficient of friction at 145 °C was 0.8 under dry sliding conditions with nitrogen alone, 0.4 for both diallyl phthalate and lauryl methacrylate, and 0.5 with vinyl octadecyl ether. The reductions in friction, ranging from 37-50%, constitute significant possible energy savings for applications under sliding conditions. The upper temperature limits for these monomers has not yet been explored.
At the elevated temperatures, colored wear tracks were visible to the eye after approximately 30 seconds after the start of each test. It was also noted that the color and the wear debris varied for each of the monomers. Further surface analysis was conducted by scraping wear track debris onto a gold mirror and obtaining FTIRM spectra for the wear debris. In all three cases, the wear debris spectra were very different from the standard spectra for the pure monomers. The comparison of the standard diallyl phthalate spectrum against the spectra for the wear debris showed clear evidence of polymerization and reaction with the substrate to form a soap. The spectra for the other two monomers were clearly very different from the standards, with evidence of some kind of reaction with the substrate, but no clear evidence of polymerization although it could not be completely ruled out. It was noted that the signal to noise ratio for the lauryl methacrylate and vinyl octadecyl ether wear debris was not as good as those for diallyl phthalate.

2.1.5.2 PIN-ON-DISK TESTS

Recently, Tripathy [19] conducted several alumina-on-alumina pin-on-disk experiments with selected monomers in a 1% wt. mixture in hexadecane. In this study, five addition type monomers were tested, i.e., lauryl methacrylate, diallyl phthalate, vinyl acetate, methyl-2-acrylamido-2-methoxy acetate, and vinyl octadecyl ether. The use of these monomers reduced alumina wear by an
average of 63%, 80%, 57%, 56% and 9% respectively. The first four monomers are capable of polymerizing by either a radical or anionic mechanism or both. The poorer performance of the vinyl octadecyl ether was attributed to its cationic mechanism of polymerization. The condensation monomer reduced wear by an average of 40%. Friction was not significantly affected by the addition of any of the monomers in hexadecane.

Tripathy also investigated the wear behavior of these monomers at elevated temperatures of 50-150 °C. All of the monomers retained their wear protection abilities throughout this temperature range with significant improvements in some cases.

In a subsequent study, Tritt [20] repeated several pin-on-disk experiments with several monomer additives in hexadecane under higher loads and higher speeds than previously explored by Tripathy. In general, it was found that at least some of the monomers were extremely effective in reducing wear under low speeds, (0.25 m/s sliding speed) at various loads, and ineffective at the highest speed tested, (1.0 m/s sliding speed).

It would certainly be inappropriate to conclude that these monomers would work well in a system with completely different substrates (such as metals) based solely from experimentation with ceramic substrates. The author believes this work to be extremely relevant from the point of view that these monomers can be delivered to the substrate at extremely low concentrations and be very
effective. The reactions between the monomers and a different substrate will undoubtedly be very different, although it is hypothesized that the monomers would be more effective in a metal system because metals are much more chemically active than ceramics, hence a greater potential exists for a reaction between the monomer and the substrate. High localized surface temperatures due to rubbing contact and exoelectron emission in a metal system are also likely to promote polymerization on the surface.
2.2 EXISTING AND EMERGING FUEL LUBRICITY PROBLEMS

As mentioned earlier, the search for newer and cleaner burning fuels has introduced new and greater problems in the areas of fuel lubricity. Liquid hydrocarbon fuels need to possess a degree of lubricating ability to protect sliding surfaces in fuel injection valves, fuel pumps and other moving parts. In some cases, improved metallurgy can reduce the rate of certain wear mechanisms, but often fuel additives are needed to protect fuel pumps, injectors and other components. A few areas where fuel lubricity problems have emerged have been investigated and are discussed in the following sections. Past work with monomers that have polymer-forming abilities indicate that they may be ideal solutions to each of these fuel lubricity problems. Existing techniques in testing and ranking fuel lubricity have also been investigated.

The term ‘lubricity’ is often used carelessly in the literature. For the purpose of clarification, it is defined in this work as: if two lubricants posses the same viscosity and one has better friction and wear characteristics in a particular tribological system than the other, then it is said to have better lubricity. This term can be misleading because it can only apply to a series of lubricants under specific boundary conditions. A lubricant may have good lubricity characteristics in one system, and very poor lubricity characteristics in a different system, depending on the dominant wear mechanism(s) and the specific chemical reactions that take place between the substrate and the lubricant in that particular system. Due to the very low viscosity of most fuels, most fuel systems
operate under boundary lubrication conditions, usually requiring some sort of chemical reaction between constituents in the fuel and the surface of the substrates to provide suitable wear protection.

2.2.1 DIESEL FUELED ENGINES

Several recent reports have been published regarding the lubricity of diesel fuels. In some areas, particularly in highly populated urban regions, legislative limits have been imposed on the amount of sulfur and aromatics that highway diesel fuels may contain. The federal government imposed a limits as of October 1, 1993 that all highway diesel fuel must have a maximum sulfur level of no more than 500 ppm (0.05%). Such fuels were also limited to a maximum aromatics content of 35%. California regulations require a maximum of 10% aromatics content in addition to the low sulfur content [23].

The hydro-treating process to reduce aromatics and sulfur levels in diesel fuel is also known to reduce the lubricating properties of the fuel. Several studies conducted by Wei et. al. [24-26] showed that the addition of sulfur impurities increase wear problems in diesel fuel. It was concluded that the hydro-treating process that reduces the sulfur content in diesel fuels also reduces the polar impurities, nitrogen and other reactive components that can react with substrate surfaces and form protective films that enhance the fuel's lubricity characteristics. Wei found that nitrogen-containing components tended to reduce wear problems in diesel fuels, but only in concentrations far in excess

LITERATURE REVIEW
of what is typically found in diesel fuels [27]. The aromatics content was also found to be directly proportional to a fuel's lubricity. A series of ball on cylinder and other different test geometries produced reasonably conclusive evidence that there is a strong linear relationship between the lubricity of diesel fuel and the aromatics content in the fuel [6].

In addition to the environmental concerns that are driving refineries to produce cleaner burning fuels, a new fuel lubricity problem has developed in the US Army due to an attempt to adopt a single battlefield fuel source. The US Army is attempting to employ aviation turbine fuel for use in all compression-ignition ground vehicles. The replacement of diesel fuel with neat Jet A-1 during operation desert storm produced a significant increase in the frequency of fuel pump failures [28]. Although work is now being conducted to more clearly understand the main sources of the failures, it is known that at least a number of these failures can be directly attributed to the lower viscosity and poorer lubricity characteristics of aviation fuel with respect to diesel fuel.

The trend of more severely refined fuels is expected to continue due mainly to the substantial growth rate in the population of compression-ignition equipment and increased concern over environmental air quality. As a result, an increase in fuel lubricity wear problems is on the rise. Environmentally friendly fuel additives must be developed that can protect engine parts from the catastrophic wear mechanisms encountered with low lubricity fuels.
2.2.2 ALCOHOL FUELS

It is well known and documented that lubrication of spark-ignition equipment is much more severe when fueled with alcohol fuels than with gasoline [29-32]. Methyl alcohol, or methanol, represents one of the most promising alternative fuels available today for use in current internal combustion engines. Methanol can be derived from alternate energy sources, such as coal, natural gas, and organic biomass materials [32]. Methanol is of particular interest over other alternate fuels because it will operate in current engine designs with a minimal conversion effort and cost compared with other alternatives. Methanol is currently one of the most economical alternatives to gasoline when considering unit energy/dollar. Methanol fuels are very clean burning and have lower HC emissions than gasoline when burned in a spark-ignited internal combustion engine. Unfortunately, the net heat of combustion of methanol is only about half of typical gasoline, but it does have a very good octane rating (109), which allows engine designs with higher compression ratios resulting in improved thermal efficiencies [81].

The use of methanol in internal combustion engines has resulted in excessive engine wear, particularly in the upper cylinder bore region of the engine. Several theories have been offered to account for this wear which is about seven or eight times worse when an engine is fueled with methanol than gasoline. The most widely accepted theory is that due to methanol's low volatility, it can condense on the combustion chamber cylinder walls and wash
away protective lubricant films, particularly during cold start-up conditions [29,30]. This “wall washing” theory is supported by the fact that engine wear has been found to be much more severe under cooler engine operating conditions (engine start up) and the majority of the wear occurs near top dead center of the cylinder, where the cylinder liner is exposed to the unburned liquid methanol.

In addition to the fact that the protective lubricant film gets washed away from the surface of the cylinder liner, the combustion products of methanol are very corrosive and are free to attack the surface of the cylinder liner. Formic acid is a carboxylic acid combustion by-product of methanol and a very aggressive organic acid. It is believed that the formation of this acid during the combustion process leads to excessive corrosive wear to the cylinder liner.

The dominant wear mechanisms in methanol fueled engines have been debated and are not completely agreed upon in the literature. It could be mainly corrosive wear or it could be caused from adhesive welding that occurs between the piston ring and cylinder liner due to the loss of a protective oil film. The overall wear is undoubtedly a result of many wear mechanisms, but is generally agreed upon that it results from the loss of a protective lubricant film brought on by the washing of the cylinder liner with methanol in liquid phase.

Several solutions to this problem have been proposed which include improved metallurgy, complete vaporization of methanol before entering the combustion chamber, and improved lubricants and fuel additives. The ideal
solution would be an effective additive that is inexpensive, environmentally friendly and easily obtainable.

Ethanol is another possible energy alternative, with an energy content slightly higher than methanol. Similar lubrication problems exist between the use of ethanol and methanol, and its cost per gallon is significantly higher. The economic incentives currently favor the use of methanol.

2.2.3 AVIATION FUEL LUBRICITY

Problems associated with aviation turbine fuels may be traced back to the early 1960’s [33]. Aviation fuels are very pure, solvent like fluids with low viscosities and poor lubricity characteristics. Problems with gear tooth wear in aviation fuel pumps in the 1960’s produced the need for a standard bench test that correlates well with field performance. By far, aviation fuel lubricity problems have been investigated more thoroughly than all other hydrocarbon fuels. To date there exists a remarkable amount of disagreement in the literature about the effect that different fuel constituents have on fuel lubricity. This may be due, at least partly, to the lack of a clear definition of lubricity.

Appeldoorn and Dukek [33] conducted a series of studies to evaluate the lubricity of different aircraft fuels and the effect of different constituents on fuel lubricity. Ten different fuels had been selected for this study, ranging in viscosity, boiling range, hydrocarbon type, and degree of refining. Four test methods were imposed to evaluate wear using different fuels: the Ryder gear
test, the Vickers vane pump, the four ball wear tester, and the Furey ball-on-cylinder test. Only the ball-on-cylinder test produced results that were consistent with field performance of the fuels in all ten cases.

The ball on cylinder lubricity evaluator has been adopted by the US Air Force and has been accepted as the standard for evaluating the lubricity of aviation fuels both with and without anti-wear additives [34]. This test procedure (which is discussed in greater detail in the next section) has been widely used to evaluate jet fuel lubricity.

Fuel contamination and moisture content is often responsible for equipment wear and failure. These effects are often mistaken for inadequate fuel lubricity.

2.2.4 FUEL LUBRICITY ASSESSMENT TECHNIQUES

Many wear test configurations have been suggested to evaluate fuel lubricity including the Lucas Dwell tester, reciprocating wear rigs, and the four-ball test configuration. By far the most widely accepted test configuration for evaluating fuel lubricity is the ball-on-cylinder lubricity evaluator, first introduced by Furey [8].

ASTM Standard D 5001-90a [34] utilizes the BOCLE and has been adapted by the US Air Force since the early 1960's as the standard test for evaluating the lubricity of aviation fuels. This test utilizes a 49 mm diameter steel cylinder that rotates at a constant speed of 240 rpm with a 12.5 mm
diameter steel ball loaded against it using a mass of 1 kg hung on the end of a lever arm. This equates to a sliding speed of about 515 mm/s and contact load of 9.81 N.

The cylinder is partially immersed in the test fluid which maintains the cylinder in a wet condition and continuously provides the ball/cylinder contact region with a fresh supply of the test fluid. Because the BOCLE is very sensitive to contamination problems, special care must be taken to prevent contamination of the test fluid and test equipment. The apparatus is enclosed to allow a controlled environment with a relative humidity of 10%.

The wear scar diameter generated on the test ball after 30 minutes is used as a measure of the lubricating properties of the fluid. Three tests are conducted with each fluid and the results are rejected if any of the three wear scars differ by more than 0.03 mm. An average wear scar diameter of 0.85 mm or less passes the test. It should be noted that wear volume is a function of wear scar diameter to the fourth power.

Although the BOCLE has been used as a standard to evaluate aviation jet fuels for over three decades, no standard has yet been developed to evaluate the lubricity of other fuels. A weighty amount of work has been conducted recently by Lacey et al. [35,36] to adapt the BOCLE for use in evaluating the lubricity of other fuels. Lacey has criticized the ASTM method of rating the lubricity characteristics of aviation fuels because the standard only tests under lightly loaded boundary lubrication conditions. Surface oxide layers and films
that form on the surfaces of the ball and cylinder from the fuel can prevent asperity contact from occurring between the ball and cylinder particularly with low contact forces. The oxide and film layers are usually weak compared to the bulk material(s) and continuously form and wear away. This is characterized as corrosive wear and the standard ASTM BOCLE test is very sensitive to this wear mechanism.

In a fuel system however, there exist many different contact loads and geometries between parts in relative motion. A recent study conducted by Lacey [37] which involved the inspection of 15 military fuel pumps that had failed during operation desert storm indicated that corrosive wear was not the dominant source of fuel pump failure. In several cases, it was hypothesized that the source of failure was due to misalignment or parts out of spec., but the failure rate was significantly more recurrent after the substitution of diesel fuel with Jet A-1. The standard BOCLE testing procedure was used to compare the lubricity of different fuels, and the results obtained by Lacey are presented in Figure 2.2
A subsequent series of bench tests were conducted by Lacey to study the mechanisms of failure in military fuel pumps using Jet A-1 [38]. In general, Lacey concluded that the results of the standard BOCLE test is at least directionally correct in regard to overall pump wear, but that it was less effective at predicting wear of components under higher contact stresses where adhesive welding and abrasive wear mechanisms appear to be dominant. This weakness was most evident in highly loaded pump components using Jet A-1. Standard BOCLE tests seemed to slightly overestimate wear with diesel fuel compared with other fuels, perhaps due partly to the higher viscosity of diesel fuel over other fuels. The detailed test results can be found in the literature.
In an attempt to present more thorough information about a fuel's lubricity characteristics, Lacey subsequently developed a wear mapping technique [39]. Three dimensional wear maps are generated by using the BOCLE under a variety of controlled test conditions. Two parameters are plotted against the resulting wear scar diameter which is always plotted on the vertical axis. Since severe adhesive damage always occurred with ball wear scars above 1mm in diameter, Lacey labeled the vertical axis form 0 to 1mm. Any wear scar diameter above 1mm was arbitrarily plotted as 1 on the wear map, creating a flat plane that represents unacceptable performance on the wear map. Figure 2.3 depicts three dimensional wear maps constructed by Lacey that were constructed using the ball-on-cylinder test device.

Although a considerable amount of information can be provided by a single wear map with two simultaneous variables, there are many parameters that have a significant influence on wear. It was suggested that five three-dimensional wear maps are required for a given lubricant/material pair: speed and load, speed and temperature, load and temperature, load and time, and speed and time. Although more work obviously still needs to be conducted in the area of rating fuel lubricity, the BOCLE test shows good potential for reasonably good correlation if ratings could be set up that consider several different test parameters. Obviously, the existing ASTM standard does not account for the entire picture.
Figure 2.3: Wear Maps for a:  
(a) Poor Lubricity Fuel  
(b) Good Lubricity Fuel [39]
Onion and Suppeah observed thin gel-like films that formed on lubricated surfaces within diesel injection equipment [40]. Tests were conducted using a rotating cylinder against a flat plane. An electrical resistance method was used to monitor when contact occurred between the surfaces. Onion reported that this very thin gel-like surface film formed almost immediately after startup and continued to increase in thickness after several hours of running. This film was easily destroyed with a small puncture and then re-formed. Tests were conducted with benzene, kerosene and heptane and no similar surface films were observed. Unfortunately, no attempt was made to characterize the surface film chemically, and there was no analysis of the constituents in the diesel fuel that was tested. In addition, there was no mention of any type of controlled environment, which could result in contamination and severely affect the results of the experiment.
2.3 THE TWO-STROKE, SPARK-IGNITION, INTERNAL COMBUSTION GASOLINE ENGINE

The two-stroke cycle engine was invented in England by Sir Dugald Clerk, approximately 10 years after the first four stroke engine, which was first built in Germany by Nicolaus Otto in 1876 [41]. Today, two-stroke engines are being manufactured to be employed in a large variety of different applications.

Legislative pressure on exhaust emissions in some countries has produced a swing to a four-stroke replacement in some cases. The possibility for the long term survival of the two-stroke engine will depend mainly on the manufacturer’s ability to develop a two-stroke engine that will meet environmental legislation and maintain a competitive cost with its four-stroke counterpart.

2.3.1 THE ADVANTAGES AND APPLICATIONS OF THE TWO-CYCLE GASOLINE ENGINE

With only three moving parts, the simple two-cycle engine can be manufactured at very low production costs. Easy maintenance and servicing are a result of the simplicity of the two-stroke design.

When compactness and power/weight ratios are the main design criteria for a given application, the two-stroke engine is the clear choice over the four-stroke design. For the same brake mean effective pressure (bmep) assumed,
the two-stroke engine needs only half the engine speed, or only half of the displacement for the same engine power output. Because the four-stroke engine needs to maintain rotational inertia during its scavenging stroke, it often requires a crankshaft with added mass, contributing to additional size and weight in a single cylinder engine. The added intake and exhaust valves required with the four-stroke design add to the complexity, cost and weight of the engine.

The two-stroke engine is ideally suited for portable equipment due to its missing oil sump, allowing the advantage of operation in any inclined or inverted orientation. The "once through" lubrication system in a two-cycle engine allows it to have a unique advantage in applications where the device is subject to be operated upright, inverted, on its side, or any intermediate position.

Two-stroke engines are easier to start than a four-stroke engine with the same power output. This is due to the lower trapped compression ratio and smaller displacement of the two-stroke engine. A very viscous oil sump in cold conditions can also make pull or kick-starting a task with a four stroke engine. The main advantages of the two-stroke engine are summarized in Table 2.3.

<table>
<thead>
<tr>
<th>Table 2.3: Advantages of the Simple Two-Stroke Gasoline Engine</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Compact Design</td>
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<tr>
<td>• High Specific Output</td>
</tr>
<tr>
<td>• Easy Cold Start</td>
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<tr>
<td>• Simple Maintenance</td>
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<tr>
<td>• Insensitivity to Inclination or Orientation</td>
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</table>
Table 2.4 lists some of the many applications in which two-stroke engines are employed.

<table>
<thead>
<tr>
<th>Agricultural Equipment</th>
<th>Passenger Cars</th>
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<tbody>
<tr>
<td>Asphalt Cutters</td>
<td>Scooters</td>
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<tr>
<td>Brushcutters</td>
<td>Small Aircraft</td>
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<tr>
<td>Chain Saws</td>
<td>Snowmobiles</td>
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<tr>
<td>Electric Generators</td>
<td>Spraying Equipment</td>
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<tr>
<td>Go-Carts</td>
<td>Sprinkling Equipment</td>
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<tr>
<td>Golf Cars</td>
<td>Tillers</td>
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<tr>
<td>Ground Boring Machines</td>
<td>Tree Sprayers</td>
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<tr>
<td>Ground Milling Machines</td>
<td>Walk Behind Mowers</td>
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<tr>
<td>Mopeds</td>
<td>Water Scooters</td>
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<tr>
<td>Motorcycles</td>
<td>Water Pumps</td>
</tr>
<tr>
<td>Outboard Motors</td>
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2.3.2 SCAVENGING

The simple, loop-scavenged, spark ignition engine is generally naturally aspirated and crankcase scavenged. This means that a fresh charge is aspirated by the bottom side of the piston during the upward or compression stroke, and compressed when the piston is moving back towards the crankshaft. Because the crankcase is used in the process of scavenging, it cannot have wet sump lubrication as in the four-stroke engine, therefore roller, ball, or needle bearings are necessary to support the crankshaft and connecting rod(s).
Usually a carburetor controls the mixing and metering of fuel and air into the crankcase, therefore resulting in a homogeneous combustion process. There are four main intake systems that can be employed between the carburetor and the crankcase. The most simple, and least expensive solution of intake control is the piston ported design, controlled by the piston skirt, which is the lower edge of the piston closest to the crankshaft. During compression, the piston moves past the intake port of the crankcase, which allows a fresh charge from the carburetor to enter the crankcase. The complete scavenge process is depicted in Fig. 2.4. After the combustion in a two-stroke cycle engine, the piston moves downwards, closing the opening to the carburetor and temporarily sealing off a fresh charge in the crankcase. As the piston continues to move downwards, the exhaust windows are opened, releasing the expanding waste gases into the exhaust. Shortly after this blowdown period, the upper edge of the piston moves past the openings to the transfer port(s), which allows the fresh charge to exit the crankcase and enter the combustion chamber. During this process, there is a period of time of which the transfer ports and exhaust ports are both open to the combustion chamber allowing some of the fresh charge to "short circuit" directly out through the exhaust. This inherent characteristic of the piston ported design cannot be completely eliminated because the port timing is symmetric. The crankshaft can be offset to help improve the port timing, but the
benefits have been found to be hardly worth the additional manufacturing costs involved due to the increased complexity of the design [41].

Short circuiting is an undesirable characteristic of homogeneous charging and needs to be minimized to optimize performance and reduce hydrocarbon emissions.

The three other intake systems commonly employed are rotary disc inlets, which are commonly used in racing engines, reed valve inlets, and a combination of piston and reed valve control. These systems are thoroughly covered in the literature [41,42] and do not differ greatly from the piston ported engine described above. These other porting designs, although slightly more expensive, have been applied to optimize the port timing of the two-stroke engine to optimize power output in certain speed ranges and reduce the amount of short circuiting.
Figure 2.4 Two-Cycle Engine Stages of Operation [41]
The process of removing the burned gasses from the combustion chamber and replacing them with a fresh charge is referred to as scavenging. The most common scavenging process is referred to as loop-scavenging. This design, patented in 1908 by P.A. Kind, as defined in the patent claim, is that "...at least one pair of scavenge (transfer) ports should be directed in such a way that the direction of the resultant stream of the streams passing through the said ports in the opposite direction to the exhaust windows" [42]. In short, the transfer ports are directed into the combustion chamber in the opposite direction from the exhaust window(s), in an attempt to minimize the effect of fresh charge directly exiting the combustion chamber, which is the process referred to as "short circuiting." The transfer ports are arranged on each side of the cylinder in such a way that the fresh charge flows to the rear side of the cylinder, opposite to the exhaust window, in an upsweep angle. Ideally, the scavenge flow follows the contour of the combustion chamber in an upsweep direction, cleaning the spark plug zone and then looping down to the exhaust port region.

The cross-scavenging process is defined by an opposite arrangement of transfer ports across from the exhaust ports with a deflection device on the piston crown to prevent (or at least minimize) short circuiting. The shape of the piston crown is often susceptible to develop "hot spots" causing pre-ignition and damage to the piston crown.
The uniflow scavenging process employs exhaust valves installed in the cylinder head and actuated by a camshaft that rotates with the crankshaft. This design adds to the complexity and cost of the two-stroke design and does not produce any benefit over a well developed loop-scavenged design in terms of scavenging efficiency. Opposed piston, double piston u-type, and poppet valve control loop scavenging are among a few other scavenging designs that are commonly employed in multi-cylinder two-stroke designs.

Perfect displacement scavenging is the ideal condition in which all of the exhaust gases are completely replaced with a fresh charge. In practice, the fresh charge mixes with some of the unburned gases and the ideal condition for this is called perfect mixing scavenging, whereby all of the retained exhaust gases completely mix with the fresh charge. The real situation is actually a combination of displacement, mixing and short circuit scavenging.

2.3.3 LUBRICATION

Although there are many factors that must be considered in the design of a two-stroke gasoline engine for a particular application, recent designs have been almost entirely dictated by environmental concerns [43]. Probably the most critical aspect of improving two-stroke engine emissions is the development of more effective lubricants and more efficient lubricating systems.
2.3.3.1 LUBRICATING SYSTEMS

The oldest and most common method of lubricating the simple two-stroke gasoline engine is through the use of a pre-mixed, “total loss” lubricating system [41]. Since the crankcase is used in the scavenging process, it cannot contain a reservoir of lubricating oil. The lubricating oil is carried in the fuel and coats the crankshaft bearings, connecting rod bearings, and piston-cylinder unit as it is carried in a fuel mist through the crankcase and into the combustion chamber, eventually leaving the engine after being exposed to the combustion process.

When fuel and oil droplets strike the warm surfaces of engine parts which are in sliding and rolling contact, the fuel vaporizes and leaves an oil film behind to lubricate rubbing surfaces, as shown in Fig. 2.5. Since most of the fuel will vaporize when reaching warm engine part surfaces, the viscosity of the lubricant plays an important role in being able to provide a hydrodynamic film and minimize asperity contact. Since the piston reverses direction twice every revolution, a break-down in hydrodynamic lubrication results and boundary lubrication conditions exist. How the lubricant reacts chemically on and with the substrate is very important under boundary lubrication conditions.

Four-stroke crankcase oils were used in the earliest two-stroke engines [44]. Due to the problems with exhaust port blockage, piston ring sticking, spark plug fouling, combustion chamber deposits and unpleasant exhaust smoke, it
was immediately clear that the lubricant requirements of the two-cycle engine were much different than its four-stroke counterpart.

![Diagram of oil and fuel droplets forming a film on a surface.]

Figure 2.5: Oil Film Formation in Two-Cycle Engine Lubrication

Since it is desirable to produce the cleanest exhaust emissions possible, it is usually advantageous to keep the lubricant concentrations to a minimum. This results in a boundary lubrication problem because there is simply not enough lubricant on the engine parts to provide a hydrodynamic, or even mixed lubrication regime. Satisfactory lubricant compounds must be capable of providing adequate wear protection under boundary lubrication conditions.

Typically, an engine manufacturer recommends a lubricant that has been developed specifically for the particular engine being sold, most commonly at a volumetric ratio in the gasoline of about 1 part oil to 50 parts gasoline. Some highly developed lubricants have been effective at ratios as low as 1:100, but
typically in very limited applications and under restricted operating conditions [45].

The pre-mixed lubrication system typically works well around the concentration of 1:50 as mentioned above, and when the fuel consumption rate can be directly related to the lubrication needs of the engine. There are times however, where the latter is not the case.

Callis et. al. [11] mentioned, for example, when a motorcycle is “coasting” along a downward slope for extended periods of time. This is a case where the throttle remains at idle, drawing minimal amounts of fuel into the engine, yet the engine runs at high speeds, requiring more than a minimal amount of lubricant. Another example is when outboard motors are run at idle for long periods of time at the dock before being shut-off, possibly for an entire season. The amount of oil delivered to the cylinder liners, for example, is very low during this idle period. This leaves an extremely light coating of oil in the engine to protect it from oxidation and corrosion during several months of off-season storage.

In an attempt to eliminate the need of an operator to measure and mix specific amounts of fuel and oil, an oil metering system was developed. This type of lubricating system requires the operator to fill an oil reservoir with two-cycle oil each time the engine is re-fueled. The oil is then mixed in-line with the fuel, by some sort of oil pump driven by the crankshaft, before entering the crankcase. This type of system has been developed to meter the oil into the fuel
at varied ratios, dependent most commonly by engine speed, throttle opening or a combination of the two and not necessarily the fuel consumption rate.

The most advanced lubrication designs have been developed to lubricate the most sensitive engine components directly. Oil grooves are machined into the crankshaft and oil is metered to the bearings through these grooves. This type of lubrication system allows a lower consumption of oil because it is directed towards the critical areas of engine lubrication. Surprisingly, Laimbock [42] stated that the cylinder-piston unit is not the dominant limit for leaning the oil quantity in a well-developed two-stroke engine. In his studies, it was found the most sensitive part against leaning the oil mixture to be the connecting rod / crankshaft bearing. Other reports have ranked the piston and cylinder bore as the most sensitive area of lubrication [45]. It is likely that this issue depends mainly on engine design metallurgy, and the lubricant being used, but almost all of the literature considers both of these regions as critical areas of lubrication.

McCaffree stated the most critical deposit control requirement to be the prevention of ring sticking [32]. Ring sticking allows the cylinder walls to be exposed to the combustion products, causing excessive varnish buildup and significant losses in engine output and efficiency. Furuhma [46] reported that the occurrence of ring sticking prohibits the piston from dissipating heat by thermal conduction through the rings and cylinder, resulting in excessively high piston temperatures. It has been generally agreed that the use of keystone or ‘L’
rings dramatically reduces the occurrence of ring sticking in two-stroke engines [46,47].

It is commonly reported that deposit formation is much more notable under long periods of continuous running then with stop-start type operation. Schilling [22] also reported that the use of a lower viscosity oil usually has a lower deposit forming tendency than a higher viscosity oil, even when used in greater ratios.

2.3.3.2 LUBRICANT REQUIREMENTS

Depending on the particular application, the priority of lubricant requirements may differ from case to case. The overall requirements, however, are generally the same for all two-stroke applications. Table 2.5 summarizes the main development criteria of a two-cycle oil.
Table 2.5: Important Considerations in the Development of a Two-Stroke Lubricant

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<table>
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<tbody>
<tr>
<td>Ecological impact</td>
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<tr>
<td>Piston scuffing (seizure)</td>
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<tr>
<td>Bearing protection</td>
</tr>
<tr>
<td>Exhaust system blocking</td>
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<tr>
<td>Rust and corrosion prevention</td>
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<tr>
<td>Deposit-induced pre-ignition</td>
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<tr>
<td>Combustion chamber deposits</td>
</tr>
<tr>
<td>Ring sticking</td>
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<tr>
<td>Spark plug fouling</td>
</tr>
<tr>
<td>Spark plug bridging</td>
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<tr>
<td>Lacquer and carbon deposits</td>
</tr>
<tr>
<td>Good miscibility with the fuel</td>
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<tr>
<td>High Flash Point</td>
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</table>

A flow chart representation of lubricant requirements with respect to different engine areas is presented in Fig. 2.6.
Figure 2.6: Lubrication Problems of 2-Cycle Engines

* Separate Lubrication Systems
2.3.3.3 CONVENTIONAL LUBRICANTS

Conventional two-stroke lubricants have typically been able to provide satisfactory wear, scuffing, and detergency at ratios in the fuel of about 2% by volume [48,49]. Generally speaking, it has been found that high molecular weight lubricant components form the most durable surface oil films on engine components, hence provide good anti-scuffing and anti-seizure protection by preventing metallic contact and adhesive welding. Unfortunately, higher molecular weight oils tend to be more susceptible of forming deposits in the combustion chamber and contribute to exhaust port blockage, piston ring sticking and spark plug fouling. Lubricant manufacturers have been working to optimize formulations that account for the trade-off between wear protection and cleanliness, often by leaning towards higher molecular weight formulations with improved detergents.

By far, the most commonly discussed two-stroke additives in the literature over the past 25 years are bright stock and polyisobutylene (PIB) [51-55].

Bright stock is a high viscosity blending stock that is used in the formulation of heavy-duty lubricants for truck, automobile, and aircraft services [51]. It is often added in the formulation of two-stroke lubricants to increase oil viscosity, thus improving the anti-scuff properties of the lubricant. A large number of articles have discussed the effects of bright stock in lubricant formulations which include a broad range of testing scenarios many of which
employ two-cycle engine bench tests [52-54]. The results have been remarkably consistent throughout the years in regard to the effect of bright stock in a two-stroke lubricant to an extent that further evaluation of the effects of bright stock seem redundant. In two-stroke lubricant formulations, it has been found that the addition of bright stock significantly increases the lubricant’s ability to prevent engine scuffing and seizure, up to a concentration in the lubricant of about 20%. The addition of bright stock beyond this concentration was found to provide little additional wear protection and was found to have a pronounced negative effect on engine cleanliness, exhaust port blockage and ring sticking. Bright stock has also been found to produce environmentally unacceptable amounts of exhaust particulate emissions. This can be attributed mainly to the high aromatics content in bright stock which does readily break-down in the combustion process.

Polyisobutylene is a common additive in the highest performance, more expensive Japanese two-stroke engine lubricants being used today [56]. It has been found to be comparable to bright stock in regard to it’s ability to protect engine parts from scuffing and wear. The main advantage of PIB is that it produces considerably less smoke in the exhaust gases. PIB is tacky, therefore adheres well to engine parts. PIB that is sucked into the combustion chamber readily undergoes thermal decomposition and is burned. It has been found that the higher the molecular weight of PIB that is added, the less exhaust smoke is
observed. The reasoning behind this is that higher molecular weight additives tend to form larger droplets that are more likely to stick to engine parts than be carried out with the exhaust gases. Similar to the use of bright stock, higher molecular weight PIB and higher concentrations of PIB are found to increase combustion chamber deposits and ring sticking. It should be noted that PIB and bright stock are not biodegradable.

A significant amount of recent work has been conducted with jojoba based lubricant formulations [57,58]. Jojoba is a wild shrub originally found growing in the southwest American desert. The jojoba shrub was introduced in India back in 1965 in an attempt to green the deserts of Rajasthan state. It is estimated that the land in India under jojoba cultivation will increase to over 50,000 hectares by 2000 AD. The seeds of jojoba contain an oil that has been found to be a very effective lubricant, comparable with mineral oil base stocks. The main rationale for the development of a jojoba based lubricant is its favorable biodegradability characteristics and the need for a renewable replacement for hydrocarbon sources. Although tests conducted using a Shell Four Ball Wear Tester as per ASTM D 2266 showed exceptional anti-scuffing properties with jojoba [58], recent engine testing conducted by Gupta et. al. has shown unsatisfactory wear and scuffing protection from jojoba alone. Engine testing conducted with formulations of jojoba with around 20% bright stock, an antioxidant, and several different detergents, in a concentration in the fuel of 3%
was reported to have effective anti-scuffing, anti-wear, and good cleanliness properties. No information has been provided regarding exhaust emissions, although the presence of bright stock guarantees particulate emissions.
2.4 TWO-CYCLE ENGINE LUBRICANT TESTING TECHNIQUES

A remarkable number of different two-cycle engine testing techniques have been utilized to screen and evaluate two-cycle lubricants and additives [59-68]. The common four-ball wear test (ASTM D 2266) is one of the most widely used tests to screen two-stroke engine lubricants. Other non-engine bench tests that have been conducted include reciprocating piston ring/cylinder bore (Cameron-Plint) bench tests [59,64,68] and rotating aluminum cylinders under loaded contact [66]. It has even been argued that differential scanning calorimetry can be employed to rank lubricants by studying their exothermic reactions [67].

The objective of these test procedures is to obtain an inexpensive, short-term, repeatable and reliable test procedure that is widely accepted throughout the industry. The problem with many commonly used procedures is that they differ significantly from the environment and fail to model the mechanisms of wear that exist in an actual engine. Several cases have been documented that demonstrate that a lubricant or additive may have extremely good characteristics in one two-stroke engine design and have poor or even adverse effects in a different engine design [11]. If conventional lubricants do not exhibit consistent friction, wear and deposit characteristics from one engine design to another, it is doubtful that any simple type of test geometry can be devised outside of an actual engine that can even be used to rank two-cycle lubricant formulations.
There seems to be a pre-occupation with test repeatability in many cases, where the main concern should emphasize the relevance of the test to an actual two-stroke power-plant.

Dozens of engine bench test procedures have also been devised throughout the years to evaluate different lubricant formulations. These procedures range in test time from Yamaha's 70 minute test procedure to those which require testing for as long as a few weeks [60]. The most widely used engine bench test procedure to evaluate air cooled two-cycle lubricants is the ASTM D 4863 - 88 [63]. This test program, which is often referred to as the ASTM piston tightening test, utilizes a small, single cylinder engine with an aluminum piston and cast iron cylinder bore. The engine parts are manufactured to tolerance ranges that are specified in the ASTM procedure. In addition, the cooling fins on the engine are machined off. A two hour engine break in is conducted at full throttle with a 20:1 fuel to lubricant ratio, with cooling air provided by an external fan. All test running is performed using a 150:1 fuel to oil volumetric ratio. During the test, the engine is run at Wide Open Throttle (WOT) for 25 to 30 minutes to establish thermal equilibrium, then the cooling air is stopped. The output torque of the engine is monitored as a function the spark plug gasket temperature. The drop in output torque from a spark plug seat temperature of 200°C until it reaches 350°C is recorded, and the cooling air is then restored. This test procedure is considered non-damaging to the engine.
although it is stated in the test plan that a maximum of three tests should be conducted using the same engine. The claim of this procedure is that the decrease in output torque is representative of a lubricant's ability of preventing contact between the cylinder and bore, hence its ability of preventing adhesive welding and piston scuffing. This test procedure is typically conducted with a "qualified" reference oil to be used in comparison of the test reference oil.

Interestingly enough, there is no mention in this designation of any measurement of the time it takes for the engine to reach the maximum temperature of 350°C. The assumption that the decrease in output torque can represent the degree of surface contact and damage going on inside the engine is simply invalid. This test provides information that can be related only to engine friction. It is also evident that the engine is run into a temperature range that may never experience during normal or even excessively severe operation in the field. The behavior of any lubricant is strongly dictated by operating temperatures in any system. If this procedure drives the engine temperature to a level that it would rarely (or never) experience in the field, then it is questionable at best that this procedure could be used to predict the quality of a lubricant for commercial use in a particular two-stroke engine design.

Since 1962, the National Marine Manufacturers Association (NMMA) has developed and updated a testing procedure to evaluate two-cycle lubricants and additives to be used in water cooled outboard motor engines. This test
procedure is commonly identified in the literature as the BIA TC-W test procedure [11]. These letters represent the Boating Industry Association Two-Cycle Water Cooled engines. This is a three-phase procedure, with each phase dedicated to evaluating a different aspect of lubricant performance. Sequence 1 is an accelerated lubricity tightening test, which is similar to the ASTM standard test mentioned previously. The ASTM test procedure is actually a refined version of the BIA TC-W phase 1 procedure, with essentially the same criterion and claims except that the BIA procedure employs a much larger, 85 hp outboard motor. Sequence 2 of the BIA procedure is a long term general performance lubricity test used mainly to evaluate ring sticking and combustion chamber deposits. This phase of the BIA procedure is run for 21 total hours with a cycle of 1 hour at WOT, 5 minutes at idle at a volumetric fuel to lubricant ratio of 50:1. At the completion of this test, the engine is disassembled and given a qualitative evaluation of ring sticking and deposit formation. Callis [11] developed a visual rating system to rank piston ring sticking. This method has been named the Oronite Rating System. The circumference (in degrees) of ring sticking is measured and converted to a number rating between 0 and 10.

The third phase of this procedure employs a 98 hour test with a 24:1 ratio to look for signs of excessive deposit formation and pre-ignition. Since pre-ignition is not a major problem with two-stroke engines using modern fuels and lubricants, the third sequence of this procedure is rarely conducted.
The weaknesses of the BIA sequence 1 procedure are the same as those discussed above for the ASTM procedure. Interestingly enough, there are no measurements to evaluate any part wear or any exhaust gas filtering to study wear debris. The deposit forming tendencies of a lubricant are important to evaluate, although the best method to date appears to be a qualitative analysis much like that described in the BIA Sequence 2 procedure.

Dozens of other engine test procedures have been developed and utilized for particular engine applications over the years. The majority of them are slight variations of the BIA TC-W and ASTM procedure mentioned above, and due to the subtle differences it would be redundant to outline them here. The results obtained from any test to evaluate any property of the oil are always compared against some standard reference oil.

The frequent changes in engine designs and materials over the years make it very difficult to designate a standard engine which can be used for a number of years as a common comparison of test results.

It is clear that the development of a test procedure to evaluate two-stroke lubricants and additives is a very complicated task and no procedure can replace the need for field testing as the bottom line in “qualifying” a lubricant. An attempt was made to develop a test procedure for this study that accounts for some of the deficiencies observed in the literature. This procedure is outlined in
the following chapter and is aimed at correlating with field operation as much as reasonably possible.
2.5 TWO-CYCLE ENGINE EXHAUST EMISSIONS

As mentioned previously, the gaseous exhaust emissions from a two-stroke engine differ greatly from its four-stroke counterpart. Several methods to lower the hazardous exhaust emissions from two-stroke engines have been reported in the literature and a summary of the methods and results are presented in this section.

2.5.1 SMALL ENGINE EMISSIONS

As a world leader in setting emission standards for small engines, CARB funded laboratory emission measurements on a number of modern two and four-cycle engine designs. Common lawn and garden equipment engines were tested such as string trimmers and walk behind mowers (WBM's). This test program, which took place at Southwest Research Institute in 1991, was developed to be used to set reasonable emission standards for small, internal-combustion engines [69]. Exhaust constituents that were scrutinized in this study included total hydrocarbons (THC), reactive hydrocarbons (RHC), methane, CO, NOx, CO2, O2, aldehydes, and particulate matter. Nine different engine designs were tested, ranging from the smallest two-stroke engines to a 20 hp four-stroke design.

The SAE Recommended Practice J1088 [70] was used as the basis of the emission measurements. This is a multi-mode test procedure where emission
measurements are taken at each steady-state mode and then weighted to obtain overall exhaust emission values. Exhaust emission results that were obtained for the nine engines are presented in Figures 2.7 through 2.10.

As depicted in the figures, the two-cycle engines had total hydrocarbon emissions that were almost an order of magnitude higher than a comparable four-stroke engine, about 18 times the allowable CARB emission limits for 1994. Although current CARB standards for particulate matter presently pertain to diesel engines, the two-stroke gasoline engines output ten times the regulated amount. Particulate emission limits would undoubtedly be implemented on two-stroke gasoline engines, should the population of two-strokes continue to grow.

---

**Total Hydrocarbons, gm/hp-hr**

![Graph showing total hydrocarbons emissions for different engine models.](image)

**Figure 2.7:** J1088 Small Engine Hydrocarbon Emissions [69]
Figure 2.8: J1088 Small Engine Carbon Monoxide Emissions [69]

Figure 2.9: J1088 Small Engine Nitrogen Oxides Emissions [69]
Carbon monoxide emissions are generally comparable between the two and four-cycle engine designs. CO emissions depend mainly on the amount of oxygen in the charge and can be increased by increasing the air-fuel ratio. Clearly, the two-cycle engines produced impressively low amounts of oxides of nitrogen, well below the regulated CARB standards even for 1999. This may become an even greater factor as engine efficiency starts to play more of a critical role in engine design. More efficient engine designs often utilize higher compression ratios which results in higher peak cyclic temperatures.
2.5.2 EMISSION REDUCTION TECHNOLOGIES

Several emission reduction technologies have been employed in an effort to reduce hazardous exhaust emissions. Before discussing the most recent efforts, some fundamentals regarding combustion and emissions will be presented here.

Gasoline is approximated as octane, the eighth member of a family of paraffins whose general formula is \( C_xH_{2x+2} \). It is important to consider that the combustion of gasoline and air occurs only between air and gasoline in vapor form, but not liquid fuel and air. The stoichiometric combustion equation for octane is as follows:

\[
2*C_8H_{18} + 25*O_2 + (25*79/21)*N_2 = 16*CO_2 + 18*H_2O + (25*79/21)*N_2
\]

The stoichiometric air-fuel ratio for this balanced equation is 15.06. If the situation is considered where the mixture is run with a 20% reduction in fuel from the stoichiometric value, i.e., there is an excess of air during the combustion process, then the combustion equation changes to the following:

\[
2*C_8H_{18} + 1.2\{25*O_2 + (25*79/21)*N_2 \} \\
= 16*CO_2 + 18*H_2O + 1.2* (25*79/21)*N_2 + 5*O_2
\]
This results in an excess of oxygen that will be contained in the exhaust gas mixture. If the situation is considered where the air-fuel mixture is 20% rich of the stoichiometric value, the following ideal equation would arise, based on the assumption that the more active hydrogen would consume all of the available oxygen before the carbon can do so:

\[
2\text{C}_8\text{H}_{18} + 0.8\{25\text{O}_2 + (25\times79/21)\text{N}_2\} \\
= 10\text{CO} + 6\text{CO}_2 + 18\text{H}_2\text{O} + 0.8(25\times79/21)\text{N}_2
\]

The exhaust gas now contains a significant amount of carbon monoxide in the theoretical gas equation.

It would seem from these equations that it would be best to operate at the stoichiometric air-fuel ratio of 15.06 to minimize hazardous exhaust emissions. However, several “real world” conditions exist that alter these equations. Some of these effects are due to a phenomenon known as “dissociation.” This results in incomplete combustion and the formation of other (often undesirable) combustion products. For example, nitrogen can combine with oxygen, particularly at elevated combustion temperatures. At extremely lean air-fuel ratios, the combustion mixture may not burn due to the lack of fuel that reaches the spark plug zone resulting in a large increase in the amount of hydrocarbon and carbon monoxide levels in the exhaust gases. A slightly lean case is
preferable because a rich mixture guarantees excessive hydrocarbons and carbon monoxide in the exhaust mixture due to the lack of oxygen.

A number of techniques have been employed in an attempt to reduce exhaust emissions from two-stroke engines. Some approaches taken and results obtained are summarized in Table 2.6.

<table>
<thead>
<tr>
<th>Approaches Taken (With References)</th>
<th>Important Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction of (hydrocarbon) exhaust emissions through the use of an in-cylinder direct injection system. Single-cylinder, air-cooled two-stroke motorcycles were equipped with fuel injection systems and tested on a chassis dynamometer using the ECE-40 testing cycle. Skip injection control was also employed to reduce irregular combustion at light loads [73].</td>
<td>• A 25% reduction in HC emissions was obtained with a solid fuel injection system over a carburetor system. (70μm SMD atomization) • A 35% reduction in HC emission was obtained with an air assisted fuel injection system over a carburetor system. - (35μm SMD atomization) • Almost 50% of the HC emissions came during deceleration and idle periods of the test cycle. • Over 50% reduction in HC emissions were obtained by employing skip injection control at light loads</td>
</tr>
<tr>
<td>Improvement of HC exhaust emissions through the use of skip injection [74]</td>
<td>• HC emissions and fuel consumption were reduced at idle by 65% and 44% respectively. • Skip injection can be employed under lightly loaded conditions to improve irregular combustion, but improvements in the control system need to be developed to account for required output torque. (Con’t.)</td>
</tr>
</tbody>
</table>

LITERATURE REVIEW
<table>
<thead>
<tr>
<th>Study of exhaust emissions by retrofitting a 125c.c. two-stroke motorcycle with a variety of catalytic converter designs [75]. ECE 40 chassis dynamometer test was employed. Three different catalyst compositions were tested: platinum, palladium, and rhodium.</th>
<th>• Platinum was most effective with the HC oxidation process. • Palladium is more reactive for CO oxidation than platinum, but is more susceptible to poisoning by exhaust constituents. • Rhodium is reactive for the reduction of CO, HC and NOx, and is more poisoning resistant than platinum and palladium. Rhodium is very scarce in nature and is therefore very expensive. • There is a trade-off between the CO and HC oxidation process because both reactions compete for available oxygen in the exhaust. The conversion efficiencies of both of these reactions can be increased dramatically by feeding oxygen into the exhaust. • The reduction in exhaust smoke opacity is approximately equal to the HC conversion efficiency.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction of pollutant exhaust emissions of a two-stroke engine by using compressed air assisted, in-cylinder fuel injection [76]. Comparisons are made with a well developed four-stroke engine with approximately the same BMEP</td>
<td>• High HC emissions at light load can be attributed mainly to irregular combustion • High HC emissions at high speeds and high loads can be attributed mainly to scavenging losses from short scavenge time. • Reductions in total HC emissions of over 50% were obtained with air-assisted fuel injection, but levels still exceeded the 4-stroke design. • Total HC + NOx emissions were lower for the two-stroke design (without exhaust after-treatment) except at very light loads.</td>
</tr>
</tbody>
</table>

As indicated from the studies outlined in Table 2.6, several existing technologies have been found to be effective at reducing overall engine emission levels, but a combination two or more of them will be necessary for the

LITERATURE REVIEW
two-cycle engine to meet the more stringent emission standards. Advances in improved lubricants prove to play a vital role.

2.5.3 EXHAUST EMISSION MEASUREMENTS

Several reports have been written that recommend a correct procedure that should be employed when measuring two-stroke exhaust emissions [77-80]. Because of the differences in the scavenging process, the lubrication system, and the combustion pressures and temperatures between the two and four-stroke engine operation, the exhaust emissions are quite different.

The inherent burning of lubricating oils in a two-stroke engine causes excessive particulate emissions. As stated earlier, almost all of the particulate emissions can be attributed to burned and unburned lubricant, and it is usually recommended to measure these emissions gravimetrically, by filtering the exhaust gases. White et al. reported that heating the exhaust line in an attempt to vaporize the lubricant droplets and measure them as hydrocarbon emissions is difficult due to the high temperatures required in the exhaust line [69]. This approach also allows the hydrocarbon fuel in the exhaust to oxidize more completely, reducing the overall hydrocarbon content in the exhaust.

As discussed previously, the total hydrocarbon content in the exhaust gases from a simple two-stroke engine far exceed those from a four-stroke engine. Several authors [42,71,79] have emphasized that the type of
hydrocarbon emissions differ between the two engine designs. Hydrocarbons emitted from a four-stroke engine have been subjected to the high combustion temperatures and pressures of the combustion process. Most of the hydrocarbons emitted from a two-stroke engine are due to the weaknesses in the scavenging process, and may need to be considered more closely when considering the toxicity of the emissions.

Shore and deVries [79] used Fourier Transform Infra Red Spectroscopy (FTIR) and Chemical Ionization-Mass Spectrometry (CI-MS) to speciate hydrocarbon emissions from a four-stroke engine using several different exhaust gas catalysts. The results showed that different operating conditions with a variety of exhaust catalysts produced altered amounts of toxic hydrocarbon emissions. Current emission standards focus mainly on total hydrocarbon emissions, but as the global concern over air quality continues to escalate, it is very likely that concerns over more specific hazardous types of exhaust emissions will emerge, and warrant a closer look between the types of emissions from each of these engine designs.
CHAPTER 3

ENGINE BENCH TESTING

3.1 EQUIPMENT

As discussed in the previous chapter, many different test procedures and configurations have been employed to evaluate two-cycle engine lubricants. Some have been shown to have greater merit than others, but there currently exists no widely agreed upon test procedure to evaluate two-stroke engine lubricants and additives.

Because no simple test geometry (such as a four ball wear tester) can even begin to model the complicated wear mechanisms in an internal combustion engine, the use of such a procedure to was quickly ruled out for the evaluation of the monomer additives. Field tests are impractical for screening new lubricants due to the large amount of time and expense involved. It was therefore decided to conduct a series of engine bench tests under loaded test conditions.

A search was conducted for available two-stroke engines. Factors considered were quality, cost, availability (of both the engine unit and parts), ease of assembly and disassembly and similarity (with respect to materials and design) of the test engine with the general population of air cooled two-stroke engines.
3.1.1 THE TECUMSEH TVXL840 TWO-STROKE ENGINE

Tecumseh model TVXL840, vertical shaft, air-cooled, two-stroke engines were selected to evaluate the wear protection abilities of the monomers. Table 3.1 summarizes some of the TVXL840 engine specifications. The design and construction of this engine is representative of most of the smaller two-stroke engines in use today. Most of the smaller two-stroke motorcycles and motor-scooters in use utilize air-cooled engines. The TVXL840 is constructed of materials most commonly used in two-stroke engine designs; such as an aluminum piston, steel piston rings and a cast-iron cylinder bore. The pre-mixed lubrication system was necessary to allow controllable variations in the fuel/oil mixture. Five engines were purchased initially, with the idea that additional units could be acquired to continue more extensive testing should the initial tests with the monomers yield promising results.

TABLE 3.1: TVXL840 Engine Specifications

<table>
<thead>
<tr>
<th>Specification</th>
<th>Specification Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>BORE (cm)</td>
<td>6.1900 / 6.1925</td>
</tr>
<tr>
<td>STROKE (cm)</td>
<td>4.6025</td>
</tr>
<tr>
<td>DISPLACEMENT (cc)</td>
<td>138.634</td>
</tr>
<tr>
<td>COMPRESSION RATIO</td>
<td>6.8:1</td>
</tr>
<tr>
<td>PISTON DIAMETER (cm)</td>
<td>6.1773 / 6.1788</td>
</tr>
<tr>
<td>RECOMMENDED OIL</td>
<td>AIR COOLED, TWO-CYCLE S.A.E. 30 OR S.A.E. 40</td>
</tr>
<tr>
<td>FUEL / OIL MIX</td>
<td>50:1</td>
</tr>
<tr>
<td>POWER</td>
<td>3.73 kW</td>
</tr>
<tr>
<td>COOLING</td>
<td>AIR</td>
</tr>
</tbody>
</table>

ENGINE BENCH TESTING
3.1.2 TEST APPARATUS

Each engine was rigidly affixed to the test bench with its shaft extended through a hole in the bench top and aligned with the axis of a 10 Hp AC motor, which was bolted on an adjustable mount directly below the engine. A schematic diagram of the set-up is depicted in Fig. 3.1. A roller clutch was installed between the motor and the engine which would engage only when the engine speed exceeded the motor speed. This was installed to prevent the possibility of the motor driving (and damaging) the engine, should the engine stall, stop, or drop below the motor speed for any reason. A flywheel was also installed between the engine and the clutch to provide additional rotational inertia to the system. This was necessary to prevent the engine speed from dropping below the motor speed during its compression stroke, which would cause the clutch to disengage and re-engage every revolution.

A reluctance transducer was installed on the test bench to pick up a discontinuity in the flywheel and it was wired directly to a digital counter, which was used to monitor engine speed during each test. The thermocouple used was a high temperature, chromel-constantan (type E) thermocouple and its leads were soldered to copper leads and then coated with polyurethane to insulate the junction. This junction was held in a 0°C ice bath as a reference while temperature was being monitored. The copper leads were then connected to an amplifier to boost the voltage signal of the thermocouple. The leads were also
connected to an IBM PC which was set-up to sample thermocouple voltage. A program was written using LabView VI software which had a variable sample rate and sample period to collect and save the thermocouple voltage data. Included in the VI was an algorithm to calculate the mean and standard deviation for each sample period. The standard deviation could be set as the criteria for saving each data block. A sudden temperature increase, for example, would result in a large standard deviation over a sampling period, telling the computer to save that data block with the time after the start of the test in which it had occurred. For the purpose of this testing it was decided to set this value at zero, and save the mean temperature over each 4 second sample period. This program also converted thermocouple voltage to temperature and displayed a strip chart temperature record on the screen during the test.
Figure 3.1: Experimental Set-up
3.2 DEVELOPMENT OF A TEST PROCEDURE

Since the critical areas of engine lubrication are unknown for this engine design and are likely to vary from lubricant to lubricant and with test conditions, a procedure was developed to inspect each engine carefully and consistently before and after each test, and to insure each engine was cleaned and assembled in a repeatable manner.

3.2.1 NEW ENGINE DISASSEMBLY AND INSPECTION

Prior to conducting each test, every engine was disassembled, cleaned, inspected and re-assembled with some new parts. The carburetor assembly, blower housing, fuel tank, and solid state ignition unit were removed from the engine block and set aside during the engine cleaning. To remove factory oil films, the engine block, along with the piston, connecting rod, crankshaft, ball bearings and governor components were soaked for a minimum of 8 hours in a naphtha solvent bath.

The muffler was removed from the engine prior to cleaning and was not re-installed during the test. Instead, an aluminum block was manufactured that held a straight pipe which was used to direct the exhaust gases into the internal combustion engine lab's exhaust ventilation system. Each new engine had a roll pin pressed into the exhaust port side of the engine block by the manufacturer, that was used to draw heat from the engine and burn hydrocarbons in the muffler.
during normal operation of the engine. Since the muffler was removed during the testing, the roll pin served no purpose. It was therefore removed, and a thread was cut into the engine block where it had been to allow simple and reproducible mounting of a thermocouple. Due to the very thin wall in most of the engine block and the transfer ports that cover a great deal of the outer cylinder, this appeared to be the best location for measuring cylinder wall temperature. Air was blown through the ports in the engine block to remove the metal chips produced while cutting the thread and then the block was carefully flushed with naphtha.

New piston rings and connecting-rod needle bearings were cleaned in an ultrasonic bath for 15 minutes, while soaking in hexane. They were then dried and weighed using a Mettler balance with an accuracy to the nearest $10^{-4}$ g. The mass of each piston ring was measured individually, and the needle bearings were measured as a set. This was done in an effort to be able compare the weight loss of these components as a function of different lubricant formulations under a set of standard testing conditions.

3.2.2 ENGINE RE-ASSEMBLY

After cleaning the engine parts, each engine was carefully assembled according to the instructions outlined in the TVXL840 Engine Manual. The
assembly procedure of the engine is depicted in block diagram form in Figure 3.2.

Figure 3.2: Block Diagram of the Engine Assembly Procedure
A few minor modifications were made to the standard assembly procedure to enable certain measurements to be made. The thermocouple was screwed into the side of the engine block and the aluminum exhaust fixture was then bolted to the exhaust of the engine to replace the muffler.

The piston and cylinder were lightly coated with the particular lubricant mixture to be used in the fuel, prior to assembly. The new connecting rod needle bearings were packed in a wax strip for ease of assembly, but the wax was dissolved during the ultrasonic cleaning to enable measurement of the mass of the set. Therefore, it was decided ‘attach’ the needle bearings to the crankshaft by coating them first with Vaseline. After the connecting rod was slipped over the needle bearings and they were constrained by the connecting rod and the shoulder on the crankshaft, the bearing assembly was submerged in naphtha to remove the Vaseline. The assembly was allowed to dry and the ball bearings and governor parts were subsequently installed onto the crankshaft.

With the bearings seated in the proper grooves in the engine block, a few drops of lubricant were applied to each of the three bearings and the two seals. The shaft was rotated several times to allow uniform coating of the lubricant over the bearing rollers. The mating surfaces between the engine block and crank-case cover were lightly coated with a liquid gasket sealer and the crank-case cover was bolted to the engine, while placing a 1/4 inch rod through the
alignment hole in the cover to insure proper alignment between the cover and the block.

The flywheel, ignition unit, blower housing, fuel tank, and base plate were then assembled according to the Tecumseh TVXL840 Engine Manual instructions.

3.2.3 INSTALLATION OF THE ENGINE INTO THE TEST APPARATUS

As mentioned previously, a flywheel was included in the design of the test apparatus to add rotational inertial to the system and reduce fluctuations in speed. Since the engine crankshaft bearings were not designed to carry a large axial load, the apparatus was designed to allow vertical adjustment of the motor to remove most of the flywheel weight from the engine bearings and support it with the motor bearings.

The first step in installing the test engine was to slide the bushing onto the engine shaft as far as it would go, while leaving enough clearance between the bushing and engine mounting plate to install the bushing jack out bolts. The flexible couplings, flywheel, roller clutch, steel shaft, and jaw coupling remained as an assembly and were supported by the motor. The electric motor was then raised to its uppermost position, and the engine was placed on the test bench, sliding the bushing into the upper coupling. The two screws were installed into the upper bushing and tightened. The motor was then lowered by turning the
upper bolt on the adjustable motor mount. While doing this, the engine base plate bolts were placed through the mounting holes to properly align the base plate with the mounting holes. The engine was lowered until the base plate just reached the surface of the test bench, then the motor mounting bolts were tightened to secure the motor at this position. The engine mounting plate nuts were installed and tightened.

The exhaust duct was then installed over the exhaust pipe, and the thermocouple junction was placed in the ice bath. The thermocouple wires were then connected to the voltage amplifier.

Careful measurement of the lubricant and fuel to be used was necessary to insure an accurate mixture. The gasoline used was 87 octane, purchased from Campus Exxon and was stored in the fuel storage area behind Randolph Hall. Since the concentration of monomer in each of the fuel mixtures was very low (0.5% or less), small inaccuracies in the measurement of the amount of monomer would affect the overall concentration of the mixture much more significantly than small inaccuracies in the measurement of the fuel. It was therefore decided to measure the monomer by mass, instead of volume, to provide greater accuracy in the measurements. Monomer samples were measured into glass bottles and were poured into the appropriate volume of fuel to acquire the desired mixture. A weight measurement was conducted to acquire the desired amount of gasoline for each test. Due to the high viscosity of the
monomer additives, gasoline was poured into the bottle several times and back into the gas can to insure that the monomer was well rinsed from the bottle.

The fuel tank on the engine was then filled with the mixture and was labeled with the particular fuel/lubricant ratio being used. The capacity of the engine fuel tank is approximately 1.0 Liter.

3.2.4 EXPERIMENTAL TEST PROCEDURE

Based on several test procedures that had been reviewed and the test apparatus that was constructed, a procedure was developed to test each engine in a repeatable manner. It was desired to test the engine under mild to severe conditions, but not to operate the engine under conditions that excessively deviate from conditions it might experience in the field. A test period of 20 hours was planned to evaluate both engine wear and deposit formation. Table 3.2 summarizes some of the test conditions.

Table 3.2  Test Conditions for Engine Bench Testing.

<table>
<thead>
<tr>
<th>Engine:</th>
<th>Tecumseh TVXL840</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel System:</td>
<td>Pre-mixed</td>
</tr>
<tr>
<td>Gasoline:</td>
<td>87 Octane</td>
</tr>
<tr>
<td>Operating Speeds:</td>
<td>2000 RPM</td>
</tr>
<tr>
<td></td>
<td>2400 RPM</td>
</tr>
<tr>
<td></td>
<td>3000 RPM</td>
</tr>
<tr>
<td></td>
<td>Controlled at 1800 RPM</td>
</tr>
<tr>
<td></td>
<td>(Loaded)</td>
</tr>
<tr>
<td>Ambient Temperature:</td>
<td>26 to 30 °C</td>
</tr>
<tr>
<td>Lubricants:</td>
<td>Monoester, Diallyl Phthalate and Selected base oils.</td>
</tr>
</tbody>
</table>
Because new needle bearings and piston rings were installed during re-assembly, a mild run-in period was included into the test procedure. This run-in period was conducted with no-load, at three different throttle settings prior to applying a load to the motor. The engine was operated for ten minutes at each of the three throttle settings of 2000, 2400, and 3000 rpm. During the entire testing period, temperature data collected and saved to a file by the computer, and speed readings were recorded in a notebook. After this thirty minute period, the engine speed was dropped below 1800 rpm and the motor was turned on. Initial testing was conducted with the engine throttle wide open. Other throttle settings could be used prior to loading the engine.

The fuel tank on the engine had a capacity of approximately 1.0 L. With this amount of fuel, the engine would run approximately 90 minutes under unloaded conditions and approximately 40 minutes when controlling the speed at 1800 rpm at wide open throttle. Several shut-down periods would therefore be required to re-fuel the engine during the planned 20 hour test. The re-starting procedure was slightly shorter than the run-in procedure. If the engine was re-started before being allowed to cool down, it was operated at 3000 rpm for ten minutes before applying the load. If the shut-down period was long enough to allow the engine to reach the ambient temperature, it would be operated at 2000 and 3000 rpm for ten minutes at each throttle setting. The re-
start procedure would be conducted to allow the engine to warm up prior to the loaded test. Table 3.3 summarizes this test procedure.

**Table 3.3: Start-up Procedure During 20-Hour Test**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>First start-up after rebuild</td>
<td>10 minutes at 2000, 2400, 3000 RPM for a total of 30 minutes then apply load at wide-open throttle</td>
</tr>
<tr>
<td>Subsequent cold-start after re-fueling</td>
<td>10 minutes at 2000 and 3000 RPM for a total of 20 min. before loading</td>
</tr>
<tr>
<td>Warm re-start (&gt; 100 °C) after fueling</td>
<td>10 minutes at 3000 RPM before loading</td>
</tr>
</tbody>
</table>

This procedure would be followed until the 20 hour test duration was completed, or until the occurrence of engine failure:
3.2.5 POST-TEST DISASSEMBLY AND INSPECTION

After each test, the engine was completely disassembled, with the exception of the carburetor assembly, which was removed from the engine block as a single unit. A careful visual inspection was conducted on each engine part to look for evidence of deposits, surface damage, wear debris and any other anomalies. These observations were documented immediately after each test.

The piston, piston rings, and crankshaft surfaces were studied using a photomacroscope, and a series of photographs were taken to document the appearance of important surface features under magnification. Scanning electron microscope (SEM) photographs of the wear scars were taken to study the damaged surfaces of the engine parts. The SEM pictures offer excellent 3-D images of the surface at very high magnification. The photomacroscope is limited by its ability to focus on a flat plane (2-D) and it has a much lower maximum magnification (80X).

The weight loss of the piston rings and needle bearings could be determined by cleaning the parts in an ultrasonic bath of hexane for 30 minutes and subsequently using the Mettler balance to measure the mass of the parts.

Damaged and undamaged part specimens and surface films were collected and saved for further examination using Fourier Transform Infrared Microspectroscopy (FTIRM). This technique is used to determine the chemical structures of the surface films, in an attempt to characterize the reaction(s) that
occurred between the lubricant and the substrate surface and those that may have occurred on the surface of the substrate. This information is critical in understanding the mechanisms of wear and lubrication of the surfaces, particularly under boundary lubrication conditions.

FTIRM is based on the principle that all molecules possess their own unique natural modes of molecular vibration, depending on the mass and orientation of the atoms, and the strength of the molecular bonding between them. The adsorption of infrared radiation will occur at the modes of molecular vibration of the surface films, and an adsorption spectra can be produced. This adsorption spectra can therefore be studied to determine the chemical make-up of the surface films.

3.3 THE MONOMERS

The monomers used in this study were dialyl phthaiate and the C₃₆ dimer acid / ethylene glycol monoester. The chemical structures for each of these monomers are depicted in Fig. 3.3. The monoester is a condensation type monomer with two functional groups per molecule. The two C-O-H chain endings can react between molecules to form a C-O-C bond and produce a polymer with a condensate of H₂O. Condensation type monomers require two functional groups in order to polymerize. The monoester used in this study was synthesized by Dr. Roman Kempinski.
Diallyl phthalate is an addition type monomer also with two functional chain endings. Each of the two carbon-carbon double bonds can be broken and changed to form a single carbon-carbon bond between two (or more) molecules. Addition polymers require only one functional group for polymerization. The diallyl phthalate used in this study was purchased from Aldrich Chemical.

<table>
<thead>
<tr>
<th>1. C&lt;sub&gt;36&lt;/sub&gt;Dimer Acid/Ethylene Glycol Monoester</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;</td>
</tr>
<tr>
<td>(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;- CH&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>CH = CH-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;7&lt;/sub&gt; C-O-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;OH</td>
</tr>
<tr>
<td>C = O</td>
</tr>
<tr>
<td>OH</td>
</tr>
<tr>
<td>MOLECULAR WEIGHT</td>
</tr>
<tr>
<td>603.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2. Diallyl Phthalate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>MOLECULAR WEIGHT</td>
</tr>
<tr>
<td>246.3</td>
</tr>
</tbody>
</table>

*Figure 3.3: Chemical Structures of the Monomers Tested*

The monomers have almost exclusively been used in a hydrocarbon carrier fluid in the past. Because it is likely that most of the gasoline evaporates
in the crankcase, mixtures of the monomers will be tested in gasoline with the addition of small amounts of a base oil, or a slightly less volatile hydrocarbon (e.g., hexadecane) to act as a carrier after the gasoline has vaporized in the engine. As the gasoline vaporizes and leaves the monomer and carrier fluid behind, the carrier fluid will help provide a medium in which the anti-wear additive can flow to localized, highly stressed surface regions.
CHAPTER 4

EXPERIMENTAL RESULTS

Photographs, photomacrographs, Scanning Electron Microscope (SEM) photographs, along with engine cylinder wall temperature plots from each test are presented with a discussion of the observations made during engine testing and disassembly. A complete summary of the test conditions during each test and the current status of each engine is included in Appendix A.

4.1 OVERVIEW OF THE ENGINE ANALYSIS AND SOME TERMINOLOGY

Prior to conducting the engine bench tests, it was unknown where the critical areas of lubrication would exist in this particular engine design using the monomer anti-wear additives. It was speculated that the critical areas of lubrication would likely occur between the piston and cylinder of the engine, or possibly the crankshaft needle bearings, which are the troubled areas of lubrication most commonly reported in the literature for two-stroke engines. It was therefore believed that the wear protection of the monomers could be measured by weight loss of the piston rings and connecting rod needle bearings from each test.

During normal engine operation, the piston undergoes heavy loading against the cylinder wall during certain stages of its cycle. During the
compression stroke, the orientation of the connecting rod, in conjunction with the combustion chamber pressures that produce a force on the piston, thrusts the piston towards one side of the cylinder. This happens to be the side of the engine on which the carburetor is mounted on the TVX-840. After the piston reaches top-dead-center, the orientation of the connecting rod reverses direction (due to the rotation of the crankshaft) and the piston is then loaded against the side of the cylinder wall where the exhaust port is located. The pressures on the piston are obviously highest during the combustion process, producing the highest surface forces between the piston and cylinder during the power stroke. For the purpose of clarification, this side will be referred to as the major thrust side of the piston. The carburetor side, as mentioned previously will be referred to as the minor thrust side of the piston. If piston scuffing did occur due to the lack of protection from the lubricant, it would normally be expected that it would occur on the exhaust port side (or both of these sides), where the contact forces between the piston and cylinder are the greatest during sliding motion.

There exist two rectangular holes on opposite sides of the piston, which allow the fresh fuel and air charge to enter the combustion chamber when these holes become aligned with the transfer port holes of the cylinder, near bottom dead center. These holes are oriented 90° from the minor and major thrust sides of the engine. As a result, one transfer port hole faces skywards, and one towards the ground when the piston is mounted in the engine.
After conducting a few tests, it became evident that the piston and cylinder wall would be the critical regions of engine lubrication. Most of the tests conducted resulted in piston scuffing, which was severe enough to cause engine seizure. These seizures occurred in less than 1 hour, well before the planned testing period of 20 hours. Because of this short duration of engine operation, it was decided that an analysis of the films and deposits on the engine parts to study the chemistry of the surface films would be much more useful than the amount of material lost due to wear during the short durations of engine operation. In addition, the severe piston scuffing produced heavy aluminum deposits on the piston rings which would result in a measured weight gain, instead of loss in the wear measurement.

4.2 PRE-TEST INSPECTION OF THE ENGINE PARTS

A few common features were found on some of the parts for each disassembled new engine. First, the surface finish of the piston was quite rough. Around the top and bottom edges of the piston, however, there were intermittent regions where the surface was very smooth and shiny. These regions appeared to be equally spaced around the entire circumference of the piston along the top and bottom edges. The top of the piston and the combustion chamber appeared to be very clean. No evidence of combustion
products were found in the combustion chamber that may have resulted from factory start-up.

To learn more about these features, contact was made with the manufacturer [81]. The aluminum engine block is cast around the cast-iron cylinder sleeve. During the cooling process, the iron sleeve warps slightly, causing the intermittent contact regions which occur between the piston and cylinder. After assembly, the engines are run for approximately 1 minute with a very pure aviation fuel at no load, and a fuel:oil ratio of 24:1 at the factory. This explains the light signs of run-in on the piston and the intermittent smooth surface regions on the piston. The reason for the high surface roughness of the piston is to retain lubricating oil in the piston and cylinder region. Figure 4.1 is a photograph of a new replacement piston and a piston that was removed from a new engine. Slight signs of run-in can be seen on the piston on the right from the brief factory start-up, particularly near the upper and lower edges of the piston.

EXPERIMENTAL RESULTS
Figure 4.1: Photograph of a Replacement Piston (left) and One Removed From a New Engine (right) Which Shows Signs of Mild Run-in.

A photomacrograph showing the edge of a run-in portion of a piston from a new engine is presented in Fig. 4.2. This photomacrograph exhibits the roughness of the machined surface and the degree of plastic deformation which portions of surface undergo during the run-in period. Note that all photomacrographs were taken such that the circumference of the piston appears
vertically in each of the figures, with the top of the piston towards the right hand side of the photomacrograph.

Figure 4.2: Photomacrograph of the Edge of a Plastically Deformed Portion of a Piston Removed From a New Engine (31.25X Magnification).

4.3 DIALLYL PHTHALATE TEST RESULTS

As discussed in Section 3.3, diallyl phthalate is an addition type monomer with two active chain endings that can attach to other molecules and polymerize. It was selected as a promising candidate for two-stroke engine lubrication due to its high molecular weight, relatively high viscosity, and favorable wear protection
performance in several tribological tests compared with other anti-wear additives and other monomers.

4.3.1 Diallyl Phthalate: 0.5% Concentration

The first engine bench test utilized a concentration of 0.5% diallyl phthalate by mass, in the fuel. The run-in procedure, as discussed in Chapter 3, was conducted at the three throttle settings of 2000, 2400, and 3000 rpm. After approximately 6 minutes of engine operation at 3000 rpm (26 minutes total), severe piston scuffing occurred, causing engine seizure. The temperature history of this test is shown in Fig. 4.3.

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**Figure 4.3:** Engine Cylinder Wall Temperature History While Using 0.5% Diallyl Phthalate as a Lubricant.
As shown in Fig. 4.3, the engine temperature stabilized at about 130 °C and 150 °C while running at 2000 and 2400 rpm, respectively. After increasing the engine speed to 3000 rpm, the temperature never stabilized, and seizure occurred at a cylinder wall temperature of about 210 °C.

Disassembly of the engine revealed that severe piston scuffing had occurred on the major thrust (exhaust port) and the minor thrust (carburetor side) of the piston. The wear scar on the carburetor side of the piston measured approximately 10 mm in width, and it covered the entire length of the piston, with the exception of about 5 mm at the lower edge of the piston skirt, where the wear scar tapered off. A photograph showing the top and the edge of major thrust side of the piston is presented in Fig. 4.4. This wear scar was about twice as wide as the wear scar on the minor thrust side of the engine, but most of the wear on this side of the piston occurred on the upper half of the piston. Very minor signs of run-in were noted on the remaining surface of the piston. The unscuffed surface was coated with very uneven gold-yellow and black deposits. These deposits were very thin and could be removed by lightly touching the surface.

EXPERIMENTAL RESULTS
Figure 4.4: Photograph of the Top, Major Thrust Side of the Piston Using 0.5% Diallyl Phthalate as a Lubricant

The combustion chamber appeared relatively clean, with no excessive deposits found on the spark plug, transfer ports, or the exhaust port holes. There were two narrow deposits of aluminum on the inside of the cylinder, 180 degrees apart, which corresponded with the wear scars on the piston. These deposits appeared much like a thin coating of dull silver paint and did not consist of a large number of visible wear particles. Figure 4.5 is a photograph of the wear scar on the major thrust side of the cylinder. The three circular holes near

EXPERIMENTAL RESULTS
the center of the photograph are the exhaust port holes. The upper portion of
the photograph shows the combustion chamber region of the engine.

![Image](image.png)

**Figure 4.5:** Photograph of the Major Thrust Wear Scar of the Cylinder Using 0.5% Diallyl Phthalate

The top of the piston was coated with a very thin, dull black material and
is depicted in Fig. 4.4. This material was easily scraped off with a razor blade
and it had a waxy texture much like a crayon. Sample surface coatings were
scraped from the piston top and sides (separately) and were collected and saved
for further chemical analysis. The piston was later cut into small specimens for
SEM surface analysis.

EXPERIMENTAL RESULTS
Aluminum wear debris from the piston had accumulated in the piston ring grooves and had trapped both piston rings in the grooves at both the wear scars. When the piston rings were later removed from the ring grooves, there were very thin, wet deposits on the rings that had not evaporated several weeks after the test. There was no evidence to indicate that piston ring sticking had occurred to suggest that excessive deposits were the cause of piston scuffing.

The crankshaft and connecting rod bearings showed no signs of premature wear or surface damage. The connecting rod needle bearings were collected and saved for future chemical analysis.

Photomacroscopic observations revealed very dark colored regions in the wear scars. The scuffed surfaces were mixed with welded and shiny abraded surface regions. Figure 4.6 is a photomacrograph of the wear scar showing very dark deposits which were typical over most of the wear scar regions.
Figure 4.6: Photomacrograph of a Piston Wear Scar Using 0.5% Diallyl Phthalate as a Lubricant (31.25X Magnification)
Figure 4.7 is a filtered photomacrograph of the scuffed piston region using 0.5% diallyl phthalate. Note the colored variations of the wear scar.

Figure 4.7: Photomacrograph of a Piston Wear Scar using 0.5% Diallyl Phthalate as a Lubricant (31.25X Magnification)

4.4 C36 DIMER ACID/ETHYLENE GLYCOL MONOESTER

This monomer was selected as a candidate for two-stroke lubrication due to its high molecular weight, high viscosity, and outstanding wear characteristics in a wide variety of similar tribological systems at very low concentrations in the past.
4.4.1 MONOESTER: 0.5% CONCENTRATION

The first engine bench test using the monoester was conducted with a concentration of 0.5% monoester, by mass, in the fuel. The run-in cycle was conducted for 10 minutes at 2000, 2400, and 3000 rpm and the engine cylinder temperature appeared to stabilize at approximately 136, 170 and 210 °C, respectively. The temperature history of this experiment is shown in Fig. 4.8. After the 30 minute run-in cycle was completed, the engine speed was reduced below 1800 rpm and the electric motor was turned on to apply a load to the engine. The engine throttle was then set wide open. The decrease in temperature around 30 minutes in Fig. 4.8 corresponds to the period when the engine speed was reduced to apply the load to the engine.

The engine ran for approximately 4 minutes after the load was applied and the cylinder temperature increased steadily during this period. When the cylinder temperature reached approximately 270 °C, engine seizure occurred. The total running time was approximately 35 minutes.
Disassembly of the engine revealed that the piston had undergone scuffing which was severe enough to cause engine seizure. About 40 percent of the piston circumference had suffered severe scuffing. Interestingly, the majority of severe damage had occurred on the upper transfer port side of the piston. Some surface scuffing was observed on the major thrust side of the piston, but there was no apparent damage centered on the minor thrust side of the piston and the lower transfer port side of the piston appeared to have undergone only minor amounts of normal run-in. A photograph of the damaged portion of the
piston is shown in Fig. 4.9. The most severe wear scars were close to the piston rings; they tapered off and became much narrower towards the piston skirt.

![Photograph of the Scuffed Piston Using 0.5% Monoester as a Lubricant](image)

**Figure 4.9:** Photograph of the Scuffed Piston Using 0.5% Monoester as a Lubricant

The lower piston ring was completely packed into the ring groove, and the upper ring was stuck in its groove about half the circumference of the piston. The piston and piston parts were completely coated with a very viscous and tacky substance. The connecting rod needle bearings were well coated with a dark brown, tacky substance and a sample of this surface film was collected from the crankshaft where the needle bearings were removed. The ball bearings
were well coated with the same sticky substance. A viscous resistance was noted when rotating the crankshaft bearings. There were no apparent signs of damage or excessive wear to any of the bearing components.

The cylinder bore was also well coated with a sticky substance. The side of the bore where piston scuffing had occurred was loaded with very fine aluminum wear debris. Figure 4.10 is a photograph of the aluminum wear debris on the cylinder wall. Note also the dark deposits in the combustion chamber region. The aluminum deposits on the side of the cylinder consisted of very thin aluminum skid marks and aluminum particles that appeared to have welded to the cylinder and broke free from the piston. The wear track on the piston consisted mainly of very fine, parallel grooves that appeared to have occurred from abrasive interaction with the aluminum particles that broke free from the piston.
Figure 4.10: Photograph of the Wear Scar in the Engine Cylinder Using 0.5% Monoester as a Lubricant.

A photomacrograph of the wear scar is shown in Fig. 4.11. Dark, welded looking deposits sat above the very shiny wear scars on the scar surface. The undamaged surfaces of the piston were well coated with a tacky substance.
The combustion chamber was coated with a dry, thick, dark-brown substance. This material was very similar in color to the deposits found on the piston, but the deposits in the combustion chamber were not tacky. The top of the piston was heavily covered with a shiny dark coating which was removed easily with a razor blade. This coating was removed in several large pieces that were very flexible. The exhaust and transfer ports showed no signs of excessive deposits that would cause plugging, but the exterior walls of the engine exhaust were well coated with a dry, dark brown film.
The lower piston ring was very difficult to remove from the piston. It was clearly stuck into the ring groove of the piston. After removing the rings, they were analyzed under the photomacroscope. Heavy deposits were noted on both rings. The lower ring appeared to be covered with slightly thicker deposits, and the underside of the rings appeared to have slightly more build-up than the top of the rings. On certain areas of the piston rings, there were visible fibers on the surface of the rings. Figure 4.12 is a photomacrograph which depicts some of the strands that were found protruding from the lower piston ring. These fibers were extremely thin and very difficult to collect due to their small size. Some of these fibers appeared to be white in color, and they protruded mainly from the outer surface of the ring which comes into contact with the cylinder. Other fibers appeared darker and thicker. These fibers were found on several areas of the piston rings, and some of them had a square cross-section which was very clear with several which had been twisted axially. It is not known if there are two (or more) different types of fibers. They could be seen only under magnification.
4.4.2 0.5% MONOESTER WITH 0.5% SEBACATE BASE OIL

Prior to this two-stroke engine testing, the monomers had always been used as an additive in some sort of carrier fluid. The gasoline would act as a carrier for the monomer additives only until it vaporized while leaving the carburetor, entering the crankcase, combustion chamber and leaving the monomer behind after vaporizing off the warm part surfaces. The low concentration of the monomer would also limit the available amount of lubricant which would be present to provide a possible hydrodynamic oil film during EXPERIMENTAL RESULTS
certain stages of engine operation. It was therefore decided to determine the
effect of using a small amount of base oil as a carrier fluid for the monomer. A
synthetic base oil, bis (2-ethylhexyl) sebacate was selected for this purpose.

The concentration of the monomer was kept at 0.5% as in the prior test,
this time with an additional 0.5% mass concentration of sebacate. The
temperature history of this test is presented in Fig. 4.13. The cylinder wall
temperatures at 2000, 2400 and 3000 rpm leveled off at 134, 156, and 212 °C,
respectively. After loading the engine, seizure occurred in just under 4 minutes
at a temperature of 248 °C. The two most notable differences regarding the
operating temperatures with and without sebacate are the differences at 2400
rpm and at seizure. The measured temperature was about 15 °C cooler at 2400
rpm with the addition of 0.5% sebacate. In fact, the temperature actually began
to drop after about 7 minutes at this speed, an occurrence that had not been
observed before. The engine with the addition of 0.5% sebacate underwent
seizure at a much lower temperature (about 20 °C less), but it was also loaded
at a lower temperature. The overall run time (of 35 minutes) was about the same
for both tests.
Figure 4.13: Engine Temperature History Using 0.5% Monoester
Plus 0.5% Sebacate

The engine parts were very wet and well coated with a tacky substance. The appearance of the interior engine parts was much wetter than with the monoester alone, most likely due to the presence of the base oil. Figure 4.14 is a photomacrograph of the thick deposits found covering the piston surface. The piston was scuffed on two main areas, near the upper transfer port and on the major thrust side. Each scuffed area was about 25 mm wide on the piston. Both piston rings were completely stuck in the ring grooves.
Because small fibers had been found on the piston rings from the first monoester test, special care was taken to make sure the sides of the piston were untouched until they were inspected under the photomacroscope. The piston and rings were inspected just a few minutes after disassembling the engine. There were several thin, white fibers protruding from the outer edges of the piston rings. One of these fibers was approximately 15 mm long and it was collected and saved. Most of these strands were very thin and short and were difficult to collect. After removing the rings from the piston, several darker,
thicker fibers were found, many on the interior side of the piston rings. The majority of these strands were found on the lower piston ring.

The piston itself appeared to have been well coated with what appeared to be a sebacate and monoester mixture. The surface of the piston was covered with a wet, dark liquid. The heavy build-up of liquid is shown in a photomacrograph in Fig. 4.15. Thin, undamaged surfaces that existed between the severe wear scars were well coated with lubricant. The wear scars themselves appeared to be covered with very dark deposits, probably from the lubricant. The surface coatings were not as tacky as they had appeared with the monomer alone, but the surface film was very viscous. The needle bearings were tacky, and a viscous resistance was noted when rotating each of the ball bearings, but not as viscous as those noted with the monoester alone.
Figure 4.15: Photomacrograph of the Liquid Build-up on the Outer Edge of the Upper Piston Ring Using 0.5% Sebacate and 0.5% Monoester as a Lubricant (31.25X Magnification)

The wear scars on the piston were covered with many patches where adhesive welding may have occurred. There were only a few notable wear particles that had broke free from the surface of the piston that ended up in the transfer port holes of the cylinder. A photograph showing the upper transfer port side of the cylinder is shown in Fig. 4.16. There was much less evidence of abrasive wear compared with the piston using the monoester alone.
Figure 4.16: Photograph of the Engine Cylinder After Piston Scuffing Had Occurred Using 0.5% Sebacate and 0.5% Monoester as a Lubricant.

The combustion chamber and top of the piston were covered with a reasonably dry, thick, glossy, dark brown film, very similar to that found with the monoester alone. Sample surface coatings were collected from the piston for further chemical analysis. The well run-in portions of the piston that remained undamaged from the test were very bright and colorful. Figure 4.17 is a photomacrograph of a run-in region near the bottom edge of the piston away from the wear scars.

EXPERIMENTAL RESULTS
Figure 4.17: Photomacrograph of the Lower Edge of the Piston After Using 0.5% Monoester and 0.5% Sebacate as a Lubricant (31.25X Magnification).

4.4.3 0.1% MONOESTER WITH 0.9% SEBACATE

Both prior tests which employed a concentration of 0.5% monoester had resulted in notable piston ring sticking. It was unknown whether the rings had been trapped in the ring grooves prior to the transpiration of piston scuffing, or as a result of this event. It was known that very heavy deposits of a thick, dark substance was found in the ring grooves, and the rings were difficult to remove from the grooves around the entire circumference of the piston, not only at the wear scars. Because of the heavy deposits found in the ring grooves, and

EXPERIMENTAL RESULTS
combustion chamber, it was decided to conduct a test with a lower concentration of the monomer and to begin with less severe operating conditions for a longer duration of time to look for evidence of excessive deposit formation and ring sticking prior to engine seizure.

4.4.3.1 90 MINUTE RUN-IN AT 2400 RPM

With a concentration of 0.1% monoester and 0.9% sebacate, the engine was warmed up at idle for 10 minutes and then set at 2400 rpm for the duration of the test. Approximately 1 liter of fuel was consumed during this period of time and the engine ran for approximately 90 minutes. As shown in Fig. 4.18, the engine temperature leveled off at about 123 °C while idling at 2000 rpm and it reached 148 °C shortly after running at 2400 rpm. The temperature slowly, but steadily decreased over the remainder of the test, with a final running temperature at 142 °C. Although the speed of the engine fluctuated between 2360 and 2400 rpm continuously throughout the test, there appeared to be no change in the average speed over the duration of the test.
Figure 4.18 Engine Cylinder Wall Temperature Using 0.1% Monoester and 0.9% Sebacate at a Speed of 2400 rpm After Warm-up.

The engine was disassembled and inspected after this 90 minute test period. Both piston rings were completely free of the ring grooves, and only minor deposits had accumulated on the top of the piston and in the combustion chamber. Photomacroscope pictures were taken of the piston and ring surfaces. The piston appeared to be well lubricated, and signs of light run-in had occurred on the piston surface. The smooth, shiny, run-in patches on the piston surface had a very colorful films on them, which appeared much like those observed with a thin film of oil floating on water. The entire piston was very wet and appeared to be well lubricated. The surface coating on the piston was very dark and appeared to be about as viscous as the sebacate. A very thin dark deposit was
found at both ends of the needle bearings, similar in color to the much thicker film found with higher concentrations of the monoester.

Wet samples were collected from the sides of the piston and the crankshaft. A thin film was easily scraped from the top of the piston, which had a texture and color very similar to those found with the previous two monomer tests. The piston was cleaned ultrasonically in naphtha and the remaining engine parts were soaked in a naphtha solvent bath. After cleaning, the engine was re-assembled with new piston rings and needle bearings. A thin film of sebacate and monoester was applied to the lubricated engine parts during assembly.
4.4.3.2 90 MINUTE RUN-IN AT 3000 RPM

After obtaining promising results at 2400 rpm for 90 minutes, it was decided to study the performance of the same mixture at a higher speed and higher temperature. The next test was conducted for 10 minutes at 2000 and 2400 rpm, and the duration of the test at 3000 rpm. The temperature plot for this 85 minute test period is presented in Fig. 4.19.

![Temperature plot](image)

0.1% Monoester, 0.9% Sebacate

**Figure 4.19:** Temperature history Using 0.1% Monoester and 0.9% Sebacate as a Lubricant for 85 Minutes.

As shown in the figure, the cylinder temperature leveled off at about 120 °C and 142 °C at 2000 and 2400 rpm, respectively. At 3000 rpm the engine temperature slowly reached 192 °C then dropped to around 182 °C, where it...
remained for almost 20 minutes. At this time, around 50 minutes into the test, the cylinder temperature increased about 10 degrees, then slowly dropped back down to about 182 °C for the duration of the 85 minute test. No notable change in speed was observed during this time.

Immediately after this test, the engine was disassembled and inspected. A visual inspection of the piston showed no notable additional run-in compared with the surface features observed after the first test was conducted with this engine. The deposits on the top of the piston were lighter than with the first 90 minute run-in, despite the higher operating temperatures. The sides of the piston appeared very wet, along with the other lubricated areas of the engine. The wet film on the piston was identical in appearance with that found with the previous test. Photomacroscopic pictures of the piston were taken and looked consistent with the surface features observed after the previous test.

Once again, the piston rings were free from the ring grooves. The ring grooves were free from notable deposits. The outer edges of the piston rings were covered with a bead of clear looking liquid. No thin fibers were noted on the piston rings as with the previous tests, but the bead of liquid on the edge of the piston ring made the edge of the piston rings more difficult to inspect under magnification.
4.4.3.3 LOADED TEST AT THE MINIMUM THROTTLE SETTING

Once again, the engine parts were cleaned and the engine was re-assembled with new piston rings and needle bearings. Since this lubricant formulation provided adequate wear protection for three hours of testing under unloaded conditions, its performance under slightly loaded conditions was explored. The engine was run through the 30 minute run-in cycle and then loaded with the motor at the lowest throttle setting. The temperature history of this test period is presented in Fig. 4.20.

![Graph showing temperature history](image)

Figure 4.20: Temperature History for the Loaded Test using 0.1% Monoester and 0.9% Sebacate
At each of the first three operating speeds, the cylinder wall temperature reached 124, 142, and 184 °C; quite consistent with the temperatures of 120, 142 and 182 °C observed in the previous test. After loading the engine at the lowest throttle setting, the engine temperature increased at a relatively slow rate in comparison with previous tests conducted under load at full throttle. During this time, the engine went through periods where it produced a sound much like that of a centrifugal pump when air is fed into the suction line. During the first few minutes of engine loading, this sound would detected for a few seconds every minute, and then the engine would sound normal. As the test continued, this noise occurred more frequently and lasted for longer periods of time. After about 11 minutes of loaded operation, it became evident that this condition was getting worse and the power to the electric motor was discontinued. Seconds later, the engine seized.

Once again, piston scuffing had occurred. Three separate wear scars were observed on the piston. The most notable wear scar was located on the exhaust port side of the piston. This scar measured 12 mm in width and started at the upper edge of the piston. It continued about midway down the piston where it tapered to 2 mm wide at the piston skirt. The other two wear scars occurred about 120 degrees from previously mentioned wear scar and each other. These wear scars were much narrower, but still quite severe. Figure 4.21 is a photomacrograph of one of the piston wear scars. The overall condition of
the piston was better than that found in the previous failures, most likely due to a lower friction force required to stall the engine at the lower throttle setting.

Figure 4.21: Photomacrograph of a Piston Wear Scar After Using 0.9% Sebacate and 0.1% Monoester as a Lubricant (31.25X Magnification)

The piston rings were relatively free from the ring grooves, and no signs of excessive build-up was found on the rings or in the ring grooves. The cylinder and combustion chamber appeared relatively free from deposits, compared with tests with higher ratios of the monoester. A photograph of the cylinder is presented in Fig. 4.22.

EXPERIMENTAL RESULTS
4.5 CONVENTIONAL LUBRICANT REFERENCE TEST

One engine was dedicated to evaluate the performance of Tecumseh's recommended lubricant. The recommended fuel:oil ratio for the conventional lubricant is 50:1 and was the ratio used for this testing. This engine was to be used to compare the operating temperatures, wear rates, and deposit formation of a 'qualified' lubricant with the experimental lubricants being tested.

A 20 hour test under loaded operating conditions was planned to be used as the reference test. Before disassembling this engine, it was installed into the
test apparatus and run under loaded conditions under wide open throttle for a total of about 85 minutes to evaluate the operation of the test equipment; (this test took place prior to any other engine testing). This engine was then disassembled and cleaned according to the standard procedure. After installing new piston rings and needle bearings, the engine was re-assembled with a thermocouple.

Each test period lasted approximately 40 minutes before the engine required re-fueling. The temperature history for this testing is shown in Fig. 4.23. As shown in the figure, the loaded operating temperature was remarkably consistent at approximately 238 °C. The sixth time the engine was placed under load, the cylinder temperature jumped form 232 °C to 256 °C in just 8 seconds and engine seizure occurred. The test time lasted about 260 minutes, 345 minutes if the tests prior to engine disassembly were included. The specific operating conditions that correspond with this temperature trace are included in Appendix A.

The appearance of the sides of the piston and the wear scar was much cleaner than that observed with the monoester and sebacate lubricant mixtures.
Two Stroke Lubricant 2.0% Conc.

![Temperature History Graph](image)

**Figure 4.23:** Temperature History for the Test Conducted Using 2.0% of the Conventional, Two-Cycle Engine Oil

One large wear scar had developed on the exhaust port side of the piston. This scar was about 30 mm wide which extended from the top of the piston and tapered to a much narrower scar near the piston skirt. A photograph of the scuffed side of the piston is presented in Fig. 4.24. Approximately two-thirds of the piston surface was well broken in. These areas had an extremely smooth, shiny, polished looking appearance. The undamaged side of the piston is shown in Fig. 4.25. The piston appeared to be very wet, and well lubricated and appeared much cleaner than the pistons that were removed from the monomer lubricant tests. The combustion chamber and piston top were both

**EXPERIMENTAL RESULTS**
coated with relatively thick, black films which adhered well to the surfaces. The crankcase parts appeared very wet, but no dark deposits were found on any of the bearings or crankshaft assembly.

**Figure 4.24:** Photograph of a Scuffed Piston Obtained Using Conventional Lubricant at a Concentration of 2.0%
Figure 4.25: Photograph of the Undamaged but Well Run-in Side of the Piston After 345 Minutes of Operation with Conventional Lubricant at a Concentration of 2.0%

Photomacrographs of the wear scar and of the run-in regions are shown in Figures 4.26 and 4.27 respectively. A remarkable amount of plastic deformation had occurred on a large portion of the piston surface as shown in Fig 4.27.
Figure 4.26: Photomacrograph of the Piston Wear Scar Using Conventional, Two-Stroke Lubricant (31.25X Magnification)
Figure 4.27: Photomacrograph of a well run-in surface of the Piston After Operation with Conventional Lubricant (31.25X magnification)

4.6 SCANNING ELECTRON MICROSCOPE (SEM) PHOTOGRAPHS

Specimens from the 0.5% diallyl phthalate and 0.5% monoester test pistons were carefully cut on a band saw at a slow speed to minimize the build-up of heat through the specimens. Damaged and undamaged piston specimens were collected for analysis. Pressurized air was blown over the specimens, to remove aluminum chips produced while cutting the pistons. Because of the tacky nature of the monoester deposits, it was more difficult to remove the
aluminum chips and any that could not be blown away with air were not
touched. A Joel JSM-35C Scanning Electron Microscope (which is located at
the Virginia Tech. Veterinary School) was used to observe the surface features
of the piston specimens.

Figure 4.28 is an SEM photograph of an undamaged surface of the piston
from the diallyl phthalate test. The bright shiny particle on the lower left corner
of the photograph is likely to be an aluminum chip produced while cutting the
specimen. SEM photographs of different regions of the scuffed sections are
shown in Figures 4.29-4.31. Several strands were observed on the scuffed
surface and many appeared to be attached at one end, like those shown in
Figures 4.29 and 4.30. Figure 4.31 is an SEM photograph of what appears to be
a flake of some sort of deposit on the wear scar. Several of each of these types
of features were found on the wear scars.
Figure 4.28: SEM Photograph of an Undamaged Portion of the Piston Surface After 27 Min. of Operation With 0.5% Diallyl Phthalate (430X Magnification)
Figure 4.29: SEM Photograph of a Scuffed Region of the Piston After 27 Minutes of Operation with 0.5% Diallyl Phthalate (120X Magnification)
Figure 4.30: SEM Photograph of the Scuffed Region of the Piston Surface after 27 Minutes of Operation With 0.5% Diallyl Phthalate (430X Magnification)
Figure 4.31: SEM Photograph of the Scuffed Region of the Piston Surface after 27 Minutes of Operation With 0.5% Diallyl Phthalate (430X Magnification)
The SEM photographs shown in Figures 4.32 and 4.33 are very smooth, well run-in portions of the piston surface from the test using 0.5% diallyl phthalate.

Figure 4.32: SEM Photograph of a Very Smooth Region of the Piston Surface After Operation for 27 Minutes using 0.5% Diallyl Phthalate (430X Magnification)
Figure 4.33: SEM Photograph of a Well Run-in Portion of the Piston Surface After 27 Minutes of Operation Using 0.5% Diallyl Phthalate. (1000X Magnification)

In comparison with the piston parts from the testing conducted with the monoester, the surface films on the diallyl phthalate piston parts were very light. Figure 4.34 is an SEM photograph of the lower surface of the lower piston ring. To the left of the photograph is the outer edge of the piston ring. Although the
piston ring appeared to be relatively deposit free, a large quantity of unusual deposits were found in the piston ring grooves, as shown in Figure 4.35.

![SEM Photograph of the Edge of the Lower Piston Ring after 27 Minutes of Operation Using 0.5% Diallyl Phthalate. (120X Magnification)](image)

**Figure 4.34:** SEM Photograph of the Edge of the Lower Piston Ring after 27 Minutes of Operation Using 0.5% Diallyl Phthalate. (120X Magnification)
Figure 4.35: SEM Photograph of the Piston Ring Groove After 27 Minutes of Operation With 0.5% Diallyl Phthalate (430X Magnification)
The monoester piston parts appeared to have surface films that were quite different from those with diallyl phthalate. Figure 4.36 is an SEM photograph of deposits found on the undamaged portion of the piston surface. Similar deposits covered much of the undamaged regions, however the thickness of these deposits varied over the surface.

**Figure 4.36:** SEM Photograph of Typical Deposits Found on the Piston Surface After 35 Minutes of Operation Using 0.5% Monoester (440X Magnification)
The damaged regions of the piston surface consisted of welded regions that were separated by smoother paths which appeared to have been abrasively damaged by wear particles. Figure 4.37 is an SEM photograph of the edge of a scuffed region of the piston. The right side of the photograph shows an undamaged portion of the specimen.

Figure 4.37: SEM Photograph of the Edge of a Damaged Portion of the Piston Using 0.5% Monoester as a Lubricant (120X Magnification)
A SEM photograph of the center of a scuffed region on the piston surface is shown in Fig. 4.38. This photograph shows typical surface features observed inside the damaged regions of the piston.

Figure 4.38: SEM Photograph of Typical Surface Features Observed Near the Center of the Wear Scars of the Piston from the 0.5% Monoester Test (120X Magnification)
Figures 4.39 and 4.40 are SEM photographs of the scuffed piston surface at higher magnification than shown in the previous figures.

Figure 4.39: SEM Photograph of the Damaged Piston Surface Using 0.5% Monoester as a Lubricant (440X Magnification)
Figure 4.40: SEM Photograph of the Damaged Piston Surface Using 0.5% Monoester as a Lubricant (430X Magnification)
Thin fibers which were observed on the piston rings using the photomacroscop were confirmed with SEM observations. Figure 4.41 is an SEM photograph of strands of material found protruding from the outer edge of the lower piston ring. This particular specimen was at the end of a long bead of material that appeared to be well attached to the surface of the piston ring.

Figure 4.41: SEM Photograph of the Outer Edge of the Lower Piston Ring From the Engine Test Using 0.5% Monoester. (440X Magnification)
The surfaces of the piston rings were covered with very uneven deposits of material. Figures 4.42 and 4.43 are SEM photographs looking down from the upper side of the lower piston ring. The outer edge of the piston ring surface is located in the upper right hand corner of these photographs. Many of the strands which can be seen on the surface of the piston ring appear as though they may have had ends which have been broken off.

Figure 4.42: SEM Photograph of Typical Deposits found on the Surface of the Piston Rings Using 0.5% Monoester (120X Magnification)
Figure 4.43: SEM Photograph of Typical Deposits found on the Surface of the Piston Rings Using 0.5% Monoester (430X Magnification)
CHAPTER 5

DISCUSSION

5.1 OVERVIEW

Perhaps the most surprising result of the testing conducted in this study was the piston seizure observed with conventional lubricant at the manufacturer recommended fuel:oil ratio of 50:1. As mentioned previously, piston scuffing occurred after about 6 total hours of loaded testing. Visual inspection of the piston clearly shows that the surface undergoes an enormous amount of run-in, e.g., plastic deformation and wear, during the first several hours of engine operation. An estimated 60-70% of the piston surface had undergone major run-in during this relatively short term of engine operation.

Despite the engine seizure that occurred while using Tecumseh’s recommended two-cycle engine-oil at a concentration in the fuel of 2%, the conventional lubricant outperformed the experimental monomer test lubricants in anti-scuffing protection. Several important factors play a role when comparing the experimental lubricant results with the conventional lubricant test. First, the experimental lubricants, (e.g., base fluid plus monomer), were tested at a mass concentration up to 1%, with the maximum concentration of the monomers up to only 0.5% by mass. Secondly, the conventional lubricant is a well developed mixture of anti-wear additives, detergents, base oils, corrosion inhibitors, rust inhibitors, and has undoubtedly been through an extensive testing program to
determine the optimum ratio of each additive for this engine application. Our experimental lubricants are simply anti-wear additives (monomers) in a base oil carrier; the optimum concentration has yet to be determined. In addition, several elements that govern the lubrication regime in a two-cycle engine are vastly different from any system in which the monomers have been previously tested. Possible reasons for piston scuffing have been hypothesized for each test and are discussed in this chapter.

Table 5.1 summarizes some of the highlights from the engine bench testing which were discussed in detail in the previous chapter.
Table 5.1: Summary of Test Results

<table>
<thead>
<tr>
<th>LUBRICANT (PRE-MIXED IN THE FUEL)</th>
<th>CYLINDER TEMP. AT 2000 RPM (°C)</th>
<th>CYLINDER TEMP. AT 2400 RPM (°C)</th>
<th>CYLINDER TEMP. AT 3000 RPM (°C)</th>
<th>CYLINDER TEMP. AT 1800 RPM LOADED (°C)</th>
<th>COMMENTS</th>
</tr>
</thead>
</table>
| Diallyl Phthalate 0.5%             | 130                             | 150                             | 210 Failure, 7 min. (Total time: 27 min.) | N/A                                  | - Scuffed piston on major and minor thrust sides  
- Failed at no-load  
- Thin yellow-gold and black surface films on the piston  
- No excessive deposits |
| Monoester 0.5%                    | 136                             | 170                             | 210 Failure, 4.0 min. (Total time: 34 min.) |                                       | *Loaded at WOT  
- Bottom ring completely stuck  
- Upper ring stuck 180°  
- Very viscous, tacky, dark deposits on all lubricated parts  
- Scuffing on the upper transfer port side of the piston |
| Monoester 0.5% plus sebacate 0.5% | 134                             | 156                             | 212 Failure, 3.7 min. (Total time: 34 min.) |                                       | **Loaded at WOT  
- Both rings completely stuck in piston grooves  
- Piston Scuffing on major thrust and upper transfer port side of piston  
- Heavy dark deposits on all lubricated parts |
| Monoester 0.1% plus sebacate 0.9% | 125                             | 143                             | 188 Test 1 (90 min. no failure)  
188 Test 2 (90 min. no failure)  
220 Test 3 (Total time: 41 min.) |                                       | *** Loaded at idle  
- No evidence of ring sticking  
- Three narrow scuffed regions on the piston starting at the major thrust side 120° apart  
- Thin, dark surface films |
| Two-stroke engine oil 2.0%        | 130                             | 145                             | 188 Failure, 238 at 256° (Total time: 340 min.) |                                       | **** Loaded at WOT  
- Total test time: 340 min.  
- Significant run-in on piston surface  
- Sides of piston appear very clean and shiny  
- One scuffed region on piston: major thrust side |

**DISCUSSION**  

156
A report by Lord et al. [83] concluded that there are three main causes of piston seizure that commonly occur in two-stroke engines. The first of these is caused when the lubricant film fails to prevent metal to metal contact from occurring between the piston and cylinder. This mode of failure is reported to occur most commonly during engine run-in. Adhesive welding can transpire between bare metal surfaces in contact and produce wear particles that detach themselves from the surface. A second common mode of piston failure can be caused by heavy build-up of carbon, lacquer (or other) deposits between the piston and cylinder which reduces the clearance between the parts. Thirdly, ring sticking followed by blow-by subjects more of the piston surface to high combustion temperatures and disallows the piston from dissipating heat by conduction through the rings to the cylinder wall. This produces localized hot spots on the piston surface and leads to piston scuffing.

**Diallyl Phthalate**

The test conducted with diallyl phthalate as a potential two-stroke anti-wear additive resulted in piston scuffing even before a load was applied to the engine. The fact that the wear scars on the piston occurred on the two thrust surfaces of the piston is a good indication that diallyl phthalate simply did not prevent metal to metal contact from occurring between the piston and cylinder. As a result, adhesive welding probably occurred between the piston and cylinder...
which resulted in a decrease in the clearance and increase in friction between the piston and cylinder.

Gold-yellow and black deposits on the piston sides were very thin and easily removed by lightly touching the surface. There was no indication on the piston or cylinder of any excessive build-up of a surface film on the piston or cylinder that could have caused engine failure. Excessive build-up of a film between the piston and cylinder would likely result in a notable increase in cylinder wall temperature due to excessive friction. The cylinder wall temperature plot for this test was very consistent with the temperatures observed with conventional lubricant at 2000 and 2400 rpm; the average cylinder wall temperatures at these two speeds were 130 and 145 °C with conventional lubricant and 130 and 150 °C using diallyl phthalate.

The piston rings had a very thin bead of a clear, wet looking liquid on their outer edges. However, they were free from the piston grooves, with the exception of the two scuffed areas where aluminum from the piston had plowed over the rings.

**C₃₆ Dimer Acid / Ethylene Glycol Monoester**

The picture appears to be much more complicated with the monoester. Every test executed using the monoester endured the thirty minute (unloaded) run-in period of the test. The tests using 0.5% monoester alone and 0.5%
monoester with 0.5% sebacate produced piston rings that were almost completely stuck in the ring grooves. The piston and cylinder bore were well coated with a very viscous and tacky film. In addition, the measured cylinder wall temperature was higher during these tests than any of the others. The addition of 0.5% concentration of sebacate with a concentration of 0.5% of the monoester to the fuel reduced the cylinder wall temperature by 15°C at 2400 rpm but was not significantly different at 2000 and 3000 rpm. It is possible that the addition of the sebacate prolonged the occurrence of ring sticking during the 30 minute run-in, which would explain the lower temperature at 2400 rpm and approximately equal temperature at the higher speed later in the test.

The test conducted with the monoester alone produced a large number of aluminum wear particles. The shiny wear tracks on the piston appeared to have been produced by these particles acting abrasively on the piston surface. Piston scuffing had occurred on the upper transfer port side and was not centered on two thrust sides of the piston. Interestingly, no scuffing was observed on over half of the piston circumference, opposite the scuffed surface. The build-up of deposits between the piston and cylinder might be the cause of scuffing in this case. Misalignment of the piston in the cylinder would likely have produced scuffing on opposite sides of the piston; this was not the case. It is difficult to compare the severity of the surface damage from test to test because damage
will continue to occur in any given test until the friction becomes high enough to stall the engine.

The addition of 0.5% sebacate with the monoester led to piston scuffing in about the same period of time as the monoester alone. The two main wear scars on the piston were towards the upper transfer port side and on the exhaust port side. If scuffing continued to occur on the piston between these two wear scars before seizure had occurred, the damage would have been almost identical to the damage observed with the monoester alone. Less tacky, but heavy deposits covered the sides of the piston. Very colorful patches were found on the smoother, run-in portion of the piston.

The heavy build-up on the piston in both of the aforementioned cases could have caused excessive friction between the cylinder and piston which lead to scuffing. It is also possible that heavy build-up in the ring groove area caused ring sticking, blow-by and excessive piston temperatures.

Heavy deposits were found on all of the internal engine parts with both of the 0.5% monoester concentrations, which included the crankshaft, connecting rod, needle and ball bearings, piston top, and the combustion chamber.

Because heavy build-up was so prevalent with 0.5% concentration of the monoester, a lower concentration was tested under unloaded conditions at constant speed for a longer duration of time. A 0.1% concentration of the monoester was mixed with a 0.9% concentration of sebacate in gasoline.
Running this mixture for 90 minutes at 2400 rpm produced only light piston deposits and run-in. This test was repeated at 3000 rpm for about 85 minutes to look for deposit formation that might occur at higher operating temperatures. The piston looked even cleaner than it did after the first test at 2400 rpm. The cylinder wall temperature plot from this test, (Fig. 4.18) shows two instances where the temperature reached almost 10 °C above the average steady state temperature of 182 °C. The unexpected temperature increase after about 50 minutes of operation is particularly interesting; however, the reason for this temperature increase is unknown. Very little, if any additional surface changes were found on the engine parts after this test at 3000 rpm.

During the loaded portion of the test, the engine produced a sound that may have come from metal-to-metal contact between the piston and cylinder, and then it would recover. As the test continued, the sound would last longer and occur more frequently. At the point where it was evident that the condition was going to continue to get worse, the load was removed from the engine and it stalled a few seconds later due to piston scuffing. This sound was not observed during any of the other loaded tests, possibly due to the lower throttle setting used in this particular test.

The surface area of these scuffed regions was small compared with the previous tests, which is likely due to the lower throttle setting and lower frictional force required to stall the engine.
The reason for the piston scuffing in this case is quite puzzling. The same mixture that provided adequate wear protection under non-loaded conditions failed quickly after reducing the engine speed and applying a light load to the engine. Possible reasons for the failure under load include (a) slightly higher operating temperatures that were obtained during the test, possibly causing thermal degradation of the anti-wear additives, (b) higher surface stresses which may remove protective films quicker than they could reform on the surface, (c) the monomer may somehow interfere with changes that transpire on the surface during run-in, or (d) the build up of degradative material may have reduced the clearance between the piston and cylinder. These and other possible reasons for piston scuffing are discussed in greater detail in the next section.

**Conventional Lubricant**

Although scuffing had occurred long before the planned 20 hour testing period, some very useful information was obtained about the engine and test method after conducting this test. First, under loaded operating conditions, the piston surface continued to change significantly due to wear and/or plastic deformation even after the first 90 minutes of running under load.

The fact that scuffing had occurred only after approximately six hours of testing would suggest that the operating conditions are too severe. A lower
throttle setting could be used prior to loading the engine with the electric motor, which would lower the piston thrust forces. It is known that the low speed, high load condition is the most severe from the standpoint of engine lubrication. High loads and low speeds favor boundary lubrication conditions.

The scuffed region of the piston occurred on the exhaust port side, which is also where the surface of the piston had shown the most amount of deformation due to wear or plastic deformation after the first 90 minutes of operation under load. Although this failure was not expected, the very smooth surface features on a large portion of the piston indicated that the heavy loading on the piston placed the system in quite severe boundary lubrication conditions.

The engine parts appeared to be well wetted with lubricant in all test cases. However, if the distribution of lubricant throughout the engine is considered, it is possible that continuous operation at the low end of the engine speed range may starve certain localized regions of the engine from being well lubricated. From the standpoint of good lubricant distribution in this engine design, it is likely that the more turbulent the air flow is through the crankcase, the better the distribution of lubricant will be. This may be, at least in part, the reason this engine failed using the recommended conventional lubricant mixture.

The sides of the piston appeared very clean in comparison with those that were tested using the monoester and diallyl phthalate. The piston top and combustion chamber were coated with a thick black coating that adhered to the
surface more tenaciously than the deposits found with any of the monomer additives. This engine was subjected to higher operating temperatures for a longer duration of time than any of the other tests, which might explain the stronger bond to the surface.

No signs of ring sticking were observed, and no deposits of any type were observed on the piston rings using the photomacroscope. The piston rings were uniformly coated with thin liquid, but no signs of a build up of any material was noted.

The cylinder wall temperature of about 238 °C was remarkably consistent and steady each time the load was applied to the engine.

5.2 PHOTOMACROGRAPH OBSERVATIONS

Photographs of the piston, crankshaft, and piston rings were taken immediately following every engine disassembly. Those that best represent the general observations have been presented in the previous chapter.

Thin strands of material were found on the piston rings with both tests conducted with a concentration of 0.5% monoester. The heavy deposits observed on several lubricated engine parts with this concentration suggests that a concentration of 0.5% of the monoester is excessive. Further chemical analysis to characterize the surface films may help to confirm this hypothesis.
5.3 SEM OBSERVATIONS

As presented in the previous chapter, piston samples from tests with each monomer were inspected using a Joel JSM-35C Scanning Electron Microscope, located at the Virginia Tech. Veterinary School. The advantage of this SEM is that it doesn’t require any prior surface preparation of the samples, and it can handle relatively large specimens up to 25 mm in diameter. Samples are placed in a vacuum, and any surface features that have poor electrical conductivity or are in poor electrical contact with the specimen appear much lighter than the bulk specimen due to the build up of an electrical charge.

The monoester piston samples were sparsely covered with regions of brown and of black deposits. These deposits appeared quite thick under SEM magnification. The formation of these deposits on very unworn portions of the piston suggests that the monoester may have reacted or polymerized on portions of the piston where high surface stresses did not occur, possibly due to high surface temperatures. However, the chemistry of the surface films has not yet been determined. Samples are currently being studied using FTIRM to determine the chemical structures of the surface films.

Several thin strands of material were observed lying on the surface of the piston specimens, but it was difficult to verify what they were or where they came from. Very heavy deposits were observed on the outer edges of the monoester piston ring samples. They covered most of the outer edges of the piston rings,
both on the top and bottom surfaces of the piston rings. Careful inspection of the piston ring was conducted, and most of these surface features appeared to be well attached to the surface.

Although very light surface films covered the diallyl phthalate piston, these films were not as pronounced using the SEM as those found on the monoester samples. Several thin, flake-like layers that had been partly lifted from the piston surface were found on the wear scars. It is difficult to determine whether these flakes were aluminum or some other material. In addition, some long, thin fibers were found that appeared to be stuck to part of wear scars.

For the diallyl phthalate test, notable deposits were not consistently observed on the piston surface. A few clusters of deposits were near the outer edge of the piston rings in much smaller quantities than those observed with the monoester. Surprisingly, the piston ring grooves were well packed with a complicated three-dimensional web of material. The material was flattened into a plane on the bottom of the grooves, probably where it came into contact with the piston rings when they were installed.

The deposits on the piston and piston ring specimens were clearly very different for each monomer and can undoubtedly be attributed, at least in part, to the anti-wear additives. Further chemical analysis of the collected specimens and surface films will help to explain what chemical reactions took place on the surfaces.
Several key factors play an meaningful role in boundary lubrication. Factors that need to be considered in this difficult lubrication problem are discussed in detail in the following section. Some of these factors could be isolated in a laboratory test apparatus to more completely understand the behavior of the monomer additives with respect to each variable. These factors are listed in no particular order, however, Section 5.5 summarizes these factors and highlights those which are most likely to have interfered with the anti-wear mechanisms of the monomers.

5.4 IMPORTANT FACTORS THAT PLAY A ROLE UNDER BOUNDARY LUBRICATION CONDITIONS

The tribological behavior inside a two-stroke engine is very difficult to model from both mechanical and chemical standpoints. Specific aspects of the monomer performance, (e.g., thermal characteristics) might be explored in a conventional lab type environment, such as a pin on disk machine, to aid in understanding how the monomers might behave in a two-stroke engine.

Sliding Speed

The anti-wear abilities of the monomers are undoubtedly related to kinetics of film formation. For a given monomer, the rate of polymerization depends upon the type of polymerization reaction (e.g., addition or step-reaction), the temperature at which polymerization will occur for the particular

DISCUSSION
monomer, possibly the rate of exoelectron emission, and other catalytic effects that may tend to effect the rate of film formation. In addition, some time may be required for the polymer to develop a durable surface film chemically. The sliding speed of the system therefore plays an important role in selecting an anti-wear additive. Calculated piston speeds, as a function of crank angle, for the TVXL840 are plotted in Fig. 5.1. The piston speeds are based on the 4 engine speeds employed in this experimental study and the geometry of the Tecumseh, TVXL840 engine. The relevant equations and engine geometry are presented in Appendix C.

As Fig. 5.1 shows, the sliding speed of the piston reaches almost 8 m/s during mid stroke in each direction. For a monomer to provide adequate anti-wear protection, it must have the ability of forming and replenishing a surface film at a rate which will provide adequate wear protection during the various speeds throughout the piston cycle. Unfortunately, the effect of sliding speed on the wear protection of a given monomer is very difficult to model or to isolate experimentally. Surface temperatures are strongly affected by sliding speed.
Figure 5.1: Piston Sliding Speed as a Function of Crank Angle at Various Engine Speeds

Contact Pressure

In addition to the sliding speed, the contact pressure between the surfaces in relative motion may influence the rate of polymer film formation and removal. Therefore, contact pressure may carry an important role in developing a suitable monomer for the purpose of an anti-wear additive. Piston contact forces have been calculated for the TVXL840 and are presented in Appendix C. The pressure-volume diagram used to calculate the piston thrust load was extrapolated from experimental data obtained from a similar, slightly larger two-stroke engine with approximately the same compression ratio. The estimated piston speeds and corresponding loads demonstrate the relationship between as
a function of crank angle. A rough estimation of the piston thrust loads predicts that loads reach over 1000 N between the piston and cylinder. The highest loads occur just after top-dead-center and at relatively low sliding speeds.

The contact pressure of sliding surfaces is possibly more important than the overall forces being carried between the surfaces in sliding motion. The real area of contact must be known in a particular system to estimate surface pressures. For a given contact force, the real area of contact between aluminum and cast-iron, for example, would generally be greater than that between cast-iron and cast-iron. This is of course due to the much lower hardness of aluminum than cast-iron. Localized surface temperatures would also tend to be higher where there are higher contact stresses. A formed polymer tribolayer would likely endure longer in a system with lower contact pressures.

**Monomer Concentration**

Ideally, the tribopolymerization concept is based on the conception that the monomers polymerize on rubbing surfaces only in localized contact zones where high temperatures and possibly where freshly exposed surface exist. Because some surfaces are more chemically active than others, the rate of film formation may differ from substrate to substrate. In addition, some systems may experience high surface temperatures where sliding contact does not occur.

For a given monomer, the rate of film formation could be controlled to some extent, by the concentration of the monomer in the carrier fluid. If the rate
of film formation does occur (for any reason) at a rate in excess of what is necessary to provide adequate wear protection, build-up of a polymer could occur and lead to deposit problems. In the case of piston lubrication, excessive deposits could lead to ring sticking, excessive piston friction forces, and could tend disallow the piston from dissipating heat by acting as an insulator between it and the cylinder.

Temperature Effects

One of the most important factors of the tribopolymerization mechanism in two-stroke engine anti-wear protection is the effect of temperature on the rate of film formation, and on the thermal degradation of the protective film. The temperatures experienced in the two-stroke engine testing exceed those in which any of the monomer additives have been previously tested. The bulk temperature of the system may also be high enough to promote polymerization away from the contact regions to cause deposit problems or prevent the bulk of the anti-wear additive form getting to the loaded contact regions. The thermal characteristics of different monomers should be explored to screen candidate monomers for this application.

For a given monomer, it is hypothesized that a minimum surface temperature is required for polymerization to occur. Therefore, for a given system and monomer, it is postulated that there is a temperature range over which a monomer would be effective.

DISCUSSION
A common tribological system, such as a pin-on-disk device could be utilized over a range of pre-selected temperatures to screen candidate monomers for this high temperature application. Despite the significant differences between a simple test device and the complicated wear mechanisms in a two-stroke engine, the temperature at which a particular polymer decomposes thermally could be examined separately.

Mechanical Properties and Surface Finish of the Substrates

During the first few hours of engine operation, asperity contact occurs between parts in sliding and rolling contact causing plastic deformation and wear of the surfaces. This occurs until the real area of contact between the surfaces increases enough to elastically support the forces transmitted through the contact region. The plastic deformation and wear that new parts undergo during the early stages of operation is a phenomenon often referred to as run-in.

It may be important to understand how the formation of a polymer film might affect the run-in process. For example, tiny wear particles that may ordinarily get washed away from the contact zone during run-in with a conventional lubricant, might become embedded in a polymer film and abrasively damage the surfaces. On the other hand, if small asperity peaks break off during the run-in process and ordinarily re-attach themselves to the surface, the monomer could somehow interfere with that process, possibly by coating the particles and preventing metal to metal contact between the wear
particle and the surface. The machined surfaces of the piston and cylinder are intentionally made very rough to retain suitable amounts of conventional lubricating oils in the contact regions. Possibly, the rough surface features wear abrasively on the formed polymer film.

The amount of plastic deformation that occurs on the surfaces during run-in, therefore, may be very important. The machining tolerances, surface roughness and hardness of the substrates dictate the amount of run-in that will occur for a given system. It may be worthwhile to study the effect of surface roughness on wear using different monomers as anti-wear additives. If the amount of plastic deformation of the substrate plays a role, then the effect of other mechanical properties such as hardness should be considered.

**Chemical Reactions and Competition**

The effectiveness of the tribopolymerization approach to boundary lubrication is strongly influenced by chemical reactions that occur at the surface and also in the carrier fluid between the monomers and the constituents in the gasoline, the combustion products, and any surface films on the lubricated substrates. There could be competition between the monomers and constituents in the gasoline for the surface of the freshly exposed surface regions. In addition, additives in the gasoline could react with the monomers while in the bulk fluid. A third factor is the possibility of chemical decomposition of the
formed tribolayer, by reacting with the combustion products or other elements in the system.

5.5 SUMMARY

This is clearly a very complicated lubrication problem and the role which each of the aforementioned factors plays is very difficult to isolate. As stated previously, two-stroke engine lubrication is very difficult to model and predict using any simple laboratory test device. The most likely reasons for the inadequate piston lubrication are briefly summarized in Table 5.2 below. Factors which the author believes are most significant are discussed later in this section.
<table>
<thead>
<tr>
<th>Mechanism of Failure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Decomposition</td>
<td>- Excessively high operating temperatures leads to thermal decomposition of the monomer(s)</td>
</tr>
<tr>
<td>Concentration</td>
<td>- Excessive concentration leading to build-up or ring sticking (due to high bulk temperature also)</td>
</tr>
<tr>
<td></td>
<td>- Inadequate concentration to allow a durable film to form</td>
</tr>
<tr>
<td></td>
<td>- Poor distribution of lubricant, starving critical regions from lubricant</td>
</tr>
<tr>
<td>Exoelectron Emission and Catalytic Effects</td>
<td>- Insufficient exoelectron emission to promote film formation</td>
</tr>
<tr>
<td></td>
<td>- Other (unknown) catalytic effects do not occur in this system to promote polymerization</td>
</tr>
<tr>
<td>Other Effects</td>
<td>- Formation of polymer film interferes with the heat transfer between the piston and cylinder</td>
</tr>
</tbody>
</table>

Although there are a large number of factors that could influence the effectiveness of the tribopolymerization approach of two-stroke engine lubrication, past work with monomers has produced strikingly impressive results with very similar systems. How does the tribological system of the two-stroke engine differ from those which monomers have been shown to possess exceptional friction and wear characteristics? The factors mentioned in Table 5.2 have been selected as the most reasonable reasons for the observed tribological failures using the monomers in this study. The piston and cylinder wall temperatures exceeded the upper temperatures at which the monomers have been employed in the past. In addition, it is possible that the formation of a
protective film interferes with the conductive heat transfer that normally occurs between the piston and cylinder, causing the system to operate at above-normal temperatures. Finally, the optimum concentration of monomers in the fuel is unknown. Heavy deposits of material found on the piston after several minutes of operation with the monoester indicate that the concentration used may have been too high. On the other hand, almost no deposits were noted using the same concentration of the addition monomer.

Work is now being carried out to address these issues. Monomers which polymerize at higher temperatures as well as monomers with higher temperature thermal stability are being explored. Solubility tests have been performed (in gasoline) with several higher temperature monomer candidates. Steel-on-steel, pin-on-disk tests are also being conducted to study the effect of these additives on wear. In addition, the design and construction of a higher temperature tribological test device is being considered to more completely characterize the thermal limitations of the monomer additives.

Work is also being carried to characterize the chemical nature of the surface films on the engine part surfaces. Piston samples and surface films from these tests have been sent to Dr. Bhawani Tripathy for FTIRM analysis. Information from this investigation will help to explain the types of chemical reactions which have taken place on the part surfaces.
Recommendations have been generated to study the wear performance of the monomers with aluminum-on-cast iron and possibly the effect of the surface finish of the substrates on the anti-wear performance of the monomers. These and several other suggestions for future studies are discussed in Chapter 7.
CHAPTER 6

CONCLUSIONS

A literature review was performed to investigate two-cycle engine lubrication and emission problems as well as testing techniques which have been employed to evaluate the friction, wear, and environmental effects of two-stroke engine lubricants. Because the tribopolymerization approach to boundary lubrication has produced strikingly effective friction and wear characteristics in hydrocarbon carrier fluids in the past, an additional investigation was also conducted to locate other fuel lubricity problems where this approach shows good potential. Tribological problems have been found to exist due to the poor friction and wear characteristics of diesel, jet and alcohol fuels.

A test plan was developed to evaluate the anti-wear characteristics of two monomers -- diallyl phthalate and the C_{36} dimer acid / ethylene glycol monoester -- for use as two-stroke engine lubricants. A test procedure was developed and an engine bench test apparatus was designed and constructed to carry out this objective.

Piston scuffing occurred well before the planned test period of 20 hours had expired with all the lubricants tested. Although the monomers did exemplify some anti-wear qualities under certain operating conditions, further development will be necessary to reach a satisfactory level of performance. Several
approaches which should help to provide insight into this complicated lubrication problem are presented in the following chapter. Specific conclusions from this study are listed below.

1. Under the test conditions employed in this study, the lubrication of the piston and cylinder is the limiting factor concerning engine life when using the Tecumseh TVXL840 two-cycle engine.

2. Piston scuffing had resulted on both thrust surfaces of the piston using a pre-mixed 0.5% mass concentration of dialyl phthalate in gasoline. The total test time lasted 27 minutes and engine seizure occurred prior to any loaded engine testing.

3. Three tests were conducted using different amounts of the C\textsubscript{36} dimer acid/ethylene glycol monoester in new engines. In each of the three cases, piston scuffing was not observed prior to applying a load to the engine. Piston scuffing did occur within several minutes after applying a load to the engine in all three cases.

4. The monoester was found to leave excessive deposits on the surface of the piston, cylinder, and particularly the piston rings when used alone at a mass concentration in gasoline of 0.5%. The same observation was noted after using the same concentration of the monoester with the addition of a 0.5% mass concentration of bis (2-ethylhexyl) sebacate, a
synthetic oil. The piston rings were found to be almost completely stuck in the piston ring grooves after each of the two (approximately 35-minute) tests.

5. Three hours of testing was performed with no load applied to the engine using a mass concentration of 0.1% of the monoester with 0.9% of a base oil in the fuel. Cylinder wall temperature measurements using this lubricant mixture were very close at all three throttle settings to the temperatures observed using conventional two-stroke engine oil at a concentration of 2.0% at the same engine speeds.

6. Thin strands of material were found on the piston rings after both tests in which a concentration of 0.5% monoester was used. These observations were first noted through the use of the photomacroscopic, and confirmed with SEM observations under higher magnification. Samples have been collected for chemical analysis (FTIRM) to determine if they were produced via polymerization of the monomer.

7. Using two-stroke engine oil at a fuel:oil ratio of 50:1, piston scuffing occurred after 340 minutes of operation while holding the engine speed at 1800 rpm at wide open throttle. This suggests that controlling the speed of the Tecumseh TVXLB40 at 1800 rpm at wide-open-throttle is more severe than the engine was designed to operate under for prolonged periods of time.

CONCLUSIONS
8. At least three areas where problems exist due to poor friction and wear characteristics of fuels have been identified. Tribological problems with the use of diesel fuel, alcohol fuels, and jet fuels have each been previously discussed. Past work has shown that the addition of minor concentrations of monomers can significantly improve the friction and wear characteristics of low viscosity fuels. Tribopolymerization shows good potential of being a solution to each of these fuel lubricity problems.
7.1 TWO-STROKE ENGINE LUBRICATION

1. A study should be conducted to evaluate the anti-wear performance of candidate monomers as a function of bulk temperature and contact pressure. If a simple contact geometry is employed, (e.g., a ball on disk) then a reasonable estimate of the local contact surface temperature could also be calculated. The local temperature in the contact region can often be significantly higher than the bulk temperature of the system. Each monomer additive undoubtedly possesses a minimum temperature at which it will polymerize and a maximum temperature where chemical decomposition occurs. Minimum temperatures that are required for polymerization to occur should be explored and considered for cold start and cold weather applications. The temperatures at which the surface films decompose play a major role in selecting an anti-wear monomer additive for this air-cooled engine application. Cylinder wall temperatures as high as 275°C were observed in the experiments conducted in this study. Very localized temperatures on the piston and cylinder surfaces are undoubtedly even higher.
Another possible approach of studying the thermal limitations of different monomers could be conducted through the use of Differential Scanning Calorimetry (DSC). This approach is often utilized to study the thermal characteristics, i.e., glass transition and melting temperature of various polymers. Pure monomers could be tested in addition to examining laboratory test samples which have been lubricated with monomers. This approach would not only help to determine the high temperature limitations of the monomers, but it may provide some information about the minimum temperature required for polymerization. It is known that other effects do have an influence on the rate of polymerization, e.g., exoelectron emission, but DSC would provide isolated information relating to the influence of temperature only.

A couple of modifications should be made to the test apparatus and procedure which was developed in this study. First, two 90-minute tests should be conducted with each experimental lubricant under unloaded operating conditions, the first at 2400 rpm and the second at 3000 rpm. This procedure was found to provide information about the deposit forming tendencies of the lubricant and may also provide some information about the thermal abilities of the lubricant due to the higher temperature at the higher speed. These initial set of tests could also reduce the chance of catastrophic engine failure under the more severe,
loaded operating conditions, should the initial tests reveal the formation of excessive deposits. Secondly, should further testing reveal a monomer compound which provides engine wear protection that is competitive with the results found using conventional lubricant, the test apparatus should then be modified to incorporate higher loaded engine speeds. As stated in the previous section, the loaded operating speed of 1800 rpm at wide open throttle appears to be more severe than the test engine was designed to be operated under for prolonged periods of time. For the purpose of comparing the results of future tests with results previously obtained, it is not recommended to modify the existing test apparatus unless more promising results are obtained with at least one of the monomers. If significant improvements are found with the performance of a particular monomer compound, the existing device should then be modified to transmit torque from the motor to the engine through a belt and pulleys sized to produce the desired engine speed. The twenty-hour test plan (as described in Chapter 3) could then be employed to test the wear protection abilities of the monomer(s).

4. An exhaust gas filtering system should be designed and installed into the engine test apparatus. It would be best to incorporate a filtering system into the vacuum duct to prevent placing a back pressure on the engine. Analysis of exhaust particulate constituents could help provide answers
about what happens to the piston surface during run-in. Do asperity peaks break-off and leave the engine through the exhaust? A gravimetric measurement of the filtered particulates is also necessary to compare particulate emissions of monomer additives with a conventional lubricant.

5. A channel should be added to the LabView VI to continuously measure and record engine speed. Increases in friction are likely to produce a drop in speed and an increase in cylinder wall temperatures. More accurate monitoring of engine speed may help explain what is happening when cylinder wall temperature changes are observed.

6. The effect of surface finish on monomer anti-wear performance may also be a useful study, particularly with substrates which are very soft and undergo a large amount of plastic deformation during run-in. Does a polymer film collect particles that break free from the substrates? Could a polymer film that forms early in the run-in period interfere with the flow of surface substrate material that occurs during run-in? What might happen to a durable film on the surface of the substrate if the material deforms plastically beneath it?

7. A study on the effect of sliding speed might provide some useful information about the rate of film formation. It is likely that different monomers polymerize at different rates. Unfortunately, changes in sliding speed produce changes in temperature, rate of exoelectron emission,
contact pressure, and possibly mechanical surface properties of the substrate. The effect of speed is therefore very difficult to isolate.

8. A search should be conducted for higher temperature monomer compounds for this air-cooled engine application. Certain monomers with ring structures may possess higher thermal stability and provide superior wear protection than straight chained or even branched polymer-formers.

9. It is important to recognize that the temperatures obtained in an air cooled two-cycle engine are significantly higher than those found with the operation of a water cooled two-stroke engine. It is very likely that success may be obtained with the tribopolymerization approach of lubrication in a water cooled engine with monomers that did not perform well in the air-cooled engine design. Future tests in a water cooled engine should not be contingent upon prior success in an air cooled design.

10. Since the driving force behind the two-stroke engine work is to achieve a reduction in two-stroke engine exhaust emissions, an experimental study will need to be conducted to determine the effect of any suitable lubricant on exhaust emissions. An FTIR gas analyzer should be used to speciate the exhaust emissions from the engine, should a monomer be found which provides adequate wear protection. A comparison between the exhaust emissions obtained with the conventional lubricant and the
monomer should then be carried out. A thorough study of exhaust emissions should include a comparison of emissions obtained with a four-stroke engine of comparable power output. Several authors have argued that the toxic emissions from a four-stroke engine increase over the life of the engine as cylinder bore and piston ring wear lead to increased blow-by and higher amounts of lubricating oil being incorporated into the combustion process. The emissions from a two-stroke engine do not change significantly over the lifetime of the engine.

7.2 FUEL LUBRICITY

1. There is a need for a standard test device and procedure to characterize the friction and wear qualities of a wide range of low viscosity fuels and the effect of small amounts of various additives. The ball-on-cylinder lubricity evaluator appears to be the most adequate laboratory test device due to its sensitivity to low viscosity fuels and small concentrations of fuel additives. The recent use of this device by Lacey et al. [39] to develop wear maps for different fuels employs a much wider range of speeds and loads than the device was originally designed for. A device such as this (along with a standard test procedure) should be developed if fuel lubricity research is to be conducted at Virginia Tech. The wear mapping
technique is a good method for conveying very thorough information about the wear characteristics of a particular compound.

2. An actual fuel system will be required for testing the anti-wear performance of monomers that show good potential as anti-wear additives in fuel systems. An investigation should be conducted to determine the feasibility of designing a laboratory fuel system (with a pump and fuel injectors) that has a good potential of correlating with field performance. Although a typical fuel system does not experience the high temperatures at which the monomer additives would be expected to decompose, fuel systems are required to operate at very low temperatures, possibly below temperatures at which polymerization of monomer additives will occur. An investigation should be conducted to evaluate the low temperature limitations of the monomers.
REFERENCES


APPENDIX A

TEST SUMMARY AND CURRENT ENGINE STATUS

At this time, ten Tecumseh TVXL840 engines have been purchased from Dixie Sales Company in Greensboro, NC. A summary of the test(s) conducted with each engine and the status of each engine is outlined in this section. Each engine has been numbered and stored separately in the carton in which it has been shipped. The engine numbering coincides with the order in which each test was conducted. Disassembled parts have all been packaged and stored with each engine and all part measurements are marked on the engine components. Tables A-1 through A-5 summarize the status of each engine used in this study. The final five engines will employed later to evaluate other candidate monomers or lubricant mixtures.

The first engine tested used a pre-mixed concentration of 0.5% diallyl phthalate in the fuel. This test produced piston scuffing prior to applying a load to the engine.
**Table A1: Status of Engine #1**

<table>
<thead>
<tr>
<th>Test Conducted</th>
<th>Test Summary and Observations</th>
<th>Current Engine Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diallyl Phthalate 0.5%</td>
<td>130°C at 2000 rpm (10 min.) 150°C at 2400 rpm (10 min.) 210°C at 3000 rpm (7 min.)* *Piston Siezure after 27 min. <strong>at no load</strong> - Thrust surfaces of piston severely scuffed - Thin black and brown films on piston surface that wipe away easily - SEM and photomacroscope revealed very light deposits on piston and rings</td>
<td>- Engine is disassembled - Deposits were scraped from the piston and saved - Piston and rings have been destroyed for SEM analysis - Mass of needle brgs. prior to test: 15.7995g</td>
</tr>
</tbody>
</table>

The second engine test utilized a concentration of 0.5% of the monoester in the fuel. The peak temperature at failure was much higher than that observed in any other test and a large number of wear particles were produced. Since the engine will run until enough friction occurs to cause seizure, the damage in this test may be more severe than other tests because it took longer for enough friction to cause seizure. One interesting observation from this test is that all scuffing occurred on one side of the piston and didn’t occur mainly on the thrust surfaces.
Table A2: Status of Engine #2

<table>
<thead>
<tr>
<th>Test Conducted</th>
<th>Test Summary and Observations</th>
<th>Current Engine Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoester 0.5%</td>
<td>136°C at 2000 rpm (10 min) 170°C at 2400 rpm (10 min) 210°C at 3000 rpm (10 min) 270°C at 1800 rpm (load, WOT-4 min)* *Piston severely scuffed on upper transfer port side, approx 40% of surface -Large amount of wear particles -All parts very tacky and well coated -Rings almost completely stuck -SEM showed heavy build-up on rings and piston surface -Small fibers found on rings with SEM and photomacroscope, possibly two different types</td>
<td>- Engine is disassembled - Piston and rings have been destroyed for SEM analysis - Deposits have been scraped and saved from the piston and crankshaft - Mass of needle brgs. prior to test 15.8300g.</td>
</tr>
</tbody>
</table>

The third test was conducted with Tecumseh’s lubricant at the recommended ratio of 50:1. Although the engine endured loaded operation for several hours, the occurrence of piston scuffing might suggest the high-load, low-speed operating conditions might be more severe than this engine was designed for. Later tests were loaded at partial throttle settings to compensate for the high loading.
### Table A3: Status of Engine #3

<table>
<thead>
<tr>
<th>Test Conducted</th>
<th>Test Summary and Observations</th>
<th>Current Engine Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0% Tecumseh 2-stroke oil</td>
<td>130°C at 2000 rpm (average) 145°C at 2400 rpm (average) 178°C at 3000 rpm (average) 238°C at 1800 rpm (under load at WOT) 256°C at failure, approx 5 hr, 40 min. -Failure occurred during eighth load-up -One wear scar on exhaust port side of piston only -Piston sides were very clean -Combustion chamber deposits were comparable in quantity with monomer tests, but strongly adhered to the surfaces -Approx. two-thirds of piston surface was very well run-in -No deposits were found on the piston rings and ring grooves -Engine operating speeds (rpm) (see Fig.4.23 for corresp. temp plot) 2000, 2400, 3000, 1800L, 2400, 3000, 1800L, 2400, 1800L, 2400, 1800L-Failure</td>
<td>- Aluminum deposits on cylinder liner have been removed by light sanding with 1500 grit silicon carbide paper. - Engine has been re-built with new piston - All parts are stored in original carton - Needle bearings: set 1: 15.8100g set 2: 15.7850g (now) - Piston Rings set 1: 4.7169g (uppr) set 1: 4.2809g (lwr) set 2: 4.6453g (uppr) set 2: 4.3305g (lwr)</td>
</tr>
</tbody>
</table>

The fourth test was conducted to evaluate the behavior of the monoester in a carrier fluid. Since cylinder wall temperatures were very high using the anti-wear additive by itself, a low-viscosity, synthetic lubricant was chosen as a carrier. Table A4 shows the observations made and the status of engine #4.
### Table A4: Status of Engine #4

<table>
<thead>
<tr>
<th>Test Conducted</th>
<th>Test Summary and Observations</th>
<th>Current Engine Status</th>
</tr>
</thead>
</table>
| Monoester 0.5% plus Sebacate 0.5% | 134°C at 2000 rpm (10 min)  
156°C at 2400 rpm (10 min)  
212°C at 3000 rpm (10 min)  
248°C at 1800 rpm (loaded at 40Hz)*  
*Failure under load in 3.7 min.  
- 15°C cooler than monoester alone at 2400 rpm BUT approximately equal at the other two speeds  
- Both piston rings completely stuck  
- All parts well coated with liquid resembling the lubricant mixture  
- Piston sides covered with dark brown wet deposits  
- Extremely thin, white fibers were observed on the piston rings using the photomacroscope | - Engine is disassembled  
- Deposits were scraped from the piston and crankshaft and saved  
- Mass of needle brgs. prior to test 15.8075g  
- Mass of piston rings prior to test: upper: 4.7158g lower: 4.3755g |

Heavy deposits were found on both pistons using the monoester at a concentration of 0.5%. Evidence of ring sticking was prevalent in both cases. It was therefore decided to conduct a test using a lower concentration of the monoester with a higher amount of the base oil to keep the total concentration in the fuel at 1.0%. Two tests were conducted at no-load and constant speed to evaluate the deposit forming tendencies of the mixture, prior to applying a load to the engine. Table A5 summarizes the observations and status of engine #5.
Table A5: Status of Engine #5

<table>
<thead>
<tr>
<th>Test Conducted</th>
<th>Test Summary and Observations</th>
<th>Current Engine Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoester 0.1% with Sebacate 0.9%</td>
<td>125°C at 2000 rpm (avg. 3 tests) 143°C at 2400 rpm (avg. 3 tests) 188°C at 3000 rpm (avg. 3 tests) 220°C at 1800 rpm (loaded at idle)* *Piston scuffing caused seizure 11 min. after load was applied. - Cylinder wall temperature was at least 10°C cooler at each speed than prior two tests - No evidence of ring sticking after any of the three tests - No excessive wear during either of the two 90 minute unloaded tests was observed - Periodic grinding noise during loaded test not observed during any other test</td>
<td>- Engine is Disassembled - New part masses Needle bearings: set 1: 15.8189g set 2: 15.7933g set 3: 15.7850g Piston rings: set 1: upper 4.7089g set 1: lower 4.2850g set 2: upper 4.7120g set 2: lower 4.3966g set 3: upper 4.6453g set 3: lower 4.3305g</td>
</tr>
</tbody>
</table>

The remaining five engines have yet to be tested and are awaiting results from compounds being screened on a pin-on-disk machine. Engine #5 has been prepared for testing and Table A6 lists the part measurements.

Table A6: Status of Engine #6

<table>
<thead>
<tr>
<th>Test Conducted</th>
<th>Test Summary and Observations</th>
<th>Current Engine Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBD</td>
<td></td>
<td>- Needle bearings: new: 15.8015g - Piston Rings new: 4.7300g. (uppr) new: 4.3525g. (lwr)</td>
</tr>
</tbody>
</table>
APPENDIX B

DOCUMENTATION OF TEST APPARATUS

The vertical shaft configuration of the engine added complexity to the design of the test apparatus. It was desired to apply a load (torque) to each engine without applying an excessively high load in the axial direction of the output shaft which could cause premature damage to the roller bearings in the engine. The test apparatus was designed with the motor on an adjustable mount. This would allow vertical adjustment of the motor to which could be used to support the weight of the flywheel and coupling components. The adjustment procedure, along with a diagram of the test apparatus assembly can be found in Chapter 3.

Drawings for each component of the assembly that was machined at Virginia Tech. is included in this section.
Figure B1: Thermocouple Holder

Part: Thermocouple Holder  Date: May 13, 1995
Material: Brass  Name: D. Patterson/Dr. Furey

Notes:
1. Drill as deep as possible without breaking thru end
2. Make from 7/16-14 brass rod
Figure B5: Exhaust Block

<table>
<thead>
<tr>
<th>EXHAUST BLOCK</th>
<th>DATE: JUNE 21, 1995</th>
<th>NOTES:</th>
</tr>
</thead>
<tbody>
<tr>
<td>DR. FUREY / D. PATTERSON</td>
<td>MATERIAL: ALUMINUM</td>
<td>1. ALL DIM. IN INCHES</td>
</tr>
</tbody>
</table>
.25 DIA. THRU 
8 HOLES EQ SPACED 
ON 4.375 DIA. B.C. 

\( \varnothing 6.00 \)

**NOTES:**
1. ALL DIMENSIONS ARE IN INCHES
2. ALL TOLERANCES +/- .02 
   UNLESS OTHERWISE SPECIFIED

**Figure B6:** Shaft Support Plate
APPENDIX C

THEORETICAL PISTON SPEEDS AND LOADS

The engine speed usually refers to the rotational speed of the crankshaft; commonly expressed in revolutions per minute. From a design point of view, the piston speed is probably a more important parameter, because stresses and other factors scale with piston speed and acceleration rather than engine speed. The speeds of the piston and thrust loads between the piston and cylinder are very important when considering piston lubrication.

Since the piston comes to a complete stop as it reverses direction at both ends of its stroke, a breakdown in hydrodynamic lubrication occurs. Additionally, the piston experiences the highest combustion chamber gas pressures near top dead center, during the compression and combustion of the fuel charge. These conditions guarantee a boundary lubrication regime, and the system components will undergo plastic deformation in the contact regions until the real area of contact can support the load between them. A simplified representation of the piston and cylinder geometry is presented in Fig. C1. It would be necessary to obtain a pressure-volume diagram for the particular engine design to calculate the forces between the piston and cylinder for any given crank angle, θ.
Referring to Figure C1, the piston speed can be represented as a function of the crank angle, \( \theta \), by the relation:

\[
\mathcal{U}(\theta) = \frac{\omega \cdot S}{2} \left[ \sin(\theta) + \frac{\varepsilon \cdot \sin(2\theta)}{2(1 - \varepsilon^2 \cdot \sin^2(\theta))^{1/2}} \right]
\]

Where:

\( \omega = \) the rotational speed of the crankshaft (radians per second)
\( S = \) the piston stroke
\( \varepsilon = S / 2 \cdot L, \) a geometric ratio
\( L = \) the connecting rod length

For the TVXL840 engine used in this study, \( S = 46 \) mm and \( L = 85 \) mm. The calculated piston speeds for the several engine speeds used for the experimental tests in this study, as a function of crank angle, have been presented graphically in Chapter 5.
For the TVXL840, the gravitational forces work perpendicular to the thrust forces on the engine due to the vertical orientation of the crankshaft. A force balance for Fig. C1 can be written to calculate piston side thrust:

\[
\sum F_x = m \frac{dU}{dt} = -Fr \cdot \cos(\phi) + p \frac{\pi}{4} b^2 \pm Ff + \text{when } \theta \leq 0 \\
\sum F_y = 0 = Ft - Fr \cdot \sin(\phi)
\]

with:
- \(m\) = the mass of the piston
- \(b\) = piston diameter
- \(p\) = combustion chamber pressure
- \(Fr\) = connecting rod force

The piston acceleration can be represented as a function of \(\theta\) by the relation:

\[
\frac{dU}{dt}(\theta) = \frac{\omega^2 S}{2} \left[ \cos(\theta) + \frac{\varepsilon (\cos(2\theta) + \varepsilon^2 \sin^4(\theta))}{(1 - \varepsilon^2 \sin^2(\theta))^{3/2}} \right]
\]

therefore;

\[
F_t = \left( -m \frac{dU}{dt} + P \frac{\pi}{4} b^2 \pm Ff \right) \tan(\phi)
\]

which is true only if the wristpin is not offset (which is the case in the TVXL840 design).

Although a p-v diagram is not available for the TVXL840, an experimentally determined p-v diagram for a similar, slightly larger, piston ported two-cycle engine has been presented by Blair [84] and is reproduced in Fig. C2.
Figure C2: Measured Pressure-Volume Relationship for a Single Cylinder, 400cc Two-Stroke Engine [84]

From the standpoint of lubrication, it would be necessary to know the corresponding piston speeds and forces on the thrust sides of the piston for a given crank angle, $\theta$, to determine the particular lubrication regime. For the purpose of obtaining an approximate relationship between the piston speeds and loads of the TVXL840, the x axis of Fig. C2 has been scaled to coincide with the TVXL840 and is shown in Fig. C3. The trapped compression ratios for both engines are about 7 which makes it simple to scale the domain of the pressure-volume diagram.
Figure C3: Pressure-Volume Relationship for the TVXL840 Operating at 3000 rpm (Estimated from Experimental Data from a Similar Engine at Wide Open Throttle)

Based on the estimated p-v diagram shown in Fig. C3, the corresponding piston thrust forces are presented in Fig. C4. As shown in the figure, the maximum thrust forces on the piston occur slightly after top-dead-center. The maximum forces on the major thrust side of the piston are slightly greater than three times those obtained on the minor thrust side.
Figure C4: Estimated Piston Thrust Forces Produced During the Two-Cycle Engine Combustion Process at 3000 rpm.

The lubrication regime is dictated by the sliding speed and the load carried through the contact region, in addition to the viscosity of the lubricant provided to the system. Figure C5 is a graphical representation of the sliding speed divided by the thrust forces of the piston. As shown in the figure, the combination of high thrust forces and slow sliding speeds just after top dead center, produce very low values of speed/load, indicative of a very severe boundary lubrication regime. Although the theoretical hydrodynamic film thickness also goes to zero at bottom-dead-center, the thrust loads on the piston are very low at this point, and the
piston moves from the major thrust to the minor thrust side of the cylinder at bottom-dead center.

![Estimated Piston Speed / Thrust Load Relationship](image)

**Figure C5:** Calculated Piston Speed / Thrust Load Relationship

It is clear from Fig. C5 that the piston must undergo boundary lubrication conditions at least when reaching the two ends of its stroke, and this is notably much more severe near top-dead-center. The possibility of a hydrodynamic regime being reached during mid-stroke not only depends on the viscosity of the lubricant being used in this case, but also on an adequate amount of lubricant being supplied to the contact region. At bottom-dead-center in Fig. C5, the piston speed drops to zero and a speed/load ratio becomes zero/zero. However, there are crankcase pressures that have not been accounted for which produce a force

APPENDIX C 216
on the piston in the negative x direction as labeled in Fig. C1. Since the piston speed goes through zero at BDC, the value of zero appears at 180 degrees on Fig. C5. It should not be misinterpreted, however, because this is not a severe lubrication regime due to the very low thrust forces.
VITA

The author was born on March 9, 1967 to Mr. L. Warren Patterson and Mrs. Ruth L. Patterson. During the years 1985 to 1987, he worked two years of active duty in the United States Army. He earned a Bachelor of Science Degree in Mechanical Engineering from Rochester Institute of Technology and graduated with high honors in May of 1993. He began working towards a Master of Science Degree in Mechanical Engineering at Virginia Polytechnic Institute and State University in August of 1993. Upon completion of his degree requirements, he will work for the Robert Bosch Corporation in Charleston, South Carolina.

[Signature]