



Catalysis of sunflower oil polymerization in a diesel lubrication system  
by Rajkumar Raman

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in  
Chemical Engineering  
Montana State University  
© Copyright by Rajkumar Raman (1989)

**Abstract:**

Oxidative addition polymerization of lubrication oil contaminated with sunflower oil diesel fuel was investigated in laboratory apparatus simulating conditions prevailing in a diesel engine crankcase. Primary research objectives were characterization of the catalytic roles of engine wear metals and testing of chemical additives which might suppress polymerization.

Of the common wear metals in a diesel lubrication system, only copper displays a significant catalytic role for sunflower oil polymerization. Catalysis is dominated by dissolved copper species. The extent of oxidation of the metallic copper surface was determined to be critical in determining the extent of copper dissolution.

Several commercial metal catalyst deactivators were investigated in this study. N,N'-disalicylidene 1,2-propane diamine (NNPD) was moderately effective in retarding polymerization, especially during the initiation phase, but its mechanism of action appeared to be more as an antioxidant than as a metal deactivator.

Attempts to reverse or inhibit copper catalysis by using excessive copper concentrations or adding polar acids to oil mixtures fail to succeed in any measure. However, all additive trials performed in this study were clouded by the unknown, proprietary commercial additives present in the diesel lubrication oils.

CATALYSIS OF SUNFLOWER OIL POLYMERIZATION  
IN A  
DIESEL LUBRICATION SYSTEM

by  
RAJKUMAR RAMAN

A thesis submitted in partial fulfillment of the  
requirements for the degree of

Master of Science  
in  
Chemical Engineering

MONTANA STATE UNIVERSITY  
Bozeman, Montana

January 1989

Maia  
N378  
R/415

APPROVAL

of a thesis submitted by

Rajkumar Raman

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citation, bibliographic style and consistency, and is ready for submission to the College of Graduate Studies.

Dec 20, 1988  
Date

D. L. Shaffer  
Chairperson, Graduate Committee

Approved for the Major Department

Dec 20, 1988  
Date

John T. Sears  
Head, Major Department

Approved for the College of Graduate Studies

January 26, 1989  
Date

Henry Parsons  
Graduate Dean

## STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a master's degree at Montana State University, I agree that the Library shall make it available to borrowers under rules of the Library. Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgement of source is made.

Permission for extensive quotation from or reproduction of this thesis may be granted by my major professor, or in his absence, by the Dean of Libraries when, in the opinion of either, the proposed use of the material is for scholarly purposes. Any copying or use of the material in this thesis for financial gain shall not be allowed without my permission.

Signature Rajkumar Raman

Date December 13, 1988

## ACKNOWLEDGEMENTS

I would like to thank the faculty and staff of the Department of Chemical Engineering at Montana State University for their continued support and assistance. I am thankful to Dr. Paul W. Jennings of the Department of Chemistry at Montana State University and Mr. Sid Schiff of Phillips Petroleum Company for their valuable recommendations.

Above all, I would sincerely like to thank my research advisor, Dr. Daniel L. Shaffer, for his much wanted guidance and encouragement. It is impossible to express my feeling of gratitude in words, for such has been the nature of his help throughout the course of this research project.

## TABLE OF CONTENTS

	Page
APPROVAL .....	ii
STATEMENT OF PERMISSION TO USE .....	iii
ACKNOWLEDGEMENTS .....	iv
TABLE OF CONTENTS .....	v
LIST OF TABLES .....	vi
LIST OF FIGURES .....	vii
ABSTRACT .....	ix
INTRODUCTION .....	1
THEORY .....	5
General Background .....	5
Oxidative Polymerization .....	6
Transition Metal Catalysis .....	10
Chelation .....	14
RESEARCH OBJECTIVES .....	17
EXPERIMENTAL .....	19
Apparatus and Procedures .....	19
Materials .....	25
RESULTS AND DISCUSSION .....	27
SUMMARY .....	68
CONCLUSIONS .....	70
SUGGESTIONS FOR FUTURE RESEARCH .....	72
REFERENCES .....	73

## LIST OF TABLES

Table		Page
1.	Atomic emission results (ppm) for the effect of oxygen and nitrogen on copper dissolution .....	34
2.	Dissolved metal concentrations (ppm) at the beginning and the end of a standard run ....	35
3.	Effect of 1.0% NNPD addition on the rate of dissolution of copper species .....	48
4.	Dissolved metal concentrations (ppm) of old and new commercial lubricating oils .....	51
5.	Effect of Copper foil exposure time on the dissolution of copper species .....	53

## LIST OF FIGURES

Figure		Page
1.	Reaction Kettle .....	20
2.	Oil Bath and Reaction Kettle .....	22
3.	Oil Bath and Operating Diagram .....	24
4.	Kinematic viscosity versus exposure time for commercial lubricating oil contaminated with 5% sunflower oil under standard conditions .....	29
5.	Kinematic viscosity versus exposure time for Runs 3 and 4 conducted with the addition of Lubrizol 5955-A once and twice respectively ..	31
6.	Kinematic viscosity versus exposure time for three different engine wear metals compared against a copper run and a no-copper run .....	33
7.	Kinematic viscosity versus exposure time for the addition of 1.0% ZDTP every eight hours ..	37
8.	Kinematic viscosity versus exposure time for Run 12 conducted with a dissolved copper concentration of 0.1 gmol/l .....	39
9.	Kinematic viscosity versus exposure time for three runs conducted with different initial additions of NNPD .....	40
10.	Kinematic viscosity versus exposure time showing the effect of addition of 0.50% NNPD initially (Run 13) and every 4 hours (Run 16).	42
11.	Kinematic viscosity versus exposure time showing the effect of 1.0% NNPD on dissolved forms of copper species .....	45
12.	Kinematic viscosity versus exposure time showing the effect of 1.0% NNPD addition at the start of Runs 14 and 19 in presence and absence of copper respectively .....	47

13. Kinematic viscosity versus exposure time showing the effect of copper foil removal after 4 hours in Run 22 ..... 50
14. Kinematic viscosity versus exposure time for the new stock of commercial lubricating oil .. 52
15. Kinematic viscosity versus exposure time showing the effect of copper foil removal at different times ..... 54
16. Kinematic viscosity versus exposure time showing runs made by Rewolinski [9] under standard conditions and with the addition of phosphoric acid ..... 56
17. Kinematic viscosity versus exposure time showing the effect of addition of 1.0% lauric acid at the start of Run 28 ..... 58
18. Kinematic viscosity versus exposure time showing the effect of copper foil immersed in NNPd for 11 hours at room temperature and then used in a standard run ..... 59
19. Kinematic viscosity versus exposure time showing the effect of oxidized copper foil obtained from a standard run and used in Run 30 as against a copper foil subjected to 33.5 hours of oxidation in an atmospheric oven and used in Run 31 ..... 62
20. Kinematic viscosity versus exposure time showing the effect of copper foil surface subjected to three different treatments ..... 64
21. Kinematic viscosity versus exposure time showing the effect of a copper foil subjected to prior nitrogen percolation under standard conditions ..... 67

## ABSTRACT

Oxidative addition polymerization of lubrication oil contaminated with sunflower oil diesel fuel was investigated in laboratory apparatus simulating conditions prevailing in a diesel engine crankcase. Primary research objectives were characterization of the catalytic roles of engine wear metals and testing of chemical additives which might suppress polymerization.

Of the common wear metals in a diesel lubrication system, only copper displays a significant catalytic role for sunflower oil polymerization. Catalysis is dominated by dissolved copper species. The extent of oxidation of the metallic copper surface was determined to be critical in determining the extent of copper dissolution.

Several commercial metal catalyst deactivators were investigated in this study. *N,N'*-disalicylidene 1,2 propane diamine (NNPD) was moderately effective in retarding polymerization, especially during the initiation phase, but its mechanism of action appeared to be more as an antioxidant than as a metal deactivator.

Attempts to reverse or inhibit copper catalysis by using excessive copper concentrations or adding polar acids to oil mixtures fail to succeed in any measure. However, all additive trials performed in this study were clouded by the unknown, proprietary commercial additives present in the diesel lubrication oils.

## INTRODUCTION

In the modern world of today, transportation plays an important role in the overall economic growth of any nation. Petroleum possesses the potential of being able to serve as a backbone to this progress. With the rise of crude oil costs in the early 1970's, efforts were made to search for alternate sources of liquid fuel.

Vegetable oils, being a replenishable source of energy, have attracted the attention of a number of researchers [1-8]. The fact that calorific values of plant oils are comparable to diesel fuel, posed them as a possible substitute. However, when used under standard operating conditions of a diesel engine, these oils tend to contaminate and thicken the lubricating oil system into a highly viscous mass [7].

In a diesel engine uncombusted fuel experiences a high temperature in the combustion chamber and a lower temperature in the engine crankcase. When vegetable oil is used as diesel fuel, a small part of the fuel remains uncombusted and seeps into the crankcase. Over a period of time the quantity of this unconsumed fuel in the crankcase increases. The lubricating oil/vegetable oil mixture thickens over a period of time making it impossible for the efficient working of the engine. This problem is related

to the structural chemical differences between vegetable oils and diesel fuel.

Extensive research has been and is being conducted to tackle this problem in this laboratory. The first step was to understand the various factors which might affect the thickening of the mixture. An experimental setup was constructed in order to study the various parameters. In order to simulate the conditions of a diesel engine, certain standard conditions had to be established. These may be summarized as temperature, metal catalyst concentration and chemical environment. Rewolinski [9] chose 150 C as a rough average temperature encountered by the oil as it travels through the combustion chamber and the engine crankcase. In a laboratory apparatus designed to simulate conditions of a diesel crankcase, he found that oxygen strongly influenced the thickening or polymerization of sunflower oil mixed with lubricating oil, while nitrogen did not. He also found that the rate of viscosity rise increased with increase in the concentration of vegetable oil in lubricating oil. In order to get a measurable viscosity rise within a reasonable period of time, Rewolinski standardized the oxygen flow rate percolating through the simulation apparatus to be 2.0 ml/sec and the concentration of vegetable oil to be 5.0 weight percent sunflower oil.

Jette [10] focussed his research on the role of copper as an important engine wear metal in the system. This metal was observed by Rewolinski to be more important as a polymerization catalyst than iron, another common engine wear metal. Jette found that copper was most active catalytically when present in a soluble form in the reactant mixture. This soluble form(s) was a result of copper species dissolved from a strip of copper foil present in the reactant mixture. He also found that copper acetylacetonate (CuAcAc) was effective in imitating closely the catalysis of the dissolved copper species from the immersed foil strip. He used copper foils of different sizes and found the viscosity rise due to polymerization increasing with increase in the size of the foil up to a maximum. A standard size of 2.0 cm X 5.0 cm was established for the metal foil. The probability of unwanted metal contamination was minimized by keeping the reactant mixture with the foil in a glass reactor.

Dutta [11] studied the mechanism of lubricating oil degradation in the presence of sunflower oil. He investigated the polymerization in hydrocarbon basestock oil as well as commercial lubricating oil. He primarily dealt with basestock oil to avoid the problem of the 'additive package' which is present in any commercial lubricating oil. This package typically contains numerous

chemical compounds whose chemistry is withheld by the suppliers as proprietary information.

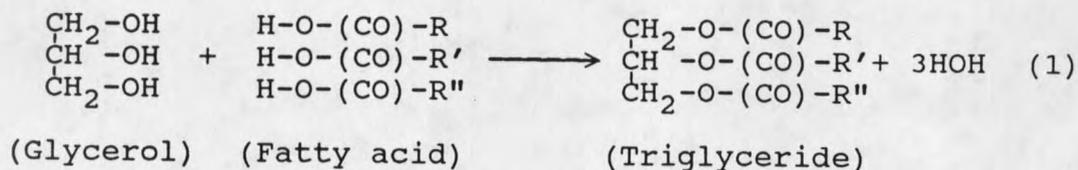
Thus, with this much prior knowledge, research on this lap of the project moved on to testing the inhibition and influence of copper and other important engine wear metals like lead, aluminium and silver, with a view to understanding the mechanism of catalysis in the sunflower oil/lubricating oil polymerization.

## THEORY

General Background

Vegetable oils in general are structurally different from diesel fuels. The former possess a high degree of unsaturation by way of double bonds between two adjacent carbon atoms. They therefore have a tendency to be attacked by oxygen and undergo addition polymerization through a free radical mechanism. Oxygen may also induce cleavage on a vegetable oil molecule to form aldehydes and ketones. Diesel fuels on the other hand primarily contain straight chain paraffins and aromatic hydrocarbons. As a result these fuels show considerable resistance towards oxidation.

Vegetable oil molecules are hydrophobic in nature. They predominantly contain glyceryl esters of fatty acids, which are known as triglycerides. These esters may be formed by reacting a glycerol molecule with three molecules of fatty acids:



R, R' and R'' symbolize the even numbered hydrocarbon chains of fatty acids with a typical range of 16-22 carbons in length. Typically, these chains are different in length as well as in the degree of unsaturation. A triglyceride molecule is made up of a glyceryl portion ( $C_3H_5-$ ) with a molecular weight of 41 and the remaining fatty acid units ( $RCOO-$ ) having a molecular weight range from 600 to over 950. These fatty acid units can contribute 96% of the total weight of the triglyceride molecule and therefore greatly influence its physical and chemical properties [12].

Many vegetable oils mostly contain oleic, linoleic and linolenic acids. These acids each have a length of 18 carbon atoms. Sunflower oil has oleic and linoleic acids as its major components. Fuel properties like oxidation resistance are directly related to the fatty acid composition of plant oils. The markedly different composition of vegetable oils suggest their properties to be significantly different from fossil hydrocarbon fuels like diesel.

#### Oxidative Polymerization

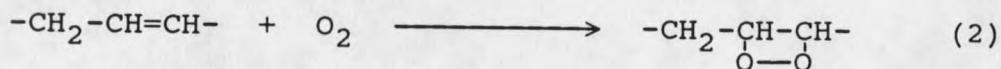
Plant oils undergo degradation by polymerization when exposed to heat and oxygen. The extent of

deterioration is a direct function of the degree of unsaturation of the fatty acid components. Atmospheric oxygen is capable of chemically attacking these oil molecules directly. This complex chemical attack is termed as autoxidation. A high degree of unsaturation in these oil molecules favors free radical polymerization to occur as a consequence of autoxidation. This oxidative degradation can be explained in the following sequential manner [13].

1. An induction period exists wherein no visible physical or chemical changes of the oil are observed. This is a result of natural antioxidants present in the oil being consumed.
2. Initiation of the oxidative chain reaction occurs. Oxygen interacts with the carbon-carbon double bonds forming hydroperoxides.
3. Conjugation of double bonds occurs followed by cis- trans isomerization.
4. Hydroperoxides decompose to form free radicals. The high concentration of these radicals makes the reaction autocatalytic.
5. High molecular weight cross-linked polymers and low molecular weight carbonyl and hydroxy compounds are

formed due to polymerization and scission reactions respectively.

The initiation mechanism of oxidative chain reactions has been a subject of controversy. Initially, this was thought to be due to the attack of oxygen on the carbon-carbon double bonds of the unsaturated fatty acids forming cyclic peroxides [14]:



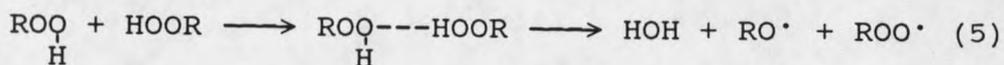
Later it was shown that the initial products contain noncyclic alpha-methylenic hydroperoxides with the double bonds still intact [15]. This suggested the alpha-methylenic carbon-hydrogen bond to be broken. However this bond has an energy of 80 kcal/mole, which is relatively strong when compared to the low availability of energy resources. Researchers have therefore concluded that the oxygen directly attacks the carbon-carbon double bond [16-19].

Autoxidation results in the formation of hydroperoxides, which when formed even in trace amounts act as catalysts. These hydroperoxides are formed as a result of the oxidative attack on the carbon-carbon double bond. As a result, rearrangement of electrons takes place with

the shifting of the double bond. This shifting is referred to as conjugation [17-18]:



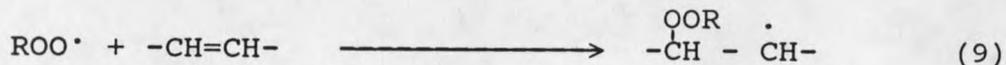
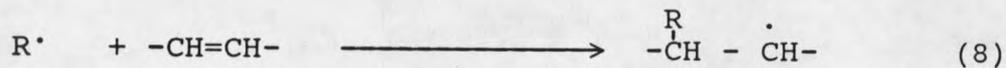
The hydroperoxides so formed may decompose to free radicals [16]:



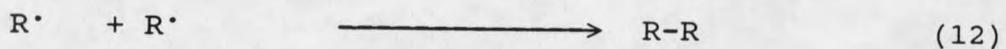
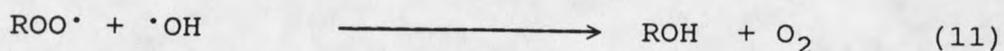
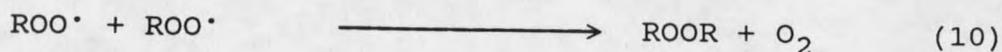
Chain propagation may occur in the following manner :



Free radicals may also attack carbon-carbon double bonds to form larger hydrocarbon free radicals [20]:



Termination reactions generally result in the formation of higher polymers from the constituent free radicals [16,20]:



#### Transition Metal Catalysis

Sunflower oil forms alkyl hydroperoxides in presence of oxygen [11]. Active, soluble forms of copper catalyze this reaction [10]. An extensive literature survey was done in the process of hypothesizing a mechanism by which copper may influence the polymerization. Fortunately, substantial information was obtained with respect to the effect of transition metal complexes in nonpolar solvents and their reaction with alkyl hydroperoxides. Copper being a transition metal (valence states 1 and 2) is in this category with other common metals namely cobalt, manganese and iron.





































































































































