



Vegetable oil dilution of diesel engine lubricating oil  
by Chance Rewolinski

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in  
Chemical Engineering  
Montana State University  
© Copyright by Chance Rewolinski (1985)

**Abstract:**

The lubricating oil environment of a diesel engine operated on vegetable oil fuel was simulated on a laboratory scale to study effects of system parameters on lubricating oil degradation, primarily excessive viscosity increase.

Initial parameters investigated for effect on viscosity increase were temperature, vegetable oil dilution level, catalyst level, and gas flow rate. Viscosity increased more rapidly for higher temperature and higher concentration of vegetable oil. Higher catalyst level accelerated the rate of viscosity increase, with copper showing a much higher catalytic activity than iron. Oxygen was required to obtain a viscosity increase, with higher oxygen flow rates slightly increasing rate of viscosity rise.

Mechanisms of acid and free radical catalysis of polymerization yielding viscosity increase were investigated. Relationship of amount of free acids in the oil to increase in viscosity was investigated by measuring total base number of contaminated lubricating oil. Amount of free acid was varied by addition of phosphoric acid, octadecylamine, and a commercial lubricating oil total base number enhancer. None of these approaches had any significant effect on viscosity increase, indicating that drop in total base number and viscosity increase are not causally related.

Free radical catalysis was investigated by periodic additions of a commercial free radical polymerization initiator to samples of contaminated lubricating oil. Viscosity response from this additive was similar in form and magnitude to that from oxygen, indicating that viscosity increase of contaminated lubricating oil is due to a free radical mechanism.

A single sulfur compound was employed to limit the copper catalyst action by poisoning. A single chelating agent was used to sequester and limit the action of solubilized catalyst. Neither of these approaches reduced the viscosity increase of contaminated lubricating oil.

Degraded lubricating oil samples were tested for lubricity by use of a four-ball wear tester. Lubricity of contaminated, degraded lubricating oil was superior in all cases to uncontaminated, degraded lubricating oil.

VEGETABLE OIL DILUTION OF DIESEL ENGINE  
LUBRICATING OIL

by

Chance Rewolinski

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

of

Master of Science

in

Chemical Engineering

MONTANA STATE UNIVERSITY  
Bozeman, Montana

July 1985

MAIN LIB.  
N378  
R328  
C.2

APPROVAL

of a thesis submitted by

Chance Rewolinski

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.

July 8, 1985  
Date

D. L. Shaffer  
Chairperson, Graduate Committee

Approved for the Major Department

July 8, 1985  
Date

John T. Sears  
Head, Major Department

Approved for the College of Graduate Studies

7-10-85  
Date

W. P. Malone  
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 acknowledgment 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 Chasice Rowolinski

Date July 1, 1985

## TABLE OF CONTENTS

	Page
APPROVAL .....	ii
ACKNOWLEDGMENTS .....	iii
TABLE OF CONTENTS .....	iv
LIST OF TABLES .....	vi
LIST OF FIGURES .....	viii
ABSTRACT .....	x
INTRODUCTION .....	1
General Considerations .....	1
Economic Considerations .....	2
Technical Problems .....	3
PREVIOUS RESEARCH .....	7
RESEARCH OBJECTIVE .....	14
MATERIALS AND METHODS .....	15
Materials .....	15
Equipment .....	15
Experimental Procedure .....	20
RESULTS AND DISCUSSION .....	22
Effect of System Variables on Viscosity .....	22
Effect of System Variables on Total Base Number .....	30
Acid Catalysis .....	34
Free Radical Catalysis .....	46
Sulfur Compounds .....	49
Chelating Agent .....	51
Wear Preventative Properties .....	51
CONCLUSIONS .....	55
RECOMMENDATIONS FOR FUTURE RESEARCH .....	57

TABLE OF CONTENTS—Continued

	Page
BIBLIOGRAPHY .....	58
APPENDICES .....	62
Appendix A—Engine Manufacturer's Association Screening Test .....	63
Appendix B—Tables of Results and Run Conditions .....	65

## LIST OF TABLES

Appendix Tables	Page
1. Run 1 Conditions .....	66
2. Run 1 Results .....	66
3. Run 2 Conditions .....	66
4. Run 2 Results .....	67
5. Run 3 Conditions .....	67
6. Run 3 Results .....	67
7. Run 4 Conditions .....	68
8. Run 4 Results .....	68
9. Run 5 Conditions .....	68
10. Run 5 Results .....	69
11. Run 6 Conditions .....	69
12. Run 6 Results .....	69
13. Run 6 Results .....	70
14. Run 7 Conditions .....	70
15. Run 7 Results .....	70
16. Run 7 Results .....	71
17. Run 8 Conditions .....	71
18. Run 8 Additive Amounts .....	71
19. Run 8 Results .....	72
20. Run 8 Results .....	72
21. Run 9 Conditions .....	72

Appendix Tables	Page
22. Run 9 Additive Amounts .....	73
23. Run 9 Results .....	73
24. Run 10 Conditions .....	73
25. Run 10 Additive Amounts .....	74
26. Run 10 Results .....	74
27. Run 10 Results .....	74
28. Run 11 Conditions .....	75
29. Run 11 Results .....	75
30. Run 12 Conditions .....	76
31. Run 12 Additive Amounts .....	76
32. Run 12 Results .....	76
33. Run 12 Results .....	77
34. Run 13 Conditions .....	77
35. Run 13 Additive Amounts .....	78
36. Run 13 Results .....	78
37. Run 13 Results .....	79
38. Additional Total Base Number Results .....	79
39. Wear Test Results .....	79

## LIST OF FIGURES

Figures	Page
1. Experimental apparatus for oil degradation. ....	16
2. Individual test cell. ....	16
3. Detail of four-ball wear tester. ....	19
4. Viscosity vs. time for 0, 20, and 100 cm copper-iron catalyst and 2000 ml/hr oxygen. ....	23
5. Viscosity vs. time for 20 cm copper and iron catalysts and 2000 ml/hr oxygen. ....	25
6. Viscosity vs. time for 0 and 20 cm copper-iron catalyst and 4000 ml/hr oxygen. ....	26
7. Viscosity vs. time for 0, 1, 3, 7, and 9 wt. % sunflower oil, with 20 cm copper-iron catalyst and 2000 ml/hr oxygen. ....	28
8. Viscosity vs. time for 5 wt. % linoleic and oleic safflower oil, with 20 cm copper-iron catalyst and 2000 ml/hr oxygen. ....	29
9. Viscosity vs. time for 120 C, with 0 and 20 cm copper-iron catalyst, and 2000 and 4000 ml/hr oxygen. ....	31
10. Total base number vs. time for 20 cm copper-iron catalyst and 2000 ml/hr oxygen. ....	32
11. Total base number vs. time for 20 cm copper-iron catalyst and 4000 ml/hr oxygen. ....	33
12. Total base number vs. time for no catalyst and 2000 ml/hr oxygen. ....	35
13. Viscosity vs. total base number for 20 cm copper-iron catalyst and 2000 ml/hr oxygen. ....	36
14. Viscosity vs. total base number for 20 cm copper-iron catalyst and 4000 ml/hr oxygen. ....	37
15. Total base number vs. time with and without octadecylamine, with 20 cm copper-iron catalyst and 2000 ml/hr oxygen. ....	41

Figures	Page
16. Total base number and viscosity vs. time for periodic additions of octadecylamine, with 20 cm copper-iron catalyst and 2000 ml/hr oxygen .....	42
17. Total base number and viscosity vs. time for periodic additions of Amoco 9231, with 20 cm copper-iron catalyst and 2000 ml/hr oxygen .....	44
18. Viscosity vs. time for addition of phosphoric acid, with 20 cm copper-iron catalyst and 2000 ml/hr oxygen. ....	45
19. Viscosity vs. time for periodic additions of Lupersol 130, with 20 cm copper-iron catalyst and 2000 ml/hr nitrogen .....	48
20. Average scar diameter vs. time for 0 and 5 wt. % sunflower oil, with 20 cm copper-iron catalyst and 2000 ml/hr oxygen .....	53
21. Average scar diameter vs. viscosity for 5 wt. % sunflower oil, with 20 cm copper-iron catalyst .....	54

## ABSTRACT

The lubricating oil environment of a diesel engine operated on vegetable oil fuel was simulated on a laboratory scale to study effects of system parameters on lubricating oil degradation, primarily excessive viscosity increase.

Initial parameters investigated for effect on viscosity increase were temperature, vegetable oil dilution level, catalyst level, and gas flow rate. Viscosity increased more rapidly for higher temperature and higher concentration of vegetable oil. Higher catalyst level accelerated the rate of viscosity increase, with copper showing a much higher catalytic activity than iron. Oxygen was required to obtain a viscosity increase, with higher oxygen flow rates slightly increasing rate of viscosity rise.

Mechanisms of acid and free radical catalysis of polymerization yielding viscosity increase were investigated. Relationship of amount of free acids in the oil to increase in viscosity was investigated by measuring total base number of contaminated lubricating oil. Amount of free acid was varied by addition of phosphoric acid, octadecylamine, and a commercial lubricating oil total base number enhancer. None of these approaches had any significant effect on viscosity increase, indicating that drop in total base number and viscosity increase are not causally related.

Free radical catalysis was investigated by periodic additions of a commercial free radical polymerization initiator to samples of contaminated lubricating oil. Viscosity response from this additive was similar in form and magnitude to that from oxygen, indicating that viscosity increase of contaminated lubricating oil is due to a free radical mechanism.

A single sulfur compound was employed to limit the copper catalyst action by poisoning. A single chelating agent was used to sequester and limit the action of solubilized catalyst. Neither of these approaches reduced the viscosity increase of contaminated lubricating oil.

Degraded lubricating oil samples were tested for lubricity by use of a four-ball wear tester. Lubricity of contaminated, degraded lubricating oil was superior in all cases to uncontaminated, degraded lubricating oil.

## INTRODUCTION

### General Considerations

America has enjoyed easy access to inexpensive, convenient fuels for a number of years. Events of the past decade have upset this pattern by causing uncertainties in the continued steady supply of energy, especially liquid fuels. These uncertainties include foreign control of a large part of current crude oil reserves and the realization that these resources are finite and nonrenewable. These conditions have prompted various researchers and government agencies to look for alternative sources of fuel.

Biomass fuels represent one source of renewable alternate energy. Falling within this broad class are vegetable oils which are candidates for replacing diesel fuel. They were among the first fuels used by Rudolph Diesel in his original engine around the turn of the century, and were later used in a farm demonstration by the Ford Motor Corporation at the 1934 World's Fair in Chicago [1]. Compared with other alternate fuels they are easy to process and handle. Although they may become replacements for diesel fuel if technical and economic obstacles are overcome, vegetable oils cannot now be produced in sufficient quantities to replace all the diesel fuel currently in use. They could, however, be utilized to ease spot shortages which occur [2].

One location where occurrences of spot shortages would be critical is the farming industry where the timeliness of the fuel supply could determine the farm's success or failure. A number of oilseed crops are currently grown on farms. If the seeds are to be processed for oil, an oil extraction plant is often located within a reasonable distance, so the system is already partially in place to guarantee farmers access to the fuel they need. To maintain this supply about 10 to 15 percent of the cultivated farmland would have to be

devoted to this use [2]. This may seem excessive, but in 1919 when the agricultural acreage used to produce feed for horses and mules was at its peak, 22 percent of harvested crop land was used for this "fuel source" [3].

The particular oilseed crop chosen would depend on locale but should have a high oil yield per pound of seed and high crop yield per hectare, and have useful side products. Examples of crops suitable for the north central United States and central Canada include sunflower, canola (or rapeseed) and safflower. Sunflower has the advantage that it may be grown on marginal lands with a minimum use of agricultural chemicals although yield may decrease. It is also suitable for most of the continental United States, e.g., Texas, both coasts, and Montana and North Dakota [4]. When grown with normal cultivation practices, sunflower also has a significantly higher energy output/input ratio than other traditional oilseed crops such as soybeans, peanuts and cottonseed [5].

#### Economic Considerations

Economic situations also influence acceptance of vegetable oil as a diesel fuel substitute. Currently, diesel fuel is readily available at about half the price of vegetable oil, but this price differential has steadily decreased over the past eight years. If vegetable oils increase in price at the same rate as inflation, and petroleum prices increase at 2 to 3 percent over inflation, then it will be about 20 years until the prices are comparable [5]. This is a difficult prediction to make as many factors are involved. Widespread use of vegetable oil will only come about when the price of diesel fuel and vegetable oil more closely approach each other. This could come about either by the steady increase in cost as oil reserves are depleted, or by emergency shortfalls caused by political reasons.

### Technical Problems

While economics provides the driving force for adopting a new fuel source, technical problems must also be overcome. Modern high speed diesel engines currently used in agriculture and transportation have been specifically designed to run on commercially available diesel fuel which is in turn refined to close specifications.

When a new fuel is used in place of the one for which the engine is designed, technical problems abound. Two methods of solution present themselves. One is to modify the engine mechanically (i.e., design the engine for the new fuel). The second is to modify the fuel and method of engine operation without making any design changes in the engine. In the United States the emphasis has been on the latter since the strategy of using vegetable oils is to supplement diesel fuel in times and areas of shortage rather than replacing diesel fuel entirely. Countries with less secure energy sources may choose the former approach. Brazil, for instance, has a national goal of replacing 16 percent of its diesel consumption with vegetable oil by 1985 [6]. Caterpillar has extended their warranty on some engines operating on up to 10 percent vegetable oil, but only in Brazil [2].

The technical problems of using vegetable oil fuels in diesel engines have been known for years. Since there was no economic incentive for their solution in the late 1920s, these problems still exist today. Problems include:

1. Difficulty with cold weather fuel handling, starting and operation. Vegetable oil is more viscous than diesel fuel, causing handling problems at low temperatures. For example, the pour point of sunflower oil is about  $-9\text{ C}$ , while that of diesel fuel is  $-18\text{ C}$  [7]. Vegetable oil is also less volatile than diesel fuel so it does not vaporize as readily as diesel fuel in a cold engine. The flash point of diesel fuel is typically about  $70\text{ C}$ , while the flash point for vegetable oils is typically about  $320\text{ C}$  [5].

2. Plugging and gumming of fuel lines, filters and injectors. In their crude state vegetable oils contain phosphatide gums, waxes and solid fines. Removal of these by refining, including dewaxing, degumming and filtering through a 4 micron filter substantially reduces these problems. Oil is often "alkali refined" where the degumming is done with an alkaline wash to neutralize the corrosive free fatty acids. If the oil were subsequently bleached and deodorized it would meet edible oil specifications [5].

3. Coking of injector nozzles, and carbon deposits and varnish on pistons and heads. This is probably also due to the low volatility of the vegetable oil, combined with the polyunsaturated nature of the vegetable oil. Since the oil does not completely vaporize, even in a warm engine, it coats the lining of the combustion chamber where it is able to polymerize, forming varnish and carbon deposits. Although diesel fuel may also cause deposits in the combustion chamber they are easily displaced during normal engine operation [8]. The deposits from vegetable oil fuels are very persistent. They have been shown to cause catastrophic failure of the engine in as little as 87 hours in a direct injection diesel engine operated on pure vegetable oil [9].

When vegetable oil is used in an indirect injection diesel engine, these deposits are almost eliminated. Some indirect injection engines have been successfully operated on pure sunflower oil for over 2300 hours at 70% load [2]. This is still much less than the expected 10,000 hour life of a diesel truck engine before a major overhaul [10].

4. Lubricating oil dilution and failure. This also seems due to the low volatility and polyunsaturated nature of the vegetable oil. Unburned or partially burned liquid fuel blows by the piston rings where it dilutes the lubricating oil. As the concentration builds up, the vegetable oil polymerizes and the lubricating oil thickens. Serious dilution can take place rapidly when the engine is operated at low rpm while under load. This problem is usually reduced when an indirect injection engine is used [2].

5. Excessive engine wear. This is caused by coking and varnish, degraded lubricating oil, and by any free fatty acids which are formed by hydrolysis of the vegetable oil during storage and combustion. Fatty acids are very corrosive at temperatures above 150 C [2].

Some of these problems could be reduced or eliminated by use of indirect injection engines. This is not a viable alternative, at least for the short term strategy in the United States, since most of the engines currently in use in agriculture and transportation are direct injection. Hence, to solve these problems work must be done to either modify the fuel or to make minor mechanical modifications of the direct injection engines currently in place.

Attempts to modify the fuel include transesterification, cracking, and use of fuel additives, with most researchers looking at transesterification. This process replaces the glycerol with three separate molecules of alcohol such as methanol or ethanol. As long as the transesterification yield is greater than 90 percent this process substantially reduces the coking and deposit problem discussed above [11]. Cold weather handling is still a problem as transesterification generally raises the pour point of the fuel. Lubricating oil dilution also continues to occur.

There are two primary criticisms of transesterification. First, it adds cost to a fuel already priced at twice the cost of diesel fuel. Second, the intent of using vegetable oil fuels to fill in during spot shortages and emergency situations will not be met since processing equipment for transesterification would need to be assembled. This applies to both farm scale and larger scale (cooperative and commercial) operations.

A number of commercially available fuel additives have been tested for elimination of the coking problem. Only a few have been found which show promise of reducing the coking problem. These will be subject to further testing [12].

Several minor engine modifications have been tried to reduce the coking problem. Work has focused on the injectors, since that is the location where coking is first noted. Modifications include injector retraction, water cooling of the injectors, and teflon coating of the injectors. None of these modifications had any effect [12].

Of the problems discussed above, lubricating oil thickening by dilution with vegetable oil is particularly suitable to laboratory study by simulation of the crankcase environment. Simulation allows more precise control of individual variables than is possible with actual engine tests. Thus, the particularly serious problem of lubricating oil failure could be at least partially quantified without recourse to expensive engine tests.

## PREVIOUS RESEARCH

Lubricating oil dilution by vegetable oil fuel is a commonly reported problem which occurs under a number of different engine test conditions. It occurs most rapidly under low speed and partial load which are the conditions favoring incomplete combustion [2, 13]. It is generally considered to occur more readily in direct injection engines, but is also reported in indirect injection engines which are usually thought to be somewhat immune to the problems caused by use of vegetable oil fuels.

Peterson et al. [2] report 160 percent increase in lubricating oil viscosity over a 100 hour oil change interval when an indirect injection engine is operated with pure linoleic safflower oil. The engines were operated at wide open throttle with the load cycled on and off at 15 minute intervals. The Engine Manufacturers Association [14] considers that a 50 percent increase in lubricating oil viscosity over the length of an oil change is an indication of test failure. The Engine Manufacturers Association standardized test for alternate fuels is shown in Appendix A.

Yarbrough et al. [15] report a rapid buildup of total solids in the lubricating oil of an indirect injection engine operated on pure degummed, dewaxed sunflower oil under full rated load at constant rpm. Lubricating oil would need to be changed two to three times more frequently than recommended by the engine manufacturer to maintain suitable lubricating oil quality.

Work has been done by several researchers in simulating the lubricating oil environment within the engine. Unless otherwise noted, lubricating oil tested by cited researchers is API CD SAE 30. Bauer et al. [16] used ASTM D.943, "Oxidation Characteristics of

Inhibited Steam Turbine Oils," as the basis for test development. Lubricating oil was intentionally contaminated with soybean oil and then exposed to heat, air, agitation, and various metals of engine construction. Samples were heated in a constant temperature oil bath. Sample containers were glass test tubes. Air was supplied through 2 mm I.D. glass tubes from high pressure cylinders. Flow rates of 1 l/hr gave sufficient agitation.

Oil viscosity was measured to determine thickening. Copper and iron together, molybdenum, manganese, chromium, and nickel were tested to determine effect on rate of viscosity increase of 10 percent soybean oil in lubricating oil. The rate of viscosity increase with copper and iron was an order of magnitude greater than the other catalysts. The range of soybean oil dilution levels tested was 0% to 10%. There was little difference in the rate of viscosity increase through 1.0%, with the rate at 3.0% slightly higher, and 10.0% significantly higher. Tests were run at 100 C and 120 C. The rate of viscosity increase was significantly higher at the higher temperature.

Adams et al. [17] tested a range of soybean oil dilution levels from 0% to 50%. Water levels from 1% to 9% were tested to simulate condensation in the crankcase. Test samples were held at 85 to 95 C, and agitated by aeration. Catalytic amounts of cobalt and manganese were tested. Viscosity increase was independent of amount of water present. No significant viscosity increase occurred in 240 hours without the added metal, but samples containing 10.0% or more soybean oil became highly viscous in 94 hours with addition of manganese and cobalt.

Engine tests with a direct injection engine were also performed by Adams and co-workers. The test schedule was based on the EMA's recommended test method. Lubricating oil viscosity measured at 75 C increased 385% after 200 hours engine operation on a 1:1 blend of soybean oil and diesel fuel. Even though lubricating oil viscosity increased only 3.2% at 100 hours of engine operation, the level of lubricating oil dilution was judged

as unacceptable by the authors due to the potential for catastrophic thickening of the lubricating oil.

Lubricating oil deterioration when contaminated with methyl esters of soybean and babassu oils was tested in a MacCoull apparatus by Siekman et al. [18]. A MacCoull apparatus, which is used to determine the corrosional effect of a test fluid on a bearing material, consists of a rotating conical shaft submerged in the oil sample to be tested. A stationary shaft supports the rotating cone with a test bearing. Catalyst is added in the form of copper baffles. Oil is sprayed off the conical shaft and runs down the side of the glass beaker containing the test apparatus and oil sample. The sample is aerated by diffusion through holes in the cover of the beaker.

Soybean oil is polyunsaturated, with an iodine number of 128 and babassu oil is essentially saturated, with an iodine number of 17. Iodine number is a measure of vegetable oil or fatty acid unsaturation, and is directly proportional to the degree of unsaturation. Dilution levels were 5.0%, 10.0%, and 20.0%. Test duration was 8 hours in all cases, and also 24 hours with 10.0% soybean oil ester. Temperatures tested were 150 C and 170 C. Kinematic viscosity at 40 C and total base number (TBN) by ASTM D 2896, "Total Base Number of Petroleum Products by Potentiometric Perchloric Acid Titrations," were evaluated as test parameters. Reduction in TBN, which indicates a drop in alkaline reserve and a rise in amount of free acids, rose with increasing contamination with ester. The effect is more pronounced with the soybean ester than with babassu ester, especially at higher dilution rates and higher temperature.

By assuming an iodine number of zero for the lubricating oil, and calculating the iodine number of the contaminated lubricating oil sample, a straight-line relationship is shown between the reduction in TBN and the amount of double bonds introduced. This indicates that acid-forming oxidation is taking place largely at points of unsaturation.

The viscosity, TBN, and percent ester (analyzed by infrared spectroscopy) were evaluated during the 24 hour test. The viscosity increased fairly quickly, doubling in 16 hours, and leveling off at 24 hours with total increase of 156%. The reduction in TBN was fairly constant with a slight leveling off at 24 hours, with a total drop of 44%. The drop of 16% in ester concentration during this time period was attributed to evaporation and reaction of the ester. The flash point of soybean oil methyl ester (methyl soyate) is 178 C [19].

Bench and vehicle testing were also done by the Siekman group using indirect injection engines fueled with pure methyl soyate. In both cases, the lubricating oil was intentionally contaminated with 5% methyl soyate. In a bench test of 100 hours, the viscosity increased to 5 times the initial value, while the TBN dropped only slightly. The soot content of the oil increased to 4.0%. The increase in viscosity was attributed to this, rather than breakdown in the antioxidant capacity of the oil. The ester content of the lubricating oil dropped from 5.2% initially to 3.2% after 75 hours. In a reference test using methyl soyate as fuel, but with uncontaminated lubricating oil, the ester content never exceeded 1.0%.

Vehicle testing was done under actual driving conditions of a light duty delivery van, with oil change intervals of 7500 km. Viscosity and TBN stayed essentially normal, with soot increasing only one tenth as much as in the bench tests.

Laboratory oxidation tests and bench engine tests were performed by Blackburn et al. [20]. The laboratory test, ASTM D 2272, "Continuity of Steam-Turbine Oil Oxidation Stability by Rotating Bomb," used a bomb to measure time required for the oil to react with a given volume of oxygen at 150 C. Tests were done on 20 lubricating oils for gasoline and diesel engines which were diluted with ethyl soyate at a level of 17%. Oxidation life of uncontaminated oil ranged from 60 to 250 minutes, while the oxidation life of contaminated oil ranged from 20 to 75 minutes.

Bench testing was done with a direct injection engine run 10 hours per day at full rated load and speed using ethyl soyate fuel. Six different lubricating oils, all SAE 30, five API CD, one API CC were tested. Samples of lubricants were subjected to conventional used oil analyses, including TBN, viscosity and loss of dispersancy by blotter spot test. Concentration of ester was determined by infrared analysis. Tests were terminated when lubricant breakdown based on loss of dispersancy occurred. In all cases, lubricating oil viscosity decreased to a minimum of about 50 percent of initial viscosity at 40 hours followed by rapid viscosity increases at 60 to 70 hours. Tests were terminated at 60 to 75 hours. Ester content of the lubricating oil increased to about 20% at 60 hours. At this time, the concentration of ethyl linolate and ethyl linolenate dropped markedly, indicating depletion of the antioxidant additives in the oil. The TBN also fell to unacceptable limits indicating increasing acid content of the oil, while insolubles and wear metals (copper, lead, and iron) in the oil increased to unacceptably high values.

Korus et al. [21] examined the effect of three commercial antioxidant diesel fuel additives on oxidative polymerization of pure, high erucic rapeseed oil. Samples were heated to 240 C in open glass beakers in a forced air convection oven. Viscosities increased more rapidly with the additive in all three cases.

Romano [22] used 25 ppm butylated hydroxytoluene (BHT), a commercial food antioxidant, in a 1:1 mixture of lubricating oil and methyl soyate. Samples were degraded by heating to 140 C and aeration with 30 l/hr air. At 100 hours the viscosity of the sample without BHT had risen one and one half times as much as the samples with BHT, while TBN in both samples was below acceptable limits. At 200 hours viscosity of the sample with BHT had risen above that of the sample without BHT. The author concluded that BHT is not a suitable antioxidant for this system.

In a survey article, Wexler [23] reviews the polymerization of drying oils or polyunsaturated vegetable oils. Primary reactions are formation of unsaturated ester hydroperoxides by reaction of the oil with oxygen, the decomposition of these materials to free radicals, and the subsequent crosslinking of the free radicals with other olefins resulting in a chain reaction or polymerization. The oxidative chain reaction is preceded by an induction period when nothing seems to occur. This is often attributed to naturally occurring antioxidants such as tocopherols. Induction periods are still observed in certain cases with material that has been rigorously purified. Hence, induction periods may be an inherent property of the material itself.

Based on radioisotope studies, the initial attack by the oxygen takes place at the double bond during the induction period. This is followed by a steady state period during which the oxygen becomes a hydroperoxide by abstracting a hydrogen from the methylenic carbon. This causes a rearrangement of the double bond to a conjugated system and places the hydroperoxide on a newly formed methylenic carbon. The double bonds are generally unconjugated prior to this reaction. Subsequent polymerization takes place by radical attack at an ethylenic carbon. Chain termination takes place when two radicals react with each other [24].

Although polymerization of neat drying oils proceeds via free radical mechanisms, presence of free acids in the lubricating oil system allows the possibility of cationic or acid catalysis, where an acid attacks the double bond directly, forming a carbonium ion with a single bond. The carbonium ion continues the chain by attacking another double bond. Chain termination can occur by ejection of a proton forming an alkene, or by reaction with an anion [24].

Wexler also discusses metal catalysis of the drying of vegetable oils. There are two groups of metals which increase the drying rate of oils. First are the participating driers which show a definite effect on the drying rate, including cobalt, lead, and manganese

which are the most active, and also cerium, copper, chromium, iron, tin, vanadium, and zirconium: Generally, these metals occur in at least two valences with the higher being less stable. They are susceptible to oxidation from the lower to the higher valence by the hydroperoxides. The second group, which enhances the activity of the members of the first group, is called the promoter catalysts. It includes calcium, zinc, and lead.

The action of the metal is not clear. They may act as oxygen carriers, stabilizing the diradical form of the oxygen. The metal may also attack the double bond directly forming a positively charged radical which would then initiate more conventional products of autooxidation. Lastly, the higher valence metal may directly attack a saturated portion of the oil molecule, abstracting a positively charged hydrogen and leaving a radical.

The valence of the metal affects its catalytic activity. For example, while metallic copper lowered the reaction rate and yield of peroxides of soybean fatty acids, cupric stearate was one of the most effective catalysts for the oxidation of linoleic acid.

Other materials, such as free radical initiators show catalytic activity toward drying oils. Examples of these are organic peroxides such as benzoyl peroxide and azo compounds such as azo-bis-isobutyronitrile. The use of 0.02% of triphenylmethoxy radical reduced the drying time of tung oil from 40 hours to 5 to 10 minutes.

Aldehydes are formed by the decomposition of hydroperoxides. Subsequent oxidation of aldehydes may account for formation of the mono- and dibasic acids reported [23].

## RESEARCH OBJECTIVE

The purpose of this investigation is to examine some of the parameters which affect degradation of lubricating oil contaminated with vegetable oil by use of an apparatus simulating a diesel engine crankcase, and to attempt to elucidate the mechanism(s) of degradation. Parameters to be studied are presence and amount of selected metal catalysts and oxygen, temperature, and level of lubricating oil dilution by vegetable oils. Total base number as it relates to the mechanism of oil degradation will also be studied.

Mechanisms to be studied are acid and free radical catalysis of polymerization of vegetable oil in lubricating oil. Acid catalysis will be studied by altering the total base number. Free radical catalysis will be examined by use of a commercial free radical initiator.

Attempts will be made to limit the action of metal catalysts by poisoning with a sulfur compound and by use of a chelating agent. Wear properties of degraded oil mixtures will also be examined by standard lubricity testing.

## MATERIALS AND METHODS

### Materials

All vegetable oils used were edible grade obtained from Agricom in Berkeley, California. Oils used were sunflower, high oleic safflower, and high linoleic safflower. Lubricating oil was Super HD II low ash MIL-L-2104C API CD SAE 30 manufactured by Amoco Oil Company, obtained under Phillips 66 Oil Company label. All chemicals were reagent grade.

### Equipment

Equipment consisted of the reactor system and analytic apparatus. The reactor system (Figure 1) was contained in a steel tank 11" high by 8" wide by 13" long, insulated with 2½" fiberglass insulation on the sides and ½" fiberboard on the bottom. The tank was filled with paraffin oil to a depth sufficient to immerse the test cells to within one inch of their tops. Bath oil was heated with a Polyscience Model 73 immersion circulating heater. Maximum temperature of the controller was 150 C, precision was 0.02 C, power output was variable from 10 to 1000 watts, and pumping rate was 13 liters per minute. A mercury thermometer accurate to 0.1 C was used to monitor temperature. This thermometer was calibrated to the ice point and boiling point of distilled water.

Gas was delivered from a high pressure cylinder through a single stage regulator to a gas header attached to the side of the oil bath. Attached to the header were 6 needle valves for flow control to the test cells and a pressure gauge to monitor gas pressure in the header. Gas was preheated before being delivered to the header by being passed through a loop of ¼" O.D. copper tubing which was immersed in the oil bath. The header was also insulated.

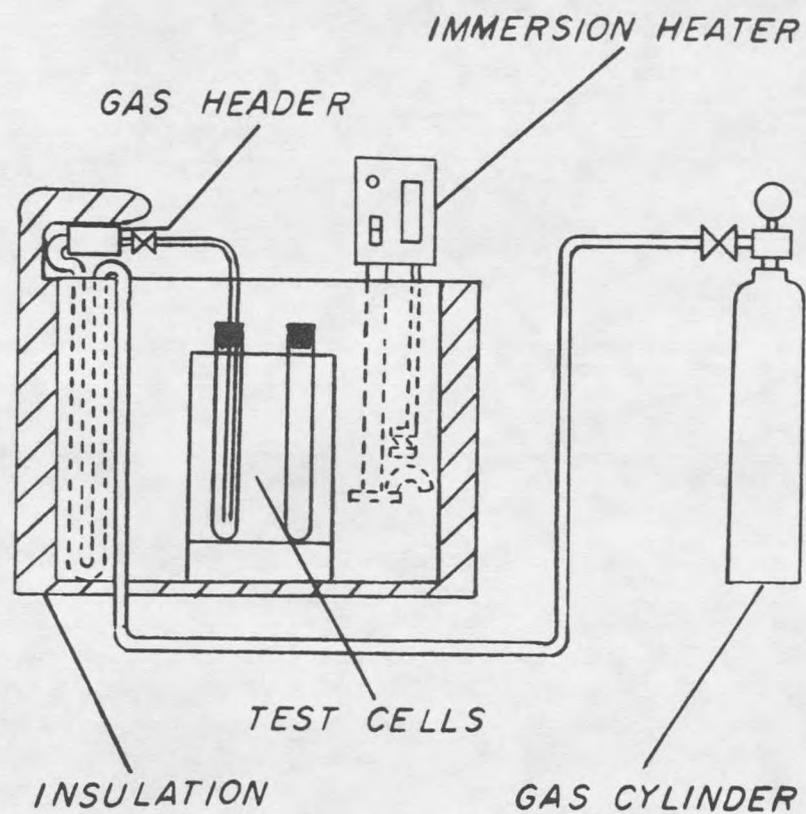


Figure 1. Experimental apparatus for oil degradation.

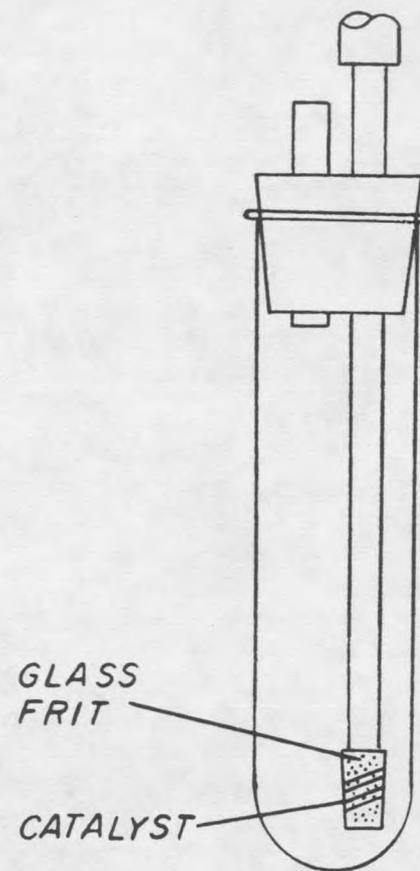


Figure 2. Individual test cell.

A temporary header with two valves was used on several runs. This header was also insulated, and the gas was preheated in a method similar to the permanent header described above.

Test cells (Figure 2) were 1" by 8" pyrex test tubes which held 50 ml sample per cell. The oil bath would accommodate 6 test cells during one run. Gas was delivered to the test cells through  $\frac{1}{4}$ " I.D. silicon rubber tubing. Gas was sparged into the sample through 7 mm glass tubes with fritted glass heads. The glass tubes were held in place with two-hole rubber stoppers so the frit was within 5 mm of the bottom of the test cells. Short pieces of 7 mm glass tubing were inserted in the second hold in the stoppers so a soap bubble flow meter could be attached to the test cells to measure flow rates.

Catalyst was introduced in the form of wire wrapped around the fritted portion of the gas inlet tube. Copper and iron wire were chosen on the basis of ASTM D 943, "Oxidation Characteristics of Inhibited Steam-Turbine Oils" [25], and the work by Bauer et al. [16]. The iron wire was 0.0090" in diameter, with a variation of 1.1% based on four measurements. The copper wire was rectangular in cross section and had an average width of 0.0112" and average thickness of 0.0024", with variations of 28.7% and 3.6%, respectively, based on ten measurements. The ratio of iron to copper surface areas per unit lengths was 1.04. When used together, equal lengths of copper and iron were used. Equal lengths of the two were used in accord with ASTM D 943, even though wear metal analysis of actual used lubricating oil shows a higher level of iron than copper. Prior to use the copper and iron wire were sanded to remove oxide coatings. They were then loosely wound together and cleaned with heptane to remove oil and grease. From this point they were handled with gloves. Runs were made with 0, 20, and 100 cm catalyst.

Two parameters were chosen as measures of oil degradation. Viscosity was chosen since elevated viscosity is the most commonly reported problem with lubricating oil used

in this service. It is relatively easy to measure and is nondestructive. It provides fairly reliable information about the degree of degradation of the oil.

Viscosity analysis was done with three Cannon-Fenske type viscometers, with a range of 100 to 500 centistokes (cSt). One was factory calibrated; the other two were calibrated using the first as a standard. Temperature was maintained at 40.0 C during viscosity measurements by immersion in a constant temperature water bath using a heater identical to the one used in the oil bath.

Total base number (TBN) was chosen since it provides a measure of the alkaline reserve [18] of the oil. As it falls to lower levels, free acids which could influence the rate of degradation of oil begin to accumulate. Total base number measurements is destructive so multiple test cells were required to determine the TBN history of a single sample. It is also a more involved procedure than viscosity measurements. Because of these considerations TBN was not measured every time a viscosity measurement was made.

Total base number was measured in accord with ASTM D 2986, "Total Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration" [26]. The back titration method was chosen as it gives sharper endpoints with some used oils, including the materials generated in these experiments. A 25 ml glass buret was used for titrant delivery, and a Beckman model SS-3 Zeromatic pH meter was used for endpoint detection.

Analysis for wear preventative properties was done according to ASTM D 4172, "Wear Preventative Characteristics of Lubricating Fluid (Four-Ball Method)" [27], by Phoenix Chemical Laboratories in Chicago, Illinois. In this test three ½" diameter steel balls are clamped together and covered by the fluid to be tested. A fourth ball of the same size is pressed with a force of 392 N into the cavity formed by the three stationary balls causing three point contact (Figure 3). The top ball is rotated for 60 minutes at 1200 rpm. Temperature is constant at 75 C. At the end of the test, the scars generated on the lower balls are

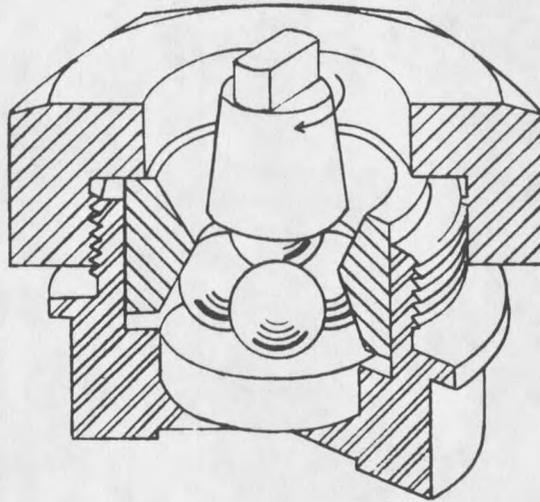


Figure 3. Detail of four-ball wear tester.

measured perpendicular and parallel to the striations. These values are averaged to give the test result.

### Experimental Procedure

To begin an experimental run about 50 gm of lubricating oil per test cell were weighed to the nearest 0.01 gm. Vegetable oil was then added to the desired concentration based on weight percent. After being mixed for a minimum of 2 minutes, 50 ml was added to each test cell. Required analysis (viscosity and/or TBN) was performed on this starting material. The fritted glass tube, with or without catalyst as desired, was inserted in the test cell and the stopper was firmly seated. The cells were then submerged to within one inch of the top of the cells.

Gas flow was started about an hour before insertion of the samples to obtain stable flows of preheated gas. Flow was adjusted to the proper rates before being attached to the test cells. After a few minutes, outlet flows of the test cells were monitored. Whenever a flow rate was used for the first time, the temperature of the test sample was monitored with a Cole-Parmer Instrument Company Model 8530-05 digital thermometer accurate to 1 C and a chromel-alumel thermocouple. These temperatures were always the same as the observed temperatures of the oil bath. Flow rates were measured every 8 to 12 hours with a 10 ml soap bubble flow meter. Flows were adjusted to within 5%, and occasionally varied by 10% from one measurement to the next. Generally, however, they were stable to within 5%. Flow rates of 2000 ml/hr and 4000 ml/hr were used.

To make measurements of viscosity or TBN all six cells were disconnected from the gas flow and removed from the bath. Ten ml samples were pipetted into the viscometer and were allowed to equilibrate for at least 10 minutes. The oil was raised above the upper mark of the viscometer by suctioning with a clean pipette bulb. Time for flow through the

viscometer was measured to the nearest 0.01 second. The sample was then returned to the test cell.

For TBN a 5 ml sample was weighed to the nearest 0.1 mg and then titrated according to ASTM D 2896 [26]. In the back titration method 120 ml of 2:1 chlorobenzene:glacial acetic acid titration solvent was added to the sample followed by addition of 10.00 ml of 0.1 N perchloric acid in glacial acetic acid. Electrodes were inserted into this solution, which was titrated potentiometrically with 0.1 N sodium acetate in glacial acetic acid. Uniform additions of 1.00 ml and 0.50 ml were made, the smaller addition size being used near the equivalence point.

When an experimental run was complete, test cells and miscellaneous glassware were cleaned with Phillips 66 nonflammable mechanics solvent, acetone, and soap and water, rinsed with water and distilled water, and air dried. Fritted glass tubes were cleaned in a similar manner followed by a 10 to 20 minute soak in hot chromic acid and rinsing with water and distilled water. They were then rinsed with acetone and suctioned to assure dryness. Viscometers were cleaned with Phillips 66 solvent, rinsed several times with acetone and suctioned. They were also cleaned with chromic acid as required.

## RESULTS AND DISCUSSION

### Effect of System Variables on Viscosity

Since the oil bath held 6 test cells per run, not all of the test cells from each run were necessarily devoted to examining the same parameter. Also, data from more than one run may be used to examine each parameter. Generally, the parameters examined were viscosity versus time for differing conditions of gas flow rate and catalyst level, total base number (TBN) versus time for differing conditions, and the effect of various additives on viscosity and TBN. Unless otherwise noted, the temperature of the oil bath was 150 C, the vegetable oil used was sunflower oil, and the dilution level was 5.0% by weight. This concentration was chosen because it is an intermediate value of lubricating oil dilution in an actual engine, where the range is from 0% to 15%. It is in the range of many other researchers' work because of this consideration.

Initially, several screening runs were performed to determine a standard set of conditions against which later runs could be interpreted. Flow rates and catalyst levels were selected such that viscosity increases took place in a reasonable length of time and gas flows gave good mixing without causing a foaming problem. A temperature of 150 C was chosen as a compromise between the crankcase temperature and the temperature encountered in the combustion areas of the engine.

Effect of catalyst level is seen in run 1, shown in Figure 4, where 0, 20, and 100 cm of copper-iron combination were used as catalyst. Flow rate of oxygen was 2000 ml/hr. Additional data for 20 cm catalyst is included from run 6, and for 100 cm catalyst from runs 5 and 11. From this data, it can be seen that rate of viscosity increase is strongly affected by catalyst level, with the rate increasing as catalyst level goes up.

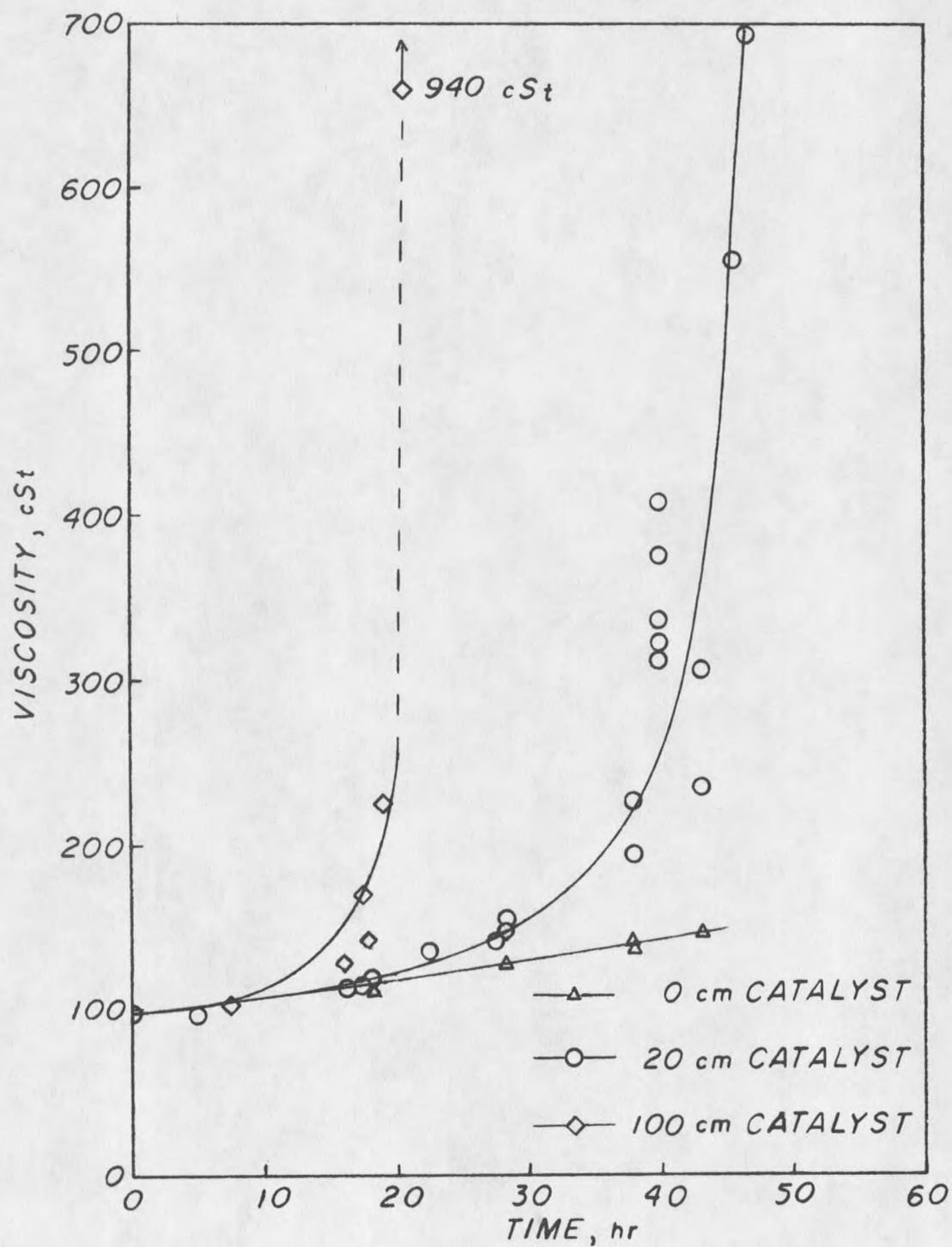


Figure 4. Viscosity vs. time for 0, 20, and 100 cm copper-iron catalyst and 2000 ml/hr oxygen.

As the work progressed, the conditions of 20 cm copper-iron catalyst, 2000 ml/hr oxygen, and a vegetable oil concentration of 5.0% by weight evolved as the standard set of conditions. The results of these conditions are shown in the center curve on Figure 4. For ease in comparison, this curve is reproduced in all the following graphs whenever appropriate. It is shown as an unlabeled dotted line.

The shape of these curves is consistent with the concept of lubricating oil thickening due to polymerization of the vegetable oil diluent. As polymerization proceeds, molecular weight, and hence viscosity, builds exponentially as progressively larger oligomers combine by addition.

Effect of copper versus effect of iron was examined in run 12, where 20 cm of copper wire was used in one cell, and 20 cm of iron wire was used in a second cell. When these results are compared with results from the standard set of conditions (shown as the solid and dotted line, respectively), it can be seen that iron has little catalytic activity, while copper has a slightly greater catalytic effect than using copper and iron together.

Copper and iron were not tested separately for catalytic activity before run 12 because other work [16,23,25] implied that both metals play a role in catalysis. Separate tests were performed to determine how much each contributed to viscosity buildup. Iron was included in the final run after this result was obtained for the sake of consistency, and because the combined presence of both metals may have subtle effects.

Effect of oxygen flow rate is seen in Figure 6, which compares the results of run 2 with the standard set of conditions. In run 2, flows of 4000 ml/hr of oxygen were used with 0 and 20 cm of copper-iron catalyst, while the standard set of conditions uses 2000 ml/hr oxygen and 20 cm copper-iron catalyst. Additional data for 20 cm catalyst is shown from run 7. Rate of viscosity increase is only slightly affected by oxygen flow rate. This is useful to note when considering the imprecision of the control of the flow rate.















































































































