



Production of diesel fuel from safflower oil by a soap-pyrolysis process
by Scott Eric Kufeld

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

The purpose of this research was to study the soap-pyrolysis process for making fuel suitable for use in a diesel engine. The process involved converting safflower oil into a soap and then pyrolyzing the soap to obtain the diesel range fuel. Commercial high-speed and medium-speed lubrication oils were investigated with five weight percent soap-pyrolysis fuel contamination relative to polymerization properties.

The first set of experiments studied pyrolysis process variables. It was observed that: fuel from soap aged three months had a greater initial kinematic viscosity than fuel from soap aged two days and both these fuels had about the same kinematic viscosity after 48 hours in the polymerization apparatus; glycerol in the soap decreased yield; fuels from soap with a 50% excess amount of Ca(OH)_2 showed less thickening after the polymerization tests than fuels from soap with a stoichiometric amount of Ca(OH)_2 ; calcium soap is superior to magnesium soap since the yield of fuel is greater; the #2 range distillate has less of an initial kinematic viscosity than the total distillate and both distillates have the same kinematic viscosity after the polymerization tests; the lighter the fraction of the total distillate the smaller the initial kinematic viscosity and the greater the viscosity increase; storage time of fuel had little effect on polymerization properties.

The second set of experiments showed that addition of Ca(OH)_2 prior to pyrolysis decreased thickening while limiting yield.

The third set of experiments found the best soap production method investigated was the fusion method with no solvent. Other methods tried were the precipitation process and using both toluene and water at different concentrations as solvents in the fusion method.

The fourth set of experiments showed that it would be desirable for the safflower oil to contain more oleic acid esters than linoleic or linolenic acid esters.

Optimization of the process showed that addition of a stoichiometric amount of Ca(OH)_2 for fusion soap production, and no Ca(OH)_2 added prior to pyrolysis, was most desirable.

The soap-pyrolysis fuels worked better as fuels in a diesel engine than safflower oil.

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of

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APPROVAL
of a thesis submitted by
Scott Eric Kufeld

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

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TABLE OF CONTENTS

	Page
APPROVAL.....	ii
STATEMENT OF PERMISSION TO USE.....	iii
ACKNOWLEDGMENTS.....	iv
TABLE OF CONTENTS.....	v
LIST OF TABLES.....	vii
LIST OF FIGURES.....	ix
ABSTRACT.....	x
INTRODUCTION.....	1
RESEARCH OBJECTIVES.....	6
EXPERIMENTAL DESCRIPTION.....	10
Soap Production.....	10
Pyrolysis.....	11
Polymerization.....	16
Acid Number.....	21
Iodine Value.....	21
Nuclear Magnetic Resonance.....	22
Distillation.....	23
Yield.....	24
RESULTS AND DISCUSSION.....	26
Pyrolysis Studies.....	26
Aged Versus Fresh Soaps.....	26
Glycerol Content of the Soaps.....	29
Fatty Acid Content of Soaps.....	32
Calcium Versus Magnesium Soaps.....	34
Distillation Results.....	35
Storage Effects.....	38
Results for Pure Linoleic Acid.....	39
Pyrolysis With and Without Calcium Hydroxide Reactant	40
Soap Production.....	43
Unsaturation Studies.....	50
Soap-Pyrolysis Process Optimization.....	56

TABLE OF CONTENTS--Continued

CONCLUSIONS.....	69
RECOMMENDATIONS FOR FUTURE RESEARCH.....	71
APPENDICES.....	72
Appendix A-Optimization Results.....	73
Appendix B-Computer Program Used for Optimization....	77
REFERENCES CITED.....	82

LIST OF TABLES

Table		Page
1.	Fatty Acid Distribution in Safflower Oil.....	3
2.	Typical Ranges for Diesel Fuel Types.....	23
3.	Fuels from Aged and Fresh Soaps.....	27
4.	Fuels from Soaps With Different Amounts of Glycerol.....	30
5.	Fuels from Soaps With Different Free Fatty Acid Contents.....	33
6.	The Total Distillate Versus the #2 Range.....	36
7.	Viscosity Results for Diesel Fuel Types.....	38
8.	Aged Versus Fresh Fuels.....	39
9.	Experiments With/Without Calcium Hydroxide Reactant.....	41
10.	Viscosity Results of Fuels With/Without Reactant.....	42
11.	Results of Fuels from Different Soaps With Solvent.....	47
12.	Yields of Fuels from Different Soaps With Solvent.....	49
13.	Results of Fuels from Different Acid Soaps.....	53
14.	Results for the Complex Method of Box.....	61
15.	Results from the 3 ² Factorial.....	62
16.	Variable Levels Used for Optimization.....	64
17.	Final Run Results.....	66
18.	Coded and Uncoded Variables for the Mathematical Model of the Soap-Pyrolysis Process.....	74
19.	Values for Surface Yield Equation Calculation...	74

20. Constants Estimate..... 75

LIST OF FIGURES

Figure		Page
1.	Soap-Making Process Apparatus.....	12
2.	Pyrolysis Apparatus With Stainless Steel Vessel.	14
3.	Pyrolysis Apparatus With Glass Vessel.....	15
4.	Polymerization Apparatus.....	18
5.	Viscometer and Temperature Bath.....	20
6.	Variable Levels for Sequential Simplex Optimization Technique.....	59
7.	Variable Levels for Complex Method of Box Optimization Technique.....	60
8.	Variable Levels for the Factorial Experimental Design.....	63
9.	Computer Program Used For Optimization.....	78

ABSTRACT

The purpose of this research was to study the soap-pyrolysis process for making fuel suitable for use in a diesel engine. The process involved converting safflower oil into a soap and then pyrolyzing the soap to obtain the diesel range fuel. Commercial high-speed and medium-speed lubrication oils were investigated with five weight percent soap-pyrolysis fuel contamination relative to polymerization properties.

The first set of experiments studied pyrolysis process variables. It was observed that: fuel from soap aged three months had a greater initial kinematic viscosity than fuel from soap aged two days and both these fuels had about the same kinematic viscosity after 48 hours in the polymerization apparatus; glycerol in the soap decreased yield; fuels from soap with a 50% excess amount of $\text{Ca}(\text{OH})_2$ showed less thickening after the polymerization tests than fuels from soap with a stoichiometric amount of $\text{Ca}(\text{OH})_2$; calcium soap is superior to magnesium soap since the yield of fuel is greater; the #2 range distillate has less of an initial kinematic viscosity than the total distillate and both distillates have the same kinematic viscosity after the polymerization tests; the lighter the fraction of the total distillate the smaller the initial kinematic viscosity and the greater the viscosity increase; storage time of fuel had little effect on polymerization properties.

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The third set of experiments found the best soap production method investigated was the fusion method with no solvent. Other methods tried were the precipitation process and using both toluene and water at different concentrations as solvents in the fusion method.

The fourth set of experiments showed that it would be desirable for the safflower oil to contain more oleic acid esters than linoleic or linolenic acid esters.

Optimization of the process showed that addition of a stoichiometric amount of $\text{Ca}(\text{OH})_2$ for fusion soap production, and no $\text{Ca}(\text{OH})_2$ added prior to pyrolysis, was most desirable.

The soap-pyrolysis fuels worked better as fuels in a diesel engine than safflower oil.

INTRODUCTION

In the mid-1980's the United States was poised insecurely between an energy crisis it had momentarily averted and an energy future it could not confidently predict. The energy crisis that lasted from 1973 to 1978 was triggered by a sudden but brief Arab embargo upon petroleum exported to the United States, quickly followed by several years of sharply rising world petroleum prices. The United States was forced to recognize it had become heavily dependent upon imported petroleum and could no longer satisfy its own rapidly rising energy demands from its existing domestic energy production. More ominously, it appeared the United States might face a shortage of petroleum within a few decades. Experts remained divided and uncertain about the future [1]. An alternative source of energy to take the place of fossil fuels might someday help alleviate this problem.

Vegetable oils show much promise as replacements or extenders for diesel fuels. Theoretically, a farmer could plant a fraction of his land in oil producing crops and use the fuel produced from this to run his entire operation. Seed oils such as safflower oil have received considerable attention as direct substitutes or additives for fuels suitable for use in a diesel engine. Safflower oil has the

attraction of being able to be grown easily in Montana. It would be of great interest to the agriculture community to see safflower oil replace diesel fuel since farmers then wouldn't have to rely on fossil fuels with fluctuating prices and finite availability, and could then be more independent and in charge of their own destiny. Researchers estimate agricultural fuel needs for the United States could be met by planting approximately 10% of the total cropland with oilseed crops [2]. As an added benefit, vegetable oil processing yields meal high in protein for animal feed as a by-product [3].

Despite the advantages of using vegetable oil for diesel fuel there are still economic problems. Collins shows that diesel prices would have to double or triple before even the best vegetable oils would become competitive [4]. In general, if a raw material such a diesel fuel becomes scarce, its price will rise. Since the relationship between price and supply is not absolute and a sign of scarcity is not a complete absence of material but rather a perception of dwindling supply by the consumer, the price of diesel fuel is always under close scrutiny [5].

The chemical difference between diesel fuel and vegetable oils is also responsible for problems: (1) vegetable oils form carbon deposits inside direct injection engines and (2) vegetable oil carried into the crankcase polymerize on contact with the lubrication oil leading to

eventual engine failure [6]. These problems are both related to differences in the chemical structure of diesel fuel and vegetable oils.

Vegetable oils are esters formed by the combination of glycerol with three fatty acids. These fatty acids are straight-chained, monocarboxylic acids that can be either saturated or unsaturated. Saturated would be without any carbon double bonds and unsaturation is a measure of the carbon double bonds. The fatty acid distribution of safflower is given in Table 1. It has been found that the carbon deposition problem can be solved by either using indirect injection engines or by transesterification. The net effect of transesterification is to replace one large triglyceride ester with three smaller esters. The principal change in physical characteristics of the transesterified vegetable oil is a significant reduction in viscosity compared to the unmodified vegetable oil. This lowering in viscosity appears to prevent the formation of carbon deposits [7].

Table 1. Fatty Acid Distribution of Safflower Oil [8]

<u>Fatty Acid</u>	<u>Percentage</u>	<u>Composition</u>	<u>No. of Double Bonds</u>
palmitic	6.4	$C_{16}H_{32}O_2$	0
stearic	3.1	$C_{18}H_{36}O_2$	0
arachidic	0.2	$C_{20}H_{40}O_2$	0
oleic	13.4	$C_{18}H_{34}O_2$	1
linoleic	76.6-79.0	$C_{18}H_{32}O_2$	2
linolenic	0.04-0.13	$C_{18}H_{30}O_2$	3

Transesterification does not necessarily prevent the previously mentioned polymerization problem. The mechanism of polymerization is thought to occur by oxygen first attacking a carbon double bond with the carboxyl groups acting as a catalyst in the reaction [9]. Therefore, the polymerization problem should be able to be solved by a modification of the chemical structure of vegetable oils. The double bonds could be removed by hydrogenation but this results in a fuel that is a solid at room temperature. Decarboxylation or removal of the carboxyl groups could be accomplished by thermal means with or without the aid of catalysts.

A project that started with work by Hiebert dealt primarily with decarboxylation and this investigation used his results and continued work in this area [10]. Hiebert found that by converting the safflower oil to a soap and then pyrolyzing the soap to obtain a liquid diesel range fuel worked the best of the techniques he tried. This modification of the chemical structure was accompanied by relatively low acid numbers (a measure of the free fatty acid content) and significant unsaturation (a measure of the carbon double bonds). This procedure significantly reduced thickening effects measured by kinematic viscosity. A 375% increase in kinematic viscosity in 64 hours is considered a failure in lubrication oil tests [11]. This current project attempted to improve and learn more about the soap-pyrolysis

process for making fuel from safflower oil that could be used in a diesel engine.

RESEARCH OBJECTIVES

The experiments performed for this soap-pyrolysis research have been divided into five tasks. The purpose of the first task was to investigate the effects of a number of pyrolysis process variables that might have been important to fuel yield and quality. Soap production was not addressed in this task; in fact, rather than starting with safflower oil, linoleic acid (its principal component at 76.6-79.0%) was used to make the soap [12]. By using a simpler, representative soap, the effects of the processing variables were expected to be more apparent and not confused by the presence of soaps from a number of different fatty acids. High speed lubrication oil was used for the polymerization tests. The high speed lubrication oil is a thirty weight oil.

Six specific process variables were investigated for this first task. First, soaps that had been aged were compared with fresh soaps to see how this affected the fuel. Second, because the soap making could be simplified if the glycerol did not have to be removed prior to pyrolysis, soap without glycerol, with an amount added equivalent to that produced in the soap making, and with an intermediate amount consistent with partial removal were compared. Third, the fatty acid content of the soaps was varied to see how this

variable affected the fuel. Fourth, calcium and magnesium soaps were compared since literature indicates these soaps have similar properties. However, the magnesium soaps would probably have lower pyrolysis temperatures which could change the nature of the fuel [13]. Fifth, a typical diesel fuel fraction of the distillate was compared to the total distillate for differences in polymerization characteristics. Also, different fractions of the distillate were compared with one another. Sixth, any changes in the fuel due to storage might have had an effect on its polymerization properties. Oxidation from contact with air could have caused polymerization. Tests were made on fresh fuels and after they had been stored for a period of time.

The experiments completed for the second task compared pyrolysis with and without the use of calcium hydroxide reactant. Linoleic acid was again used rather than safflower oil to prepare the soaps so as to not confuse the processing variables by the presence of soap from a number of different fatty acids. Another purpose of this task was to compare fuels made from pyrolysis with and without the use of calcium hydroxide reactant with both medium and high speed lubrication oils. High speed lubrication oil is a thirty weight oil and medium speed lubrication oil is a forty weight oil. The addition of calcium hydroxide was made to the soap just prior to pyrolysis.

The experiments for the third task concentrated on the soap production process. Safflower oil was used to prepare the soaps for this task since it was important to compare the fuel yields obtained from the vegetable oils using different soap production methods. A multi-step precipitation process was compared to the single-step fusion method for the production of the soaps. In addition, non-aqueous solvents with varying concentrations were investigated with the fusion method along with use of no solvent for the process.

The fourth task attempted to investigate the importance of the degree of vegetable oil unsaturation. Exploratory research in this lab has indicated that converting the safflower oil to a soap prior to pyrolysis significantly decreases the role of unsaturation in the polymerization of lube oils, but more information was necessary [14]. The approach used for this task involved converting fatty acids with various degrees of unsaturation or number of carbon double bonds to soaps and then comparing the pyrolysis products for any differences that might be found. High speed lubricating oil was used for the polymerization tests. The fatty acids used in this task would be different only in the number of carbon double bonds.

The last task was to optimize the soap-pyrolysis process for making fuel suitable for use in a diesel engine. The results from the first four tasks helped identify

important process variables and techniques that were to be optimized. It was now the purpose to put all this information together and determine the most desirable techniques and levels of variables for the soap-pyrolysis process for making diesel fuel from safflower oil.

EXPERIMENTAL DESCRIPTION

Soap Production

Two methods were used to prepare the soaps for these experiments. The fusion method was employed for most of these runs. The process consisted of the following steps. First, 200 grams of acid (oleic, linoleic, or linolenic) or safflower oil was heated to 100°C. Second, a solution consisting of the alkali hydroxide (calcium hydroxide or magnesium hydroxide) with or without a solvent (demineralized water or toluene) was vigorously stirred in. Magnesium hydroxide was only used to prepare the magnesium soaps in the pyrolysis studies. Toluene was only used as a solvent in some of the soap production experiments. Next, the soaps were allowed to cool which took several minutes. After the soaps had dried they were ground into uniform chunks using a hand grinder.

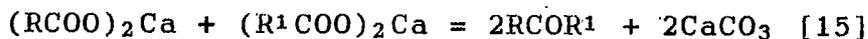
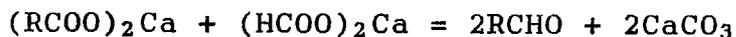
The precipitation method was also used to prepare the soaps. First, 200 grams (in some cases 180) of linoleic acid was heated to 100°C. Second, a solution consisting of sodium hydroxide and demineralized water was vigorously stirred in. This process formed a solid sodium soap. Third, the sodium soap was separated into two batches each of which was dissolved in 500 ml of water. Each batch was then mixed with a solution of calcium chloride and

demineralized water and stirred. This process of ion exchange precipitated out the calcium soap. Last, the two batches of soap were combined and washed with demineralized water to remove any sodium soap or calcium chloride since they are both water soluble and the calcium soap is not.

Soap reactions were performed at atmospheric pressure in a 1000 ml glass batch reactor with a glass top. The 1000 ml reactor and glass top were both purchased from Ace Glass, product Nos. 6506-35 and 6485-16. A thermocouple measured the temperature and a powerstat was used to control the heat supplied to the reaction vessel by a electric heating mantel. The setup for the soap making process is given in Figure 1.

Pyrolysis

Pyrolysis is the process of heating the soaps and condensing the resulting vapors to obtain the diesel fuel. Literature indicates that pyrolysis of calcium soaps leads to the formation of aldehydes (RCHO) and ketones (RCHOR¹) shown in the following reactions.



Maximum liquid temperatures were about 815°F; this maximum was chosen to prevent damage to the heating mantel. Pyrolysis reactions were carried out in a 500 ml stainless steel reactor vessel and then this was replaced by a 500 ml

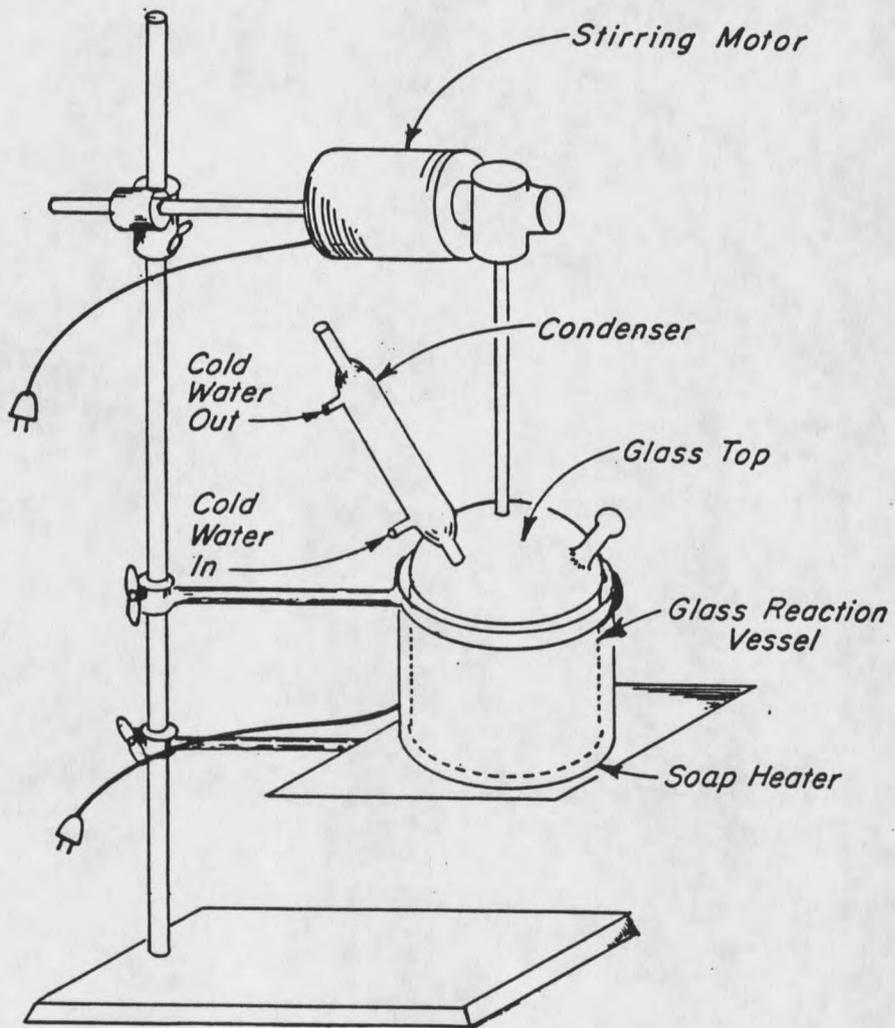


Figure 1. Soap-Making Process Apparatus

glass reactor after several experiments into the pyrolysis studies. The glass reactor was used for the rest of this project. These were both purchased from Ace Glass, product Nos. 6497-05 and 6927-22. The apparatus used with the stainless steel and glass pyrolysis vessels is given on Figure 2 and Figure 3.

The reason the stainless steel vessel was chosen in the first place was the ease of cleaning compared to the glass vessel. The change to the glass vessel in this study was implemented because the product yields were significantly lower with the stainless steel vessel than those obtained with the glass vessel during the previous investigation (DNRC Grant Agreement RAE-84-1041) [16]. This change resulted in a significantly greater yield in the current study. The possible reasons for this yield difference is discussed in the Aged Versus Fresh Soaps section of the Pyrolysis Studies.

The soap was first put into either the stainless steel or glass pyrolysis apparatus and a glass connector came out the top and was attached to the condenser. The condenser then emptied into a separatory funnel. Fiberglass insulation was packed around the top of the pyrolysis apparatus to minimize heat loss. The 500 ml glass reactor was a two-necked flask. The first neck led to the condenser where the vapor temperature was measured and the second neck was used to insert a thermocouple which measured the liquid

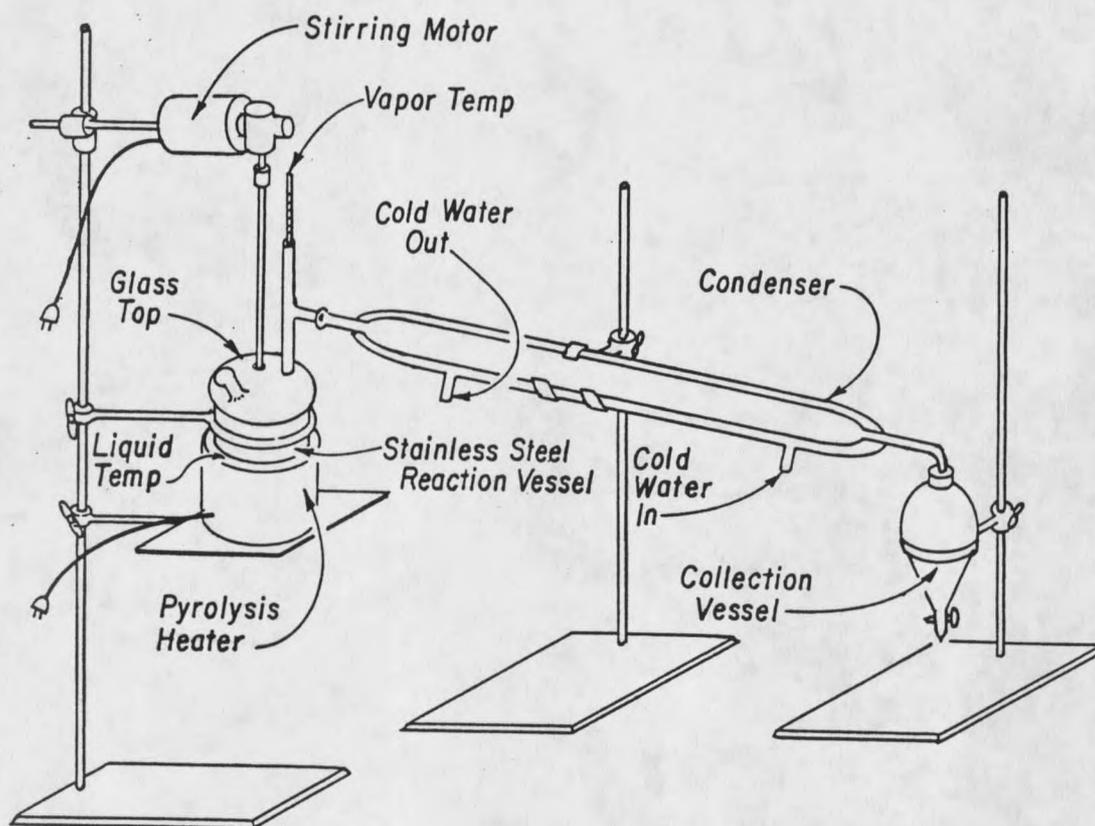


Figure 2. Pyrolysis Apparatus With Stainless Steel Vessel

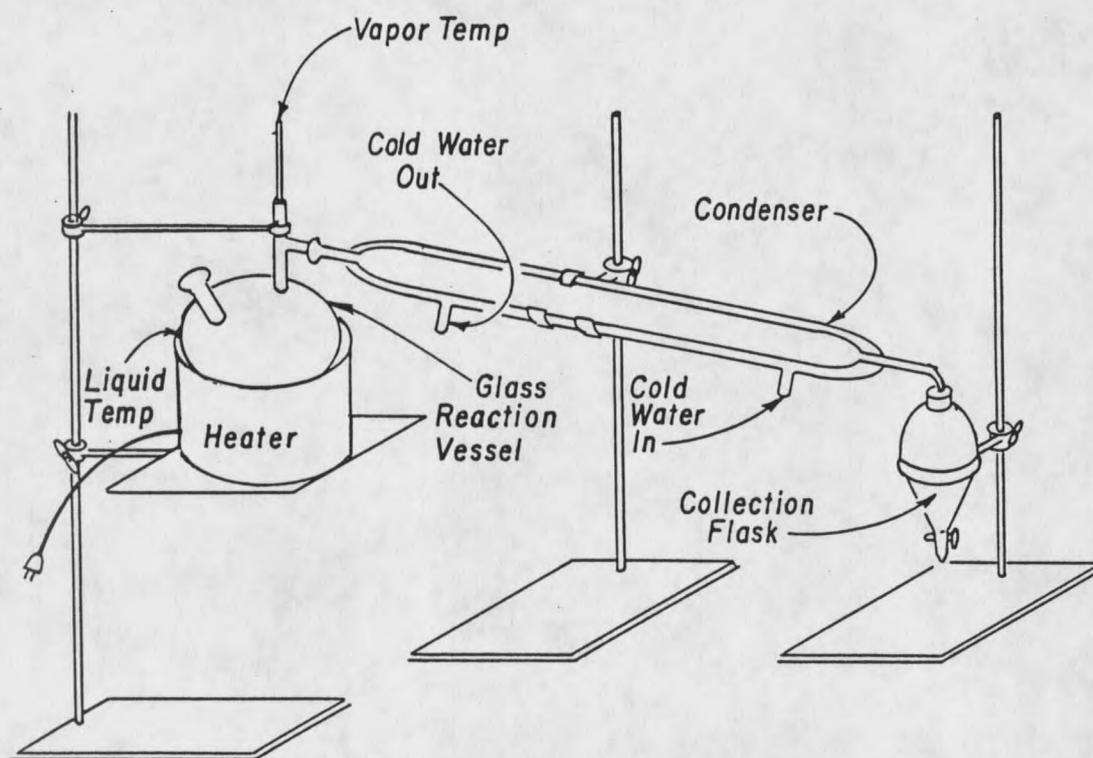


Figure 3. Pyrolysis Apparatus With Glass Vessel

temperature. A quarter-inch, glass covered magnetic stirring bar was used at the bottom of the flask to keep the soap well mixed. The 500 ml stainless steel reactor with a glass top was also used for pyrolysis. The glass top had three necks. The first neck was where the stirrer went in from the motor, the second neck was used to insert a thermocouple to measure the liquid temperature, and the third neck attached to a glass connector which joined the condenser where the vapor temperature was also measured. Heat was supplied by a different heating mantle than the one used for soap production.

Polymerization

The purpose of polymerization experiments was to simulate crankcase oil conditions in a diesel engine for determining thickening effects due to adding a 5 weight percent concentration of the fuel. The kinematic viscosity measured in centistokes was used as the measure of thickening effects. The reactions were carried out at 150°C in 100 ml glass batch reactors using 50 ml of lubrication oil. Ten parts per million of a soluble copper form (cupric acetylacetonate or CuAcAc) was used as a catalyst and oxygen was bubbled through at the rate of 3 cc per 15 seconds. The high speed lubrication oil was Amoco Super HD11 SAE 30W while the medium speed lubrication oil was Unocal SAE 40. These commercial lubrication oils

contain lubrication oil additives that affect polymerization. Since effects of vegetable oil fuel on commercial lubrication oil were the focus of this research, no attempt was made to study how additives affect the mechanisms of polymerization. The 100 ml glass reactors were put into a custom-built constant temperature bath. Eight different samples could be tested simultaneously. The apparatus was arranged so that the bath was under a hood. The polymerization apparatus is shown in Figure 4. Several pieces of equipment were used for the constant temperature bath and all were from Ace Glass. These were: adapter #11 THD 24/40, product No. 5261-37; test tube, product No. 8752-02; 300 mm pore c tubes, product No. 7202-16; 11 mm nylon bushing, product No. 7506-02; 24/40 bearing c, product No. 8042-115; adapter inner, product No. 5028-30.

Evaporation of vegetable oil fuels in the polymerization apparatus was considered. Evaporation of the soap-pyrolysis fuels would leave the lubrication oil left to be measured for thickening. Many of the experiments with the high-speed lubrication oil ended up with a kinematic viscosity approximately the same as the control polymerization tests. The control polymerization tests contained the lubrication oil and no added soap-pyrolysis fuel. Evaporation was not considered likely because of previous work [17]. While current work had measurements for kinematic viscosity initially and after 48 hours in the

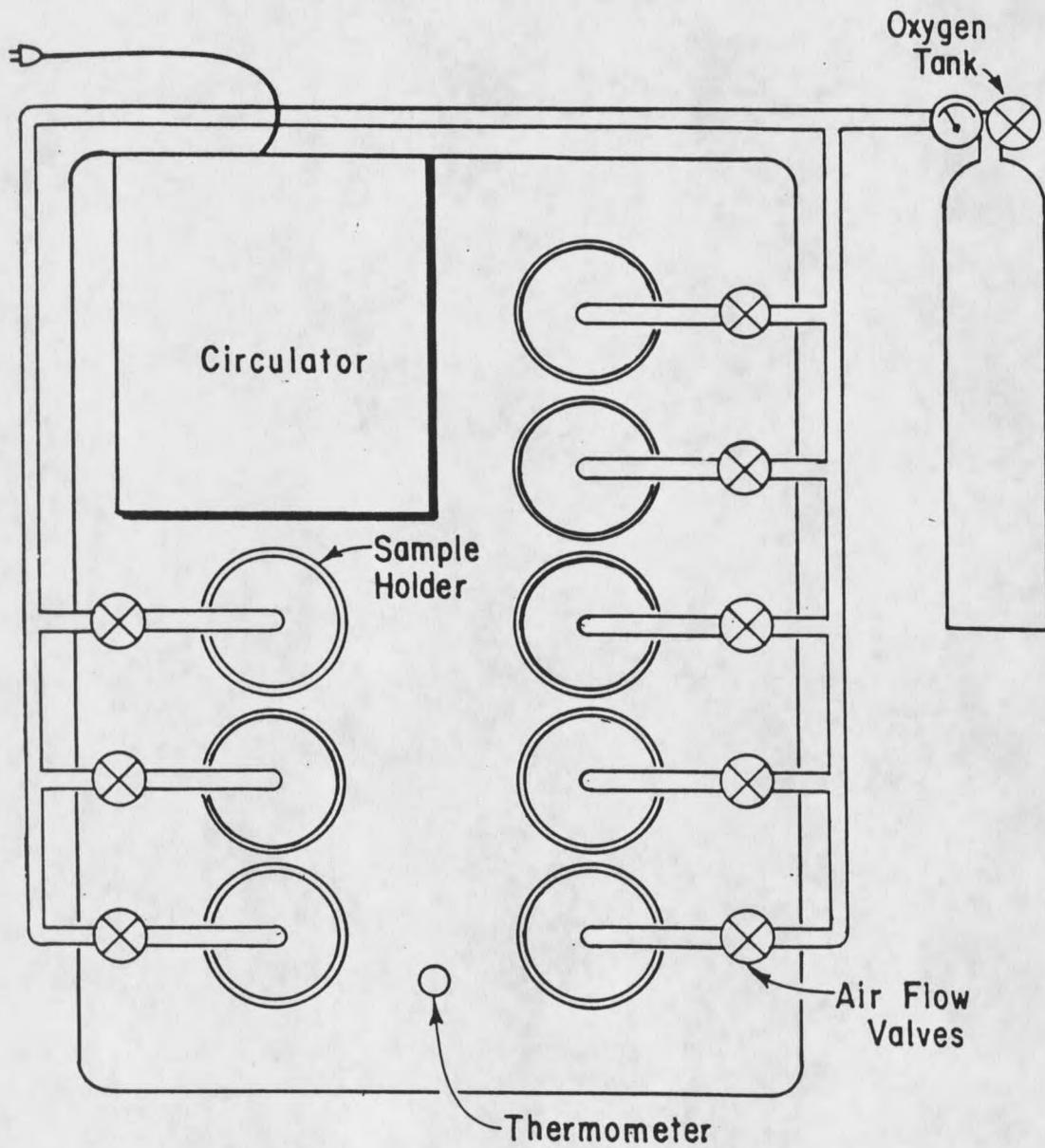


Figure 4. Polymerization Apparatus

polymerization apparatus, previous work took measurements every 10-12 hours up to 72 hours. The earlier work showed the kinematic viscosity continued to increase above the neat lubrication oil after the 48 hour measurement. Therefore, evaporation of soap-pyrolysis fuels was only a remote possibility. Future work in this area should be considered.

A viscometer was used to measure the kinematic viscosity at 40°C. A drawing of the viscometer is given in Figure 5. The technique used was to add 8 ml of sample to the viscometer and let it stand for 10 minutes. Then the time in seconds was recorded on a stopwatch as the oil traveled between two marks on the viscometer. This was then multiplied by a calibration number to convert it into kinematic viscosity in centistokes. The viscometer was a Canon-Fenske viscometer, No. L799, size 350, report No. 21859. This viscometer was calibrated at 40°C and 100°C. The initial viscosity was measured and then the sample was put into the 100 ml glass reactors which were placed in the constant temperature bath for 48 hours. At the end of this time the final viscosity reading was taken. Under previous work done on this project for the Montana Department of Natural Resources and Conservation (RAE-84-1041, Chemical Processing of Vegetable Oils to Prevent Polymerization) [18], it was shown the thickening properties of the fuel were apparent after 48 hours; the kinematic viscosity using straight safflower oil had increased 110% from about 95-200

