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

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 $Ca(0H)_2$ for fusion soap production, and no $Ca(0H)_2$ 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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by

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

of

Master of Science

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Chemical Engineering

MONTANA STATE UNIVERSITY
Bozeman, Montana

September 1988

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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ACKNOWLEDGMENTS

The author would like to thank the faculty and staff of the Chemical Engineering Department here at Montana State University for their guidance and assistance. Special thanks is extended to my research advisor, Dr. Warren P. Scarrah, for his advice, help, and encouragement. The author would also like to acknowledge Dr. Robert L. Nickelson and Dr. Daniel L. Shaffer who served on my guiding committee. Advice by John W. Olson, a fellow graduate student, in the area of polymerization is also recognized. Finally, the financial support received from the Montana Department of Natural Resources and Conservation is gratefully appreciated.

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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.

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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.

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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]

Fatty Acid	Percentage	Composition	No. of Double Bonds
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 ($RCHOR^1$) shown in the following reactions.

$(RCOO)_2Ca + (HCOO)_2Ca = 2RCHO + 2CaCO_3$

$(RCOO)_2Ca + (R^1COO)_2Ca = 2RCOR^1 + 2CaCO_3$ [15]

Maximum liquid temperatures were about 815^oF; 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

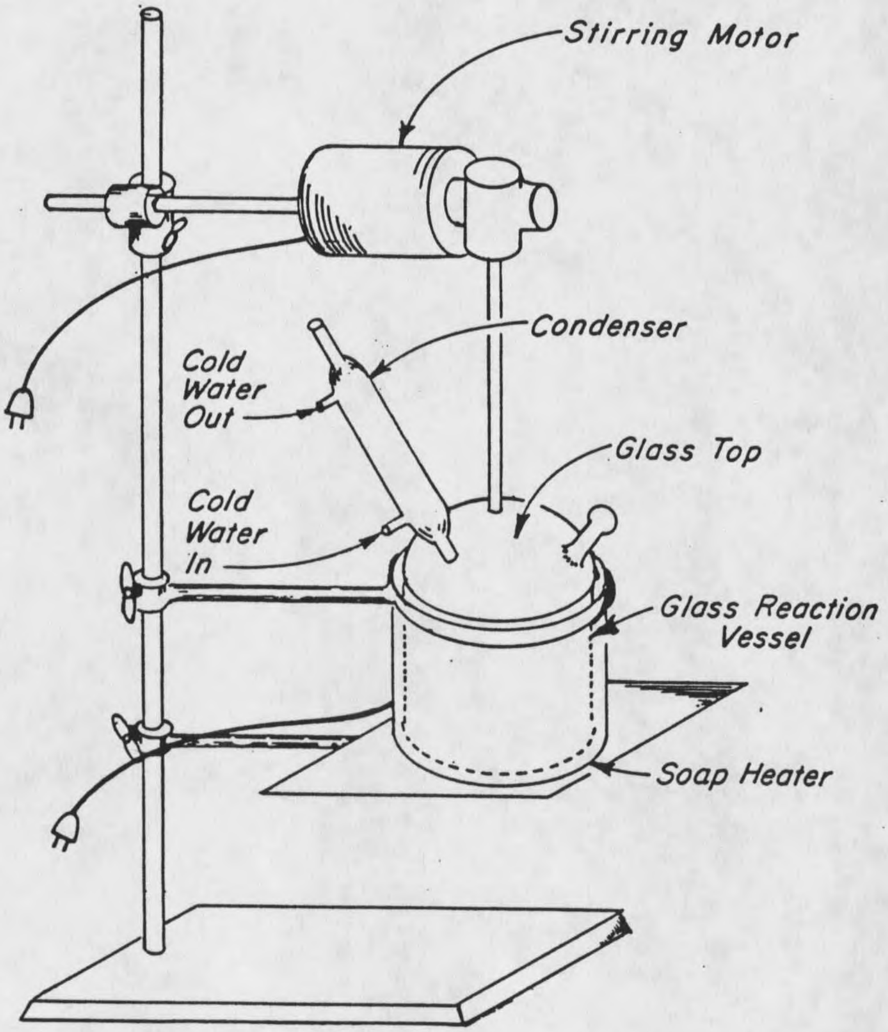


Figure 1. Soap-Making Process Apparatus

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

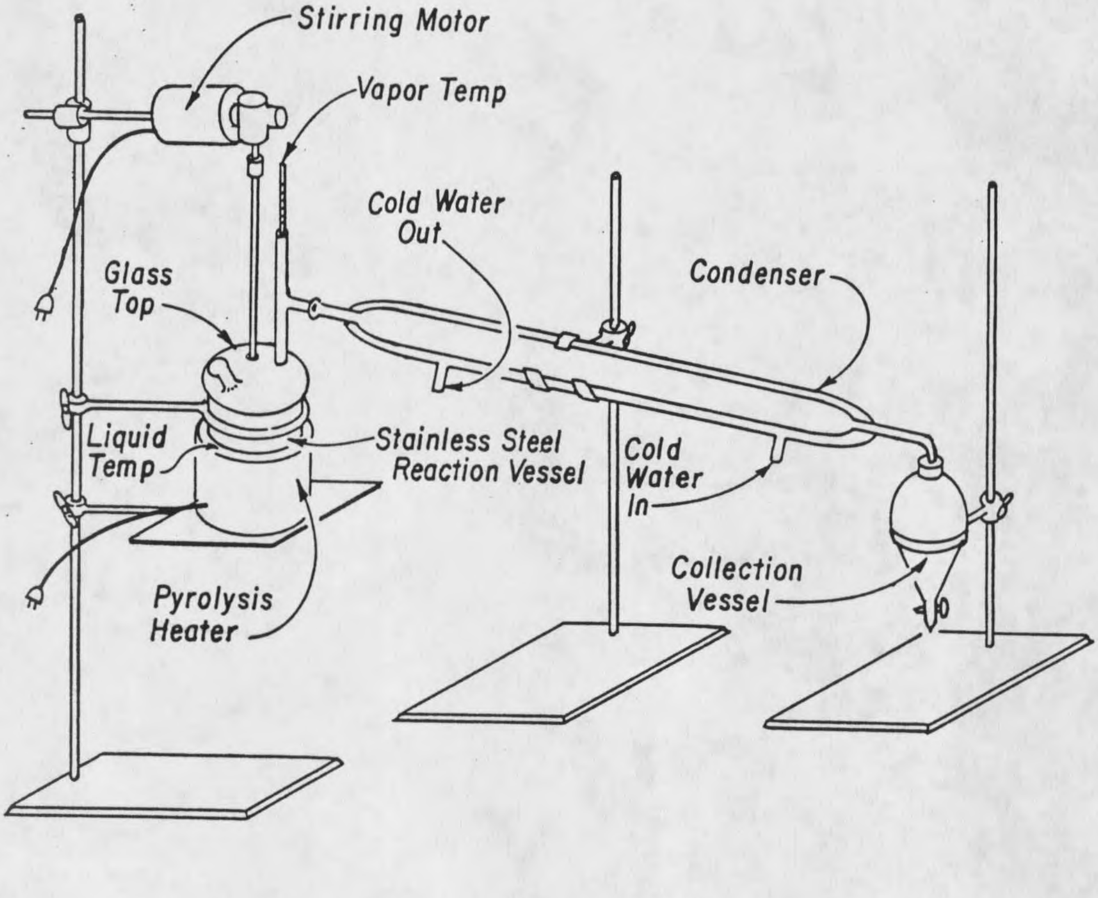


Figure 2. Pyrolysis Apparatus With Stainless Steel Vessel

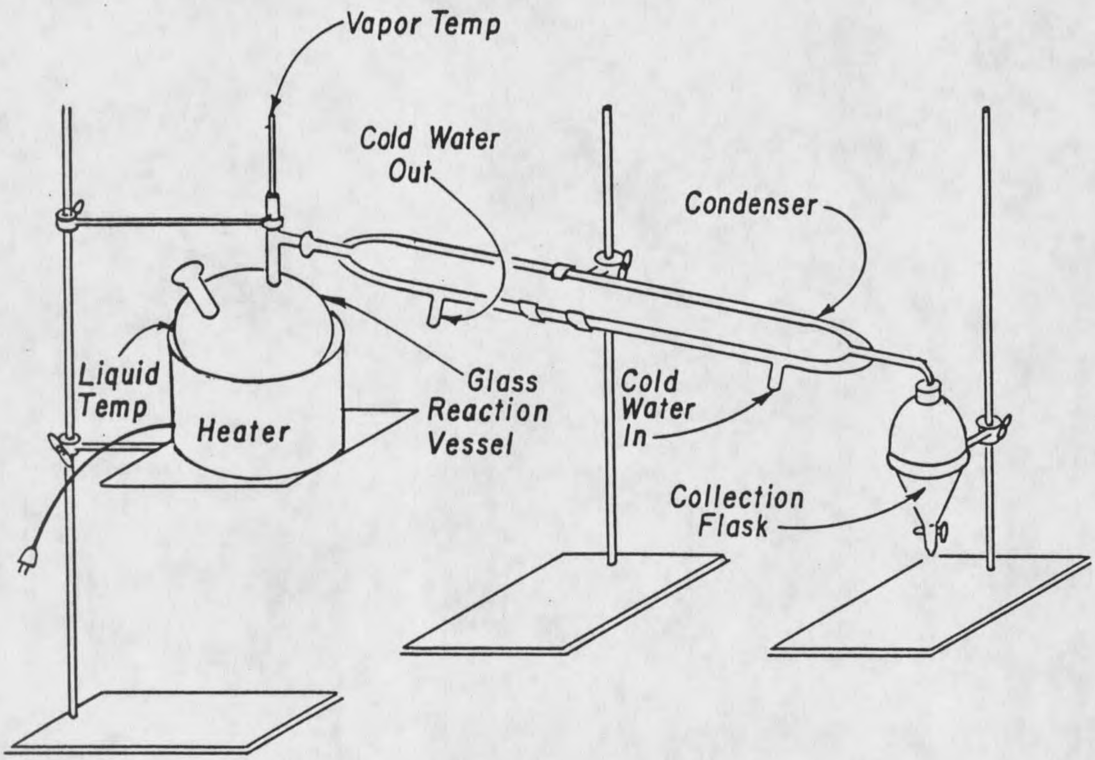


Figure 3. Pyrolysis Apparatus With Glass Vessel

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^{0}C in 100 ml glass batch reactors using 50 ml of lubrication oil. Ten parts per millon 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

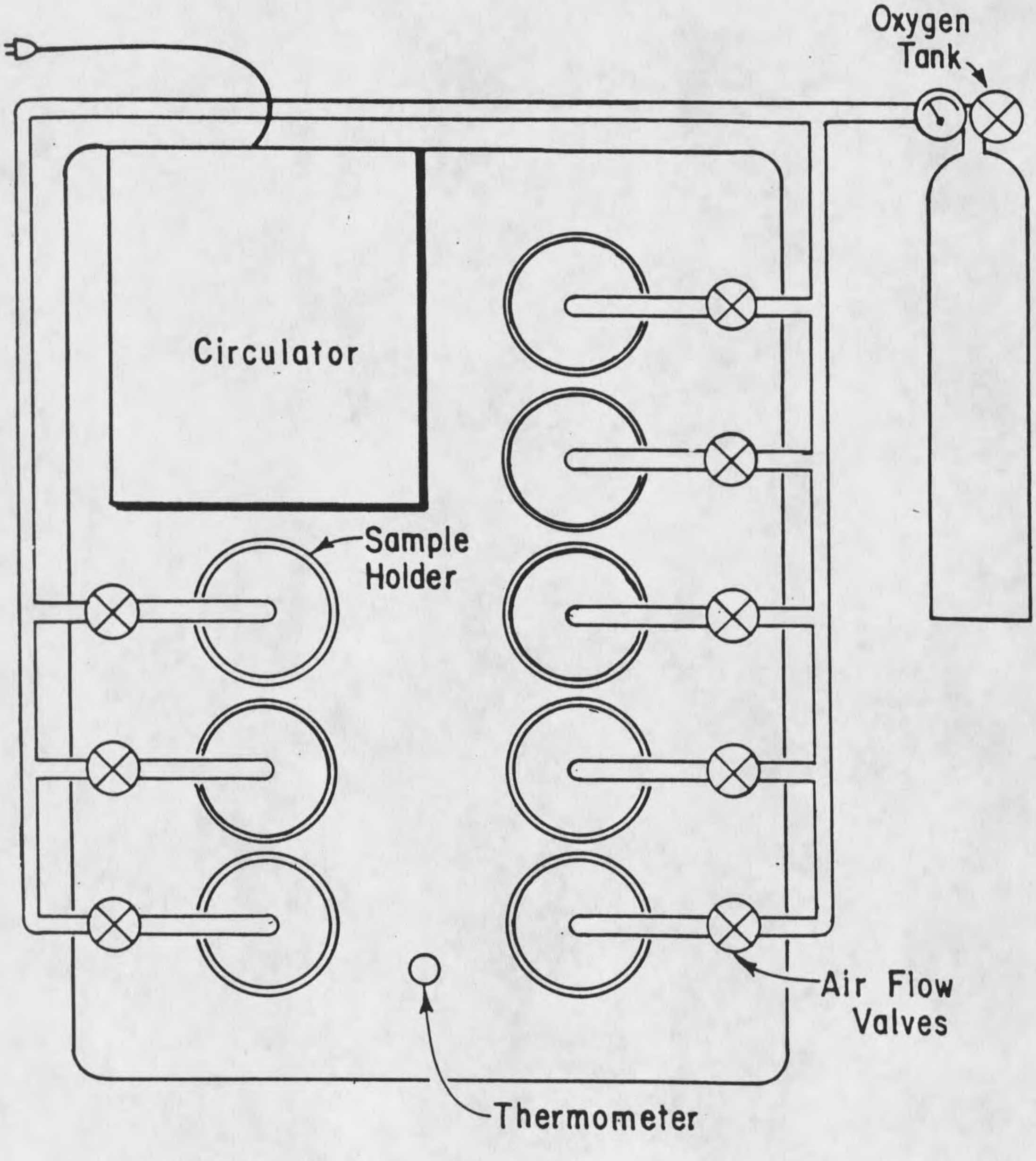


Figure 4. Polymerization Apparatus

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 in 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

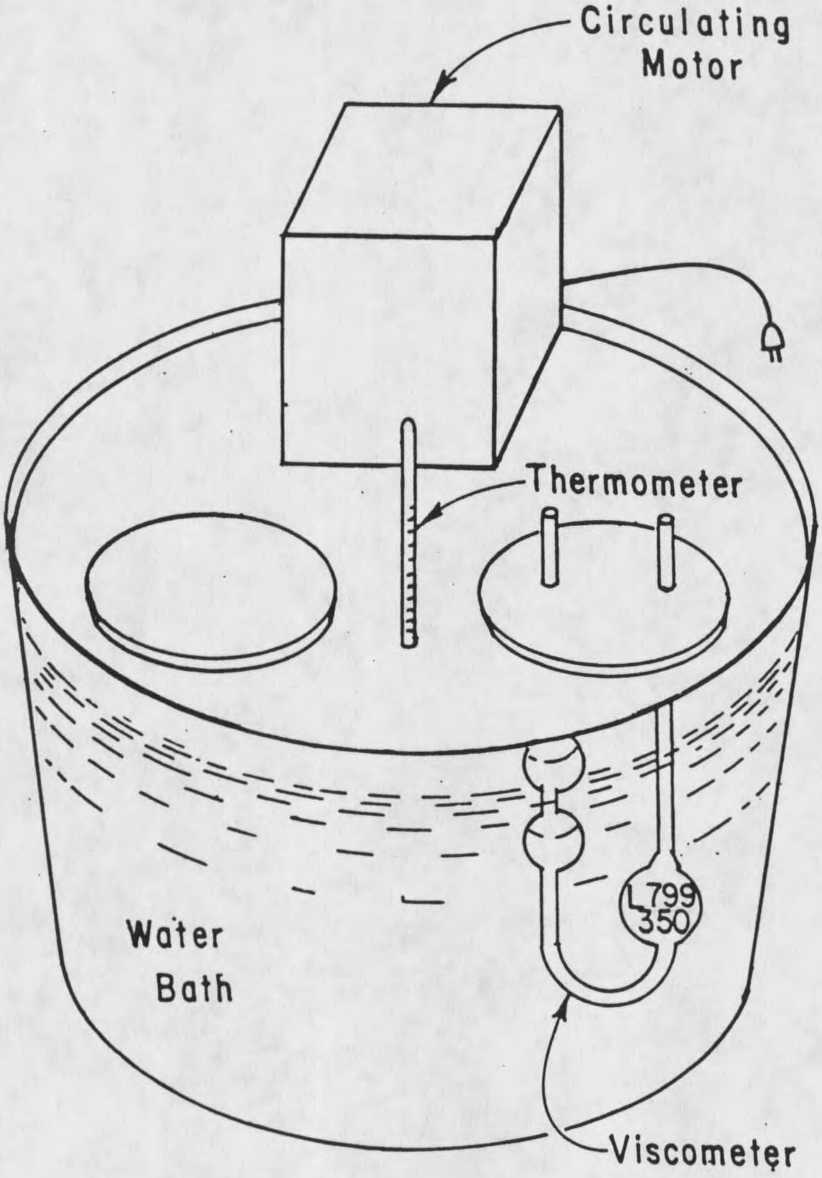


Figure 5. Viscometer and Temperature Bath

centistokes while using the safflower soap decomposition product had led to approximately a 22% increase from about 90-110 centistokes.

Acid Number

The acid number of an oil or oil product is the relative measure of free fatty acid content. The procedure used is described in ASTM D 466-78. This involved dissolving the diesel range product in 95% ethanol and heating until boiling. Then a titration procedure was used with phenothalin as the indicator until the endpoint was found. The base used for the titration was potassium hydroxide with a normality of close to 0.1.

Iodine Value

The iodine value is the relative measure of unsaturation or carbon double bonds present in the sample. The method used was the Wijs procedure performed according to ASTM D 1959-69. This method has been shown to give accurate results for oils and their derivatives with non-conjugated double bonds. These are the only type present in safflower oil and its derivatives. The procedure was to add 20 ml of carbon tetrachloride and 25 ml of Wijs solution to the diesel sample. This was to be stored in the dark for one hour. After this hour, 20 ml of 15% potassium iodide and 100 ml of demineralized water were added. This was then titrated with sodium thiosulfate solution using starch as the indicator. Simultaneously, blanks had to be titrated that were made up of 25 ml of Wijs solution, 20 ml of the 15% potassium iodide solution, and 100 ml of demineralized water.

Nuclear Magnetic Resonance

The Carbon-13 Nuclear Magnetic Resonance Spectrometer used was a Bruker WM-250 with a Aspect 2000 computer. The NMR spectra provided qualitative information about the functional groups attached to the carbon molecules. Several parameters had to be tested in order to determine the appropriate set to use for these oil products. These were receiver gain, receiver delay, and the number of scans. The receiver gain varies with the concentration differences. An appropriate receiver gain would be set so the free induction decay is two centimeters above and below the screen midline. A typical receiver gain for these samples was 1600. The receiver delay is the time between scans. This was already set by choice of the other parameter. A typical receiver delay was around two seconds for these samples. Enough scans should be taken to give a good signal to noise ratio which varies by the square root of the number of scans. As the concentration of the sample is increased, the lower the number of scans that are needed. The 1.5 ml sample of oil was mixed with 0.5 ml of solvent (deutero chloroform). This fairly high concentration required only 500 scans which gave good results.

There were several areas of interest in the NMR spectrum. The unsaturation region occurred between 110-140 parts per millon. The carboxylic acid region was found at 180 parts per millon. Esters were found at 170 parts per millon. Ketones were from 205 to 208 parts per millon. Finally, solvent had three peaks with the middle one at 77 parts per millon. All peaks were done in comparison with the solvent.

Distillation

Distillations were done to determine volatility characteristics of one set of products in the pyrolysis tests. The method used is described in ASTM D 86-78. Tom Davis, a Chemical Engineer at the Farmers Union Central Exchange in Billings, MT, provided these typical ranges for diesel fuel:

Table 2. Typical Ranges for Diesel Fuel Types

Diesel Fuel Type	Initial(°F)	Endpoint(°F)
heavier-#3	500	720
regular-#2	430	625
lighter-#1	315	520

It should be noted these ranges vary with the season.

The apparatus used included the same 500 ml glass reactor used in pyrolysis, a vapor temperature thermometer, a water cooled condenser, and a glass recovery flask. The procedure used was to heat the organic product slowly. The vapor would condense and collect in a recovery flask. The product was distilled in order of lightest to heaviest as the temperature was increased. The first and lightest material to come off was a very light yellow. As the temperature was increased the color of the product went to brown. The heaviest diesel that came off was a dark brown color with a green tint. The differently colored products did not stay separate as they mixed in the recovery flask.

Yield

Yield was calculated two ways. When the various acids were used to make the soap and in the soap production study which used safflower oil to make soap, the yield was computed per 100 grams of dry soap since the effects of the process variables were important. This was done by taking the weight of organic product collected and dividing it by the weight of soap charged minus the water product. A second way to calculate yield was used when safflower oil was charged since it was important to compare the fuel yields from the starting vegetable oils. This yield was calculated per 100 grams of total safflower oil used. This was done by taking the weight of organic product collected and dividing it by the soap charged for pyrolysis. Then this number was multiplied by the total weight of soap and divided by the weight of safflower charged.

RESULTS AND DISCUSSION

Pyrolysis Studies

Aged Versus Fresh Soaps

The first set of experiments compared polymerization properties of fuels prepared from soaps that had been aged for two months prior to pyrolysis with fuels prepared from fresh soaps aged three days before pyrolysis. The soap was prepared by the fusion method with linoleic acid and a 50% excess amount of calcium hydroxide mixed with 71 grams of demineralized water. High speed lubrication oil was used for the polymerization tests. Table 3 gives the results of these experiments. The fuels obtained from these soaps aged two different times had similar properties. The acid numbers for the fuels dried two months were both 0.7. This compares to acid numbers of 1.0 and 1.4 for fuels from soaps dried three days. The iodine values did not differ significantly from one another. The fuels from soaps dried two months had iodine values of 136 and 141 while the fuels from soaps dried three days had iodine values of 149 and 150. Therefore, no significant differences existed relative to acid numbers and iodine values. NMR spectra confirmed results of small acid numbers and significant unsaturation. The yields of the fuel from the soaps aged different times was not comparable since the pyrolysis apparatus had been changed from stainless steel to glass and will be discussed later in this section. The yield is per 100 grams of dry soap and pyrolysis was performed in the stainless steel apparatus for the soaps dried three days (fresh) and the glass apparatus was used for fuels from soaps dried two months (aged).

Table 3. Fuels from Aged and Fresh Soaps

				Viscosity	
Soap	%Yield	Iodine Val.	Acid No.	Initial (cSt)	Final (cSt)
fresh	16.7	149	1.0	65.8	109.1
				68.1	110.1
fresh	17.4	150	1.4	70.1	105.8
				69.9	107.4
aged	49.5	136	0.7	82.8	115.3
				80.1	108.8
aged	45.0	141	0.7	78.5	105.1
				77.5	107.4

The vapor temperatures observed were much lower with the stainless steel compared to the glass apparatus used for pyrolysis. When the stainless steel pyrolysis vessel was used the maximum vapor temperatures were in the range of 200-210°F. With the glass vessel the vapor temperatures got as high as 400°F.

The liquid product recovery formed several layers and was considered complete when it fell to about 10 seconds between drops of product into the separatory funnel. The lightest and first of the product to come out was a clear water layer. The organic layer was next. When the stainless steel pyrolysis vessel was used this organic layer took the form of two distinctly different colored layers. The layers were a light yellow and a dark brown. These organic layers did not stay separated when they mixed in the separatory funnel. When the stainless steel pyrolysis apparatus was used, but the rate at which heat was supplied was reduced, the organic product took another form. The product was then formed in one distinct yellow-brown mixture with the color yellow more apparent. This organic product was different again when the glass pyrolysis vessel was used. The product then usually took the form of a more uniformly colored brown liquid product with a green tint on the last of the product.

There is a possible explanation of this extreme difference in yield between the glass and stainless steel pyrolysis vessels. As the soaps were heated they vaporized in both vessels and polymerization could take place in the vapor phase. This could be more drastic when the stainless steel pyrolysis apparatus was used for two reasons. First, there was a longer retention time with the stainless steel apparatus since the glass top increased the volume causing the vapor to have a longer holding time. Second, polymerization was possibly catalyzed by components in the stainless steel vessel. The polymers could then condense and, since they would be much less volatile than the soaps, they would char rather than vaporize.

The thickening effects of the fuels obtained from the soaps dried two different times were different. The kinematic viscosity for the fuels from soaps dried two months increased an average of 36.9% while the average increase was 57.8% after 48 hours for the fuels from soaps dried three days. An interesting observation takes place when the actual numbers are examined in Table 3. The viscosities taken after 48 hours were very close and averaged 112.0 and 106.3 centistokes compared to 109.6 and 106.6 centistokes for the fuels from soaps aged two months compared to three days. The average initial viscosities of the fuels from soaps dried two months (81.5 and 78.0 centistokes) were much greater than those of fuels from soaps dried three days (67.0 and 70.0 centistokes). This shows that fuels from soaps aged the longer period of time gave fuels with greater initial kinematic viscosities. These fuels from soaps aged different times were at approximately the same kinematic viscosity after 48 hours. Some of this variation in initial viscosity might have been due to the switch that occurred in the pyrolysis apparatus.

Glycerol Content of the Soaps

The second set of experiments for the pyrolysis studies investigated the effect of glycerol content of the soaps on the fuel. The soap was again prepared by the fusion method with linoleic acid and a 50% excess amount of calcium hydroxide mixed with 71 grams of demineralized water. High speed lubrication oil was used for the polymerization tests. The results are given in Table 4. Fuels made from soaps without added glycerol were compared against fuels made from soaps with 23 and 46 grams of glycerol added. The glycerol was added prior to pyrolysis. There is only one mole of glycerol that would be produced from vegetable oils for every three moles of calcium soap. Therefore, 46 grams of glycerol is the total amount that would be produced. Correspondingly, 23 grams represents half the amount in the soap.

Table 4. Fuels from Soaps With Different Amounts of Glycerol

Glycerol Added	%Yield	Iodine Val.	Acid No.	Viscosity Initial (cSt)	Final (cst)
none	12.6	134	1.3	81.8	100.3
none	13.7	124	1.0	72.7	107.0
23g	11.6	129	1.9	74.9	110.9
23g	10.7	131	1.9	75.7	109.8
46g	5.8	---	1.6	77.8	108.5
46g	4.5	---	1.7	76.9	107.1

The glycerol content of the soaps did not change the properties of the fuel significantly. The acid numbers for the fuels from soaps without glycerol added were 1.3 and 1.0. Acid numbers for fuels made from soaps with 46 grams of glycerol added were 1.7 and 1.6. Acid numbers for the fuels from soaps with 23 grams of glycerol added were both 1.9. Iodine values showed this same consistency for the fuels that could be tested. Since the yields were only 5.8%

and 4.5% for the fuels obtained with 46 grams of glycerol added not enough product was available for an iodine value determination. Iodine values for the fuels from soaps without added glycerol were 134 and 124. Iodine values from soaps with 23 grams of added glycerol were 129 and 131. The NMR spectra once again confirmed the findings of small acid numbers and showed a significant unsaturation region.

Thickening effects of the fuels were not affected by the addition of glycerol to the soaps prior to pyrolysis. The kinematic viscosity for the fuel from soap with no added glycerol increased an average of 34.2% after 48 hours. Likewise, the kinematic viscosity increased for the fuels made with 23 and 46 grams of glycerol added to the soap an average of 46.6% and 39.4%. This leads to the conclusion that glycerol content of the soaps does not affect the performance of the fuel in a diesel engine with regard to a tendency to polymerize.

Although the glycerol content of the soap did not significantly affect the polymerization properties, it did decrease the yield calculated per 100 grams of dry soap. Yield was low because pyrolysis was done in the stainless steel apparatus. Yields obtained from soaps with no glycerol added, with adding 23 grams, and adding 46 grams were averaged to be 13.2%, 11.2%, and 5.1%. The pattern of decreasing yield with increasing glycerol added to the soap leads to the conclusion that glycerol is not desirable in the soap prior to pyrolysis.

Fatty Acid Content of Soaps

Next in the pyrolysis studies was an investigation of the fatty acid content of the soaps. The fusion method with linoleic acid was used to produce the soaps and the polymerization tests used the high speed lubrication oil. This presented a problem when an attempt was made to increase the fatty acid concentration. The first try was to heat the soap to turn it to a liquid form and add the fatty acid which would have been linoleic acid. Then the corresponding acid number could be measured. The problem was the soap would not return to a liquid form before starting to pyrolyze. Next, it was tried to add excess linoleic acid to prepare the soaps. Several runs were tried using excess linoleic acid to complete the reaction. This technique proved to be a failure. Solid soap never formed, it just remained in the liquid state. Finally, it was determined how much excess calcium hydroxide was required to produce a solid soap. After several runs it was discovered that solid soap required at least stoichiometric amounts of calcium hydroxide. The two soaps compared in this study had 50% excess and stoichiometric amounts of calcium hydroxide. This was not the initial comparison that was to be made but it was the best that could be accomplished.

The results are given in Table 5. The nature of the fuel does seem to be changed slightly by the amount of excess calcium hydroxide used. The acid numbers for fuels from soaps with a stoichiometric amount of calcium hydroxide were 6.1 and 8.1. Acid numbers for fuels from soaps with a 50% excess amount of calcium hydroxide were both 0.6. This showed a slight difference. Iodine values were also changed: 181 and 184 for fuels from soaps with a stoichiometric amount of calcium hydroxide compared to iodine values of 132 and 139 for fuels from soaps with a 50% excess amount of calcium hydroxide. This means fuels made from soaps with less calcium hydroxide had more unsaturation and more free fatty acid content. Yields were not affected by the calcium hydroxide in the soaps. Yield per 100 grams of dry soap were averaged to be 42.6% and 49.1% for the stoichiometric and the 50% excess amount of calcium hydroxide. The glass pyrolysis apparatus was used for all these experiments.

Table 5. Fuels from Soaps with Different Free Fatty Acid Contents

				Viscosity	
$Ca(OH)_2$	%Yield	Iodine Val.	Acid No.	Initial (cSt)	Final (cSt)
50%xs	43. 8	132	0.6	76.7 77.7	106.3 101.9
50%xs	54.5	139	0.6	75.9 77.6	105.1 107.4
0%xs	41.2	181	6.1	76.5 76.7	117.8 118.1
0%xs	43.9	184	8.1	76.9 76.9	120.0 121.4

The thickening of the fuel did seem to be affected by the free fatty acid content of the soaps. The kinematic viscosities increased an average of 54.5% and 36.9% for the fuels from soaps with the higher free fatty acid content and the lower free fatty acid content respectively. The major difference in this increase was in the final kinematic viscosities of the fuels. The initial kinematic viscosities were all within 1.8 centistokes. Fuels made from soaps with the higher free fatty acid content showed a tendency to polymerize faster. This probably would have been more significant if higher free fatty acid contents could have been achieved.

Calcium Versus Magnesium Soaps

The fourth set of tests for the pyrolysis studies compared calcium soaps with magnesium soaps. The magnesium soap was prepared by the fusion process with 33.1 grams of magnesium hydroxide and 59 grams of demineralized water. The results from the other tests in the pyrolysis studies were used for the calcium soap. Magnesium soaps gave such low yields not enough product was available for any tests. The stainless steel pyrolysis apparatus was used. With this apparatus a typical yield from other runs in the pyrolysis studies for the calcium soaps was around 10-15%. Magnesium soaps gave yields that approached 0%. Thus, the calcium soaps were preferred to the magnesium soaps since the calcium soaps gave a greater yield.

For a possible explanation of this difference in yield the reader is first referred to the discussion of the difference in yield between the stainless steel and glass pyrolysis vessels given in the Aged Versus Fresh Soap section of the Pyrolysis Studies. It is possible, however, that the magnesium in the soaps promotes vapor phase polymerization more than the calcium found in the soaps. If this is true it would cause decreased yield for the same reason as discussed earlier.

Literature indicates magnesium soaps might have lower pyrolysis temperatures than their calcium counterparts. In the 1920's Sato in Japan investigated the dry distillation of calcium and magnesium soaps of soybean oil. Sato found that the magnesium soaps decomposed at lower temperatures and gave heavier products than the calcium soaps [19].

Distillation Results

The pyrolysis studies next investigated the different fractions of the diesel fuel. Fuel and the fractions of the fuel corresponding to the #2 diesel range were tested with high speed lubrication oil for polymerization tests. Soap was again prepared by the fusion method using linoleic acid and a 50% excess amount of calcium hydroxide mixed with 71 grams of demineralized water. The total distillate was made up of extremely light, #1, #2, #3, and extremely heavy liquid diesel products. The #2 fraction of the total distillate was 51 weight percent of the total product and the fractions that were lighter and heavier than the #2 range fuel fraction were approximately equal. This total product was compared to the #2 range and the results are given in Table 6. This comparison proved the differences in the properties of the fuel were not significant. Acid numbers for the total distillate were 0.6 and 0.8 compared to acid numbers of 0.8 and 0.9 for the #2 diesel range. Iodine values for the total distillate were 136 and 130 while iodine values for the #2 diesel range were 141 and 138.

Table 6. The Total Distillate Versus the #2 Diesel Range

Fuel	Iodine Val.	Acid No.	Viscosity Initial (cSt)	Viscosity Final (cSt)
total	136	0.6	82.0	110.1
total	130	0.8	81.0	106.7
#2	141	0.8	62.3 62.2	108.4 108.3
#2	138	0.9	63.6 63.7	106.5 106.5

Thickening effects were different when the total distillate and the #2 diesel range product were compared. The total distillate had initial viscosities of 82.6 and 81.0 centistokes and final viscosities after 48 hours in the polymerization apparatus of 110.1 and 106.7 centistokes. The #2 diesel range had initial viscosities of 62.2 and 63.7 centistokes and final viscosities after 48 hours in the polymerization apparatus of 108.3 and 106.5 centistokes. The total distillate experienced a 32.5% average increase in kinematic viscosity after 48 hours while the #2 diesel range had a 70.6% average increase. This shows the #2 diesel range experiences a greater increase in kinematic viscosity after 48 hours in the polymerization apparatus compared to the total distillate because the initial kinematic viscosities were much greater for the total distillate compared to the #2 diesel range. After 48 hours the #2 diesel product gave about the same viscosities as the total distillate.

Next, the total distillate was separated into three fractions: lighter than #2, #2, and heavier than #2 diesel. These three fractions were then compared. Results are given in Table 7. Thickening effects were different. The lighter fraction had an 93.0% increase in kinematic viscosity. The regular #2 diesel increased an average of 70.6% in kinematic viscosity. The heavy fraction had an 27.2% increase in kinematic viscosity. All these increases were after 48 hours in the polymerization apparatus.

Table 7. Viscosity Results for Diesel Fuel Types

Fuel	Viscosity Initial (cSt)	 Final (cSt)
light	56.4	107.8
regular	62.3	108.4
(#2)	62.2	108.3
	63.6	106.5
	63.7	106.5
heavy	77.9	99.1

These results indicate that for hot weather regular #2 should be made up of diesel on the heavier side of the #2 diesel range. This is what Tom Davis, a chemical engineer at the Farmers Central Union Exchange just outside Billings, Montana, said is the case.

Storage Effects

Next, storage effects on the fuel were studied. Fuel fresh from pyrolysis was tested and compared to fuel pyrolyzed and let stand for ten weeks. Polymerization tests used high speed lubrication oil and the soaps were prepared by the fusion method with linoleic acid and a 50% excess amount of calcium hydroxide mixed with 71 grams of demineralized water. Data for these experiments is given in Table 8. Properties of the fuel were not affected by this storage process. For fuel fresh from pyrolysis acid numbers were 5.1 and 1.3. This compared to the aged fuels acid numbers of 4.2 and 0.6. Iodine values for fresh fuels were

160 and 147. The iodine values for the aged fuels were 143 and 150.

Table 8. Aged Versus Fresh Fuels

Fuel	Iodine Val.	Acid No.	Viscosity Initial (cSt)	Final (cSt)
fresh	160	5.1	77.5	111.0
fresh	147	1.3	71.7	112.0
aged	143	0.6	71.0	108.3
aged	150	4.2	85.6	108.0

Thickening effects were also similar. For fuel fresh from pyrolysis the kinematic viscosity increased an average of 49.5% after 48 hours in the polymerization apparatus. For fuel that had been aged ten weeks the kinematic viscosity increased an average of 39.1% after 48 hours in the polymerization apparatus. In conclusion, the fuel aged for ten week behaved similarly in the simulation of the diesel engine.

Results for Pure Linoleic Acid

Next, the pure linoleic acid was compared to the other results in the Pyrolysis Studies. The iodine value for the linoleic acid was 153 which was comparable to the iodine values found for the soap-pyrolysis fuels. The acid number of 155 for the linoleic acid was significantly higher than that of the acid numbers of the soap-pyrolysis fuels. The polymerization results showed an initial kinematic viscosity of 96.4 centistokes and after 48 hours one of 178.0 centistokes with the high speed lubrication oil. This is an

85% increase in thickening of the linoleic acid which is significantly more than that of the soap-pyrolysis fuels. In addition, the initial viscosity of the linoleic acid is much greater. Therefore, soap-pyrolysis fuels would work better than pure linoleic acid in a diesel engine with regard to tendency to polymerize.

Pyrolysis With and Without Calcium Hydroxide Reactant

The next step after the pyrolysis studies were completed was to investigate pyrolysis with and without the use of calcium hydroxide as a reactant. The calcium hydroxide reactant was added just prior to the heating of the soaps. A review of the literature indicated that pyrolysis with the use of calcium hydroxide as a reactant may produce hydrocarbons [20]. Hydrocarbons (RH) would be a product in the following reaction of calcium soap with calcium hydroxide:

$$(RCOO)_2Ca + Ca(OH)_2 = 2RH + 2CaCO_3$$

A charge of 12.37 grams of calcium hydroxide was the stoichiometric amount required if the soap contained no water. The precipitation soap making process was used to prepare the soaps in this group of experiments so as to insure no excess calcium hydroxide would be present in the soaps. The precipitation method used a stoichiometric amount of sodium hydroxide mixed with 86 grams of demineralized water and a 50% excess amount of calcium chloride mixed with 176 grams of demineralized water. The amount of calcium hydroxide required on a wet basis could not be calculated until after the pyrolysis with the calcium hydroxide reactant was performed because the moisture content of the soaps was unknown. It was determined after pyrolysis with the calcium hydroxide reactant was performed that the amount of calcium hydroxide required on a dry basis for the runs with the reactant was 7.16 and 6.36 grams. Therefore, 12.37 grams was a 72.8% and 94.5% excess for the two runs with the reactant.

The results are given in Tables 9 and 10. The acid numbers and iodine values of the fuel show no significant differences whether calcium hydroxide was added or not. Acid numbers for fuels made without the calcium hydroxide were 3.2 and 2.3 while acid numbers were 4.2 and 0.6 for fuels when the calcium hydroxide was added. NMR spectra did support the findings of small acid numbers and significant unsaturation. No significant differences could be determined from these results.

Table 9. Experiments With/Without Calcium Hydroxide Reactant

Run	Soap	%Yield	Iodine Val.	Acid No.
1-w/o	1	79.7	148	3.2
2-with	1	58.8	138	4.2
3-w/o	2	73.1	145	2.3
4-with	2	61.4	140	0.6

Table 10. Viscosity Results of Fuels With/Without Reactant

High Speed Lubricating Oil			Medium Speed Lubricating Oil		
	Viscosity			Viscosity	
Run	Initial (cSt)	Final (cSt)	Run	Initial (cSt)	Final (cSt)
1	76.9	115.7	1	118.9	200.6
2	76.6	109.3	2	118.6	190.9
3	72.8	115.1	3	117.2	255.9
4	77.4	109.2	4	121.5	197.7
neat lub. oil	109.3	112.5	neat lub. oil	175.0	234.2
	108.2	113.0		179.0	233.0

Yield was significantly decreased when the calcium hydroxide was added. Yields per 100 grams of dry soap were 79.7% and 73.1% when calcium hydroxide was not used prior to pyrolysis compared to yields of 58.8% and 51.4% when calcium hydroxide was used. Therefore, yield is adversely affected by the addition of calcium hydroxide prior to pyrolysis.

Polymerization tests were done with both medium and high speed lubrication oil. These results showed the kinematic viscosity increase after 48 hours in the polymerization apparatus was greater for the fuels made without the calcium hydroxide addition than for fuels with the addition. With the high speed lubricating oil or thirty weight oil the viscosity increase averaged 54.2% without the addition of calcium hydroxide and 41.8% with the addition. When the medium speed lubrication oil or forty weight oil was used the kinematic viscosity increase averaged 68.7%

(ignoring run 3) without the addition and 61.8% with addition of calcium hydroxide. Looking at the final viscosity readings for all eight runs the value of 255.9 centistokes in run 3 was the only one out of line and was probably in error. These results indicate the addition of calcium hydroxide prior to pyrolysis is somewhat beneficial in reducing thickening effects.

Control polymerization runs were also made using the lubricating oil without added soap-pyrolysis fuel. The Table 10 data indicate the high speed lubricating oil was much more resistant to polymerization than the medium speed oil; the kinematic viscosity of the former increased 3.7% and the latter increased 32.0% in 48 hours. Therefore, the addition of soap-pyrolysis fuels had comparable effects on both lubricating oils.

Soap Production

The next set of experiments investigated the effects of the soap production processes with the high speed lubricating oil polymerization tests. Until this time soap had been produced by both the precipitation and fusion methods. However, linoleic acid had been used since it was only important to investigate certain process variables. Now it was time to use safflower oil since the yield using the vegetable oil was an important variable for the soap production studies. The oil used for these experiments was mill run safflower oil from Continental Grain Company in Culbertson, MT. The safflower oil was freshly extracted from a number of common varieties. The safflower oil was raw and was kept in refrigerated storage. Even though safflower oil is made up of primarily linoleic acid the soap-making procedure was not expected to be exactly the same. This was because the reaction of linoleic acid with calcium hydroxide produced calcium soap and water while the reaction of safflower oil and calcium hydroxide produced calcium soap and glycerol. These experiments compared the fusion soap-making process with the precipitation method. Toluene and water at different concentrations were used as solvents with the calcium hydroxide in the fusion procedure. In addition, use of no solvent with the calcium hydroxide was investigated.

The results of the pyrolysis studies were used as a guide for deciding the techniques to use. First, it was decided that no advantage was gained by drying the soaps. Second, glycerol was removed by pouring off any excess and then washing with demineralized water. Third, since the magnesium hydroxide dramatically decreased yield, calcium hydroxide was chosen as the alkali hydroxide. The soap production method is outlined for both the precipitation and fusion methods in the Experimental Description section. Two batches of soap were prepared using the precipitation procedure and 180 grams of safflower oil; a solution of 25.7

grams of sodium hydroxide mixed with 77 grams of demineralized water was then added. The next step in the precipitation procedure added a solution of 26.4 grams of calcium chloride and 79.2 grams of demineralized water. The sodium hydroxide was in stoichiometric quantity and the calcium chloride corresponded to a 50% excess.

The remaining batches of soap were prepared using the fusion method. Twenty-nine grams of calcium hydroxide were used for all the fusion runs and this corresponded to a 10% excess. First, two batches of soap were prepared with 200 grams of safflower oil and a slurry containing 29 grams of calcium hydroxide and 52 grams of demineralized water. Second, two more batches of soap were prepared with 200 grams of safflower oil and a slurry with 29 grams of calcium hydroxide and 132 grams of demineralized water. Third, two batches of soap were prepared with 200 grams of safflower oil and only the 29 grams of calcium hydroxide.

The most apparent difference when the safflower oil was used instead of the linoleic acid was the length of time required for the reaction to take place with the fusion process. With the safflower oil agitation was required for 1.5-2.0 hours before the reaction was complete. When linoleic acid was used the reaction was complete in a matter of minutes. If this agitation was not sustained the soap seemed to want to separate out into two phases that looked like safflower oil and calcium hydroxide solution.

Soap was then made by the fusion method but with a hydrocarbon as the solvent instead of water. The reason this was tried was that a hydrocarbon such as toluene might provide good contact between phases. First, two batches of soap were prepared with 200 grams of safflower oil and a slurry of 29 grams of calcium hydroxide and 11 grams of toluene. Second, two batches of soap were prepared with 200 grams of safflower oil, 29 grams of calcium hydroxide, and 22 grams of toluene. Several different approaches had been initially tried for the set of runs that used toluene as the solvent. The 29 grams of calcium hydroxide were first tried with 50 grams of toluene. This produced very little soap with about 90 ml of unreacted safflower oil and glycerol. Next, 50 grams of toluene and 50 grams of calcium hydroxide were used to produce the soap. This produced more soap than the first method but it still left approximately 35 ml of unreacted safflower oil and glycerol. The soap produced by these two tactics was not enough for pyrolysis. It was then determined that toluene in the concentrations finally used worked satisfactorily along with the 29 grams of calcium hydroxide and left very little unreacted safflower oil or glycerol. Therefore, there was enough soap for pyrolysis. The time required for this reaction to take place was about 2 hours.

The test results on the fuels are given in Table 11. As in previous tests, all the acid numbers and iodine values for the fuels produced by the various soap-making methods were quite similar. Acid numbers for the fuels ranged between 0.9 and 2.7. Iodine values were in the range of 155-170. No differences existed between the fuels in the amount of unsaturation or free fatty acid content. NMR spectra were all similar for the fuels produced from different soaps and the spectra showed only a slight carboxylic acid peak and significant unsaturation. Therefore, the NMR spectra confirmed the findings of the acid numbers and iodine values.

Table 11. Results of Fuels from Different Soaps With Solvent

Soap Prep.	Iodine Val.	Acid No.	Viscosity Initial (cSt)	Final (cSt)
precipitation	158	1.5	77.3	120.2
precipitation	162	2.4	76.7	108.9
fusion 52g H_2O	151	1.9	78.9	109.8
fusion 52g H_2O	162	1.9	78.4	114.3
fusion 132g H_2O	166	2.3	82.2	117.7
fusion 132g H_2O	159	0.9	81.8	116.0
fusion 11g tol.	170	2.7	76.0	115.4
fusion 11g tol.	161	2.5	76.9	110.0
fusion 22g tol.	160	2.1	74.9	112.5
fusion 22g tol.	155	2.1	80.3	114.8
fusion	157	1.7	78.8	114.3
fusion	164	2.4	79.9	116.3

The thickening effects for the fuels obtained from soaps made by different procedures did not show significant deviation. The kinematic viscosity increase averaged 48.8% in 48 hours for the fuel from the precipitation soap. For the fuel from the fusion soap with demineralized water concentrations for the solvent of 52 and 132 grams the kinematic viscosity increased an average of 42.5% and 42.5% in 48 hours. For the fuel from fusion soap with toluene as the solvent in amounts of 11 and 22 grams the kinematic viscosity increased in 48 hours an average of 47.4% and 46.5%. The final soap was produced by the fusion method with no solvent and only the 29 grams of calcium hydroxide had a kinematic viscosity increase after 48 hours an average of 45.4%. Therefore, in respect to thickening effects in a diesel engine the fuels made from different soap-making procedures would behave similarly in a time period of 48 hours.

Two types of yields were calculated as described in the Experimental Description section and these yields are given in Table 12. The first yield was calculated per 100 grams of dry soap. The data in this table indicate that the precipitation and the fusion soap production method with no solvent gave the greatest fuel yields. The precipitation soap gave a average yield of 41.9% while the fusion soap produced with no solvent gave an average yield of 40.2%. Pyrolysis Run 10 used soap with 22 grams of toluene solvent had the greatest yield of 66.1% but this was not confirmed by its duplicate run 9 with a yield of 34.3%.

Table 12. Yields of Fuels from Different Soaps With Solvent

Soap Prep.	Yield (g fuel/ 100g dry soap)	Yield (g fuel/ 100g safflower oil)
precipitation	44.8	45.9
precipitation	38.9	
fusion 52g H_2O	24.2	23.4
fusion 52g H_2O	26.2	
fusion 132g H_2O	26.9	16.6
fusion 132g H_2O	26.4	
fusion 11g tol.	26.3	30.0
fusion 11g tol.	29.2	
fusion 22g tol.	34.3	33.8
fusion 22g tol.	66.1	
fusion	42.6	43.6
fusion	37.7	39.1

Second, a yield was calculated per 100 grams of total safflower oil used. Some of the duplicate data for this calculation was inadvertently destroyed but at least one value for each of the soaps was saved. These values along with the first set of yields provided enough information for a pattern to develop and a recommendation to be made. The yields on Table 12 show the precipitation soap process had a 45.9% yield and the fusion soap method with no solvent gave yields of 43.6% and 39.1%. In reference back to the experimental section under soap-making procedures it shows more steps, and ultimately more time, for soap to be prepared with the precipitation method rather than the simpler fusion process. Even though the fusion method is complicated slightly by the use of safflower oil rather than linoleic acid, it is still easier to perform than the precipitation method.

From the data a soap-making procedure can be recommended. First, the fuels made with these different soaps demonstrated only a negligible difference would exist in a diesel engine with regard to tendency to polymerize within 48 hours. Second, the precipitation soap-making process and the fusion method with no solvent gave the greatest yields and these were about the same. Since the fusion with no solvent is a one-step process and the precipitation a multi-step one which is harder to perform and takes more time, the fusion process is preferred. Also, use of a solvent of any kind is not recommended to achieve the greatest yield.

Unsaturation Studies

The mechanism by which polymerization proceeds has been described by Rheimich and Austin as follows [21]:

1. An induction period occurs, preceding the initiation of the oxidative chain reaction, during which no visible physical or chemical properties change.
2. Oxygen interacts with carbon double bonds to form hydroperoxides. A considerable uptake of oxygen coincides with the beginning of a perceptible polymerization reaction.
3. The polyunsaturated species undergo conjugation of double bonds and isomerization of cis to trans forms.
4. The hydroperoxides decompose resulting in free radicals

which in turn contribute to autocatalysis.

5. Production of high-molecular weight cross-linked polymers and low-molecular weight carbonyl and hydroxyl compounds occurs via a free radical polymerization and scission reactions.

The number of fatty acid double bonds should then affect reactivity. In addition, Miyashita and Takagi recently proposed that higher oxidative rates of free fatty acids than those of their methyl esters could be due to the catalytic effect of the carboxyl groups on the formation of free radicals by the decomposition of hydroperoxides [22]. It is a possibility then that number and/or position of the carboxyl groups relative to the carbon double bonds would effect the polymerization reaction.

Previous research in this lab (DNRC grant agreement RAE-84-1041, Chemical Processing of Vegetable Oil to Prevent Polymerization, [23]) indicated that the polymerization properties of the fuel produced by a soap-pyrolysis process may not be very sensitive to the quantity of unsaturation. It was found that the polymerization character was more sensitive to the free fatty acid content. The purpose of the unsaturation studies conducted here was to investigate the effect of unsaturation on polymerization with high speed lubrication oil. This was done by preparing soaps that were made from fatty acids with varying degrees of unsaturation. The fatty acids all had 18 carbon atoms with different numbers of carbon double bonds: stearic acid (saturated), oleic acid (one double bond), linoleic acid (two double bonds), and linolenic acid (three double bonds). The effect of unsaturation can be determined more specifically using the technical grade fatty acids than using a safflower oil composed of a mixture of esters made from acids with different degrees of unsaturation and different numbers of carbon atoms. Soap was prepared by the fusion method using each of the four fatty acids. An interesting observation was that the soaps from each fatty acid had a distinctive color: off-white for the stearic acid soap, light gray for the oleic acid soap, light tan for the linoleic acid soap, and medium tan for the linolenic acid soap. Pyrolysis of all the soaps except that of stearic acid produced fuels suitable for further testing. Because stearic acid is a solid at room temperature, the fuel produced from it also had a high melting temperature compared to those fuels from other fatty acids. When pyrolysis was run on the soap produced from stearic acid, the resulting fuel solidified when cooled in the condenser leading to the product collection vessel and plugged the apparatus. Since a solid fuel is not at all attractive for use in a diesel engine, it was decided to eliminate the stearic acid soap from further tests.

The results are presented in Table 13. The acid numbers of the fuels are all relatively low and indicate little free fatty acid content. The average acid numbers were 0.2 for the oleic acid soaps, 0.6 for the linoleic acid soaps, and 0.5 for the linolenic acid soaps. Since the starting acids were all monocarboxylic, i.e., they contain only one carboxylic or acid group, the acid numbers were all similar: 157 for oleic, 155 for linoleic, and 162 for linolenic.

Table 13. Results of Fuels From Different Acid Soaps

				Viscosity	
Fuel	%Yield	Iodine Val.	Acid No.	Initial (cSt)	Final (cSt)
oleic	69.2	132	0.2	79.0	97.7
acid				77.6	99.0
soap	65.4	141	0.2	76.2	95.9
				75.2	99.6
linoleic	59.4	147	0.6	79.2	109.3
acid				78.6	109.9
soap	62.7	148	0.6	78.7	106.7
				77.3	107.7
linolenic	59.1	143	0.6	79.1	104.8
acid				78.2	103.1
soap	57.4	150	0.4	78.5	107.0
				78.8	106.3

The iodine values of the fuels were all similar while those of the starting acids increased with increasing unsaturation. The values of the starting acids are understandable (106 for oleic, 153 for linoleic, and 190 for linolenic) since iodine value is a measure of the number of carbon double bonds present and oleic has one double bond, linoleic has two double bonds, and linolenic has three double bonds. However, the similarity of the iodine values of the fuels made from soaps produced from these acids is surprising. Literature has indicated that double bonds can be formed during soap-pyrolysis, particularly if calcium hydroxide is present. This would explain the increase in unsaturation in the fuel using the oleic acid soap [24]. Further literature indicates that soaps are used as driers to promote oxidation and polymerization of unsaturated vegetable oils. This would lead to a decrease in unsaturation as some double bonds are eliminated in forming larger molecules [25]. The carbon 13 NMR spectra confirmed the findings of essentially no carboxylic acid groups present and a significant amount of unsaturation.

The yield data calculated per 100 grams of dry soap indicate yield decreased as unsaturation in the original acid has increased. The average yields of fuels were 67.3% from the oleic acid soap, 61.0% from the linoleic acid soap, and 58.2% from the linolenic acid soap. In 1939 Dalal and Mehta in India cracked vegetable oils. They found that liquid product yields decreased with increasing unsaturation [26]. This pattern of decreasing yield with increasing unsaturation has therefore been documented before in vegetable oils.

Polymerization tests were performed with the high speed lubrication oil. The values from the table indicate initial kinematic viscosities for each of the fuels from different soaps were similar. These viscosities were 77.0, 78.4 and

78.6 centistokes for the fuel from the oleic, linoleic, and linolenic acid soaps. After 48 hours in the polymerization apparatus the kinematic viscosities of all the fuels had increased. The increase for the fuels was 27.3% for fuel from the oleic acid soap, 38.3% for the fuel from the linoleic acid soap, and 34.0% for the fuel from the linolenic acid soap. It is interesting to note that the values of the viscosities taken after 48 hours and the iodine values of the starting fuels are almost directly proportional. For both properties the values increased in order of oleic, linoleic, and linolenic (values for the linoleic and linolenic fuels were very close however).

The purpose of this task was to investigate the effect of unsaturation on polymerization. The previous grant funded by the DNRC [27] had suggested that the effect of unsaturation on polymerization might be less important than the free fatty acid content present. The unsaturation studies conducted here cannot distinguish between these two variables since all the starting soap-pyrolysis fuels had little free fatty content as evidenced by the acid numbers and qualitatively confirmed by the NMR spectra.

Several conclusions can be drawn from this study. First, soap made from stearic acid is undesirable since the fuel was a solid at ambient conditions. Second, it might be desirable for the vegetable oil to contain more oleic acid esters than either linoleic or linolenic acid esters. The fuel yields would probably be greater and there may be less tendency to polymerize with the lubrication oil. Finally, when virtually no free fatty acids are present iodine values serve as a good indication of polymerization characteristics.

Soap-Pyrolysis Process Optimization

This task optimized the soap-pyrolysis process for making fuel potentially suitable for use in a diesel engine. The results from the previous experiments helped identify important process variables and techniques that were used in this investigation. The purpose of the optimization study was to put all the prior results together and determine the combination of most desirable techniques and levels of variables for the process.

Several variables were observed from the previous experiments that affected the fuel and were optimized here. First, the Pyrolysis Studies tests addressing the Fatty Acid Content of the Soap indicated that the amount of calcium hydroxide added to the linoleic acid during soap production might affect polymerization characteristics. This optimization used safflower oil instead of linoleic acid to produce the soaps since it was important to compare fuel yields from the vegetable oil and not just properties. Therefore, the first variable optimized was the amount of excess calcium hydroxide added to the safflower oil to make the soaps. The lower constraint on the amount of calcium hydroxide added to 200 grams of safflower oil was 0 grams of excess (stoichiometric) or 26.3 grams. Second, it was shown when pyrolysis was performed with the addition of calcium hydroxide reactant that the addition of calcium hydroxide to the linoleic acid prior to pyrolysis decreased thickening while limiting yield. This was the second variable optimized. The lower constraint on this variable was to add no (0 grams) calcium hydroxide prior to pyrolysis.

Several techniques were also found to affect the fuel. First, the Pyrolysis Studies under the Glycerol Content of the Soaps found that glycerol in the soap decreased yield. Therefore, the glycerol was removed by washing the soaps with demineralized water and pouring off any on the surface of the soap. Second, the Soap Production Studies indicate that the soap should be prepared by the fusion method with no solvent. This procedure was used to prepare all the soaps for this milestone.

Optimization of the process included several steps. The yield of the fuel was selected for optimization. The polymerization characteristics were considered to be less important because all the soap-pyrolysis fuels were good and quite consistent in this respect. First, the sequential simplex optimization procedure was used as long as possible [28]. The number of variables to be optimized was 2, so the number of vertices in a simplex was 3. The simplex vertices corresponded to the various levels of the variables. After comparing the three experiments, a decision was made to discard the worst experiment. The location of the new experiment was calculated by using simple rules and this resulted in a new simplex. This technique was abandoned when it was found that the constraints were starting to be violated, i.e., it would require using less than the amount of calcium hydroxide required to produce the soaps or a negative (impossible) amount of calcium hydroxide added prior to pyrolysis. This made it futile to maintain the original shape of the simplex (See Figure 6).

The Complex Method of Box [29] was next implemented to locate the optimum. The Complex Method of Box is superior to the simplex method in that the shape of the pattern of experimental runs can be changed; this allows for continued experimentation without violating any variable constraint. This technique used 4 vertices which again corresponded to the levels of variables (See Figure 7). The location of the next experiment was found again by discarding the least desirable point and using simple rules to find the new point in the complex. From this method the optimum appeared to be at values of 0 excess grams of calcium hydroxide for soap production and 0 grams of calcium hydroxide added prior to pyrolysis. The results of this procedure are given in Table 14 and it does indicate the yields at or very near this point were the greatest while the kinematic viscosities of

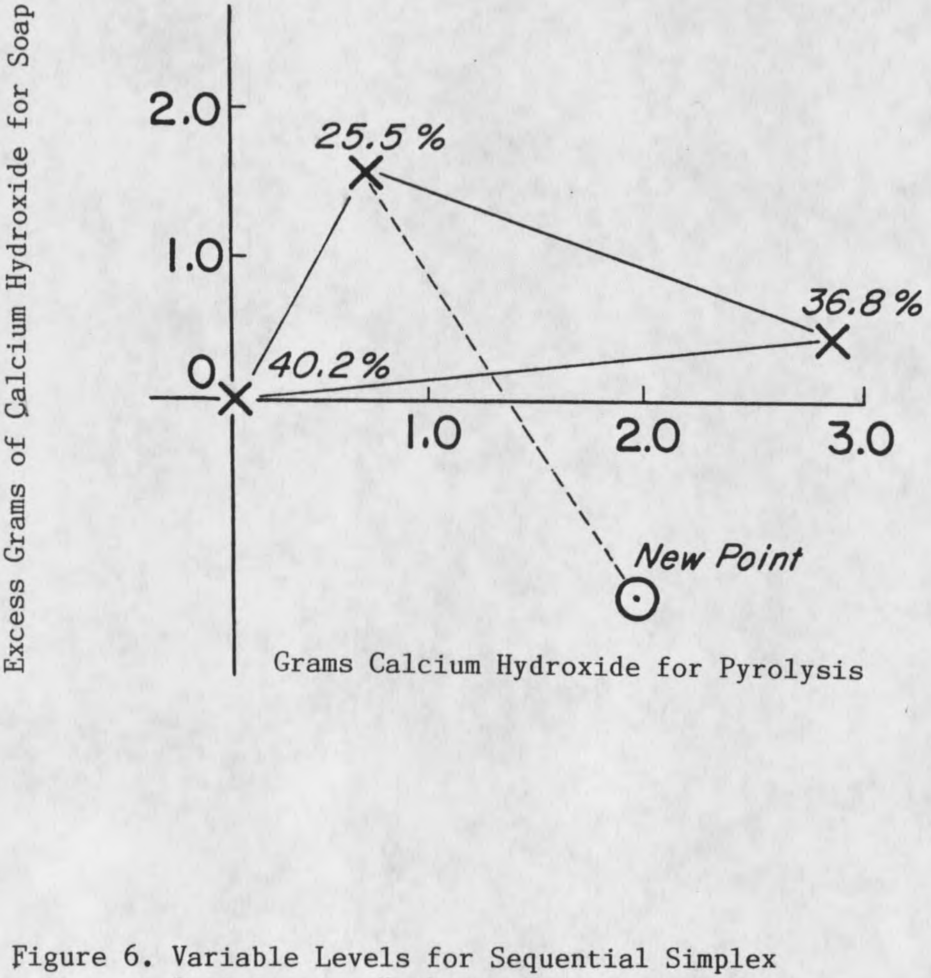


Figure 6. Variable Levels for Sequential Simplex Optimization Technique

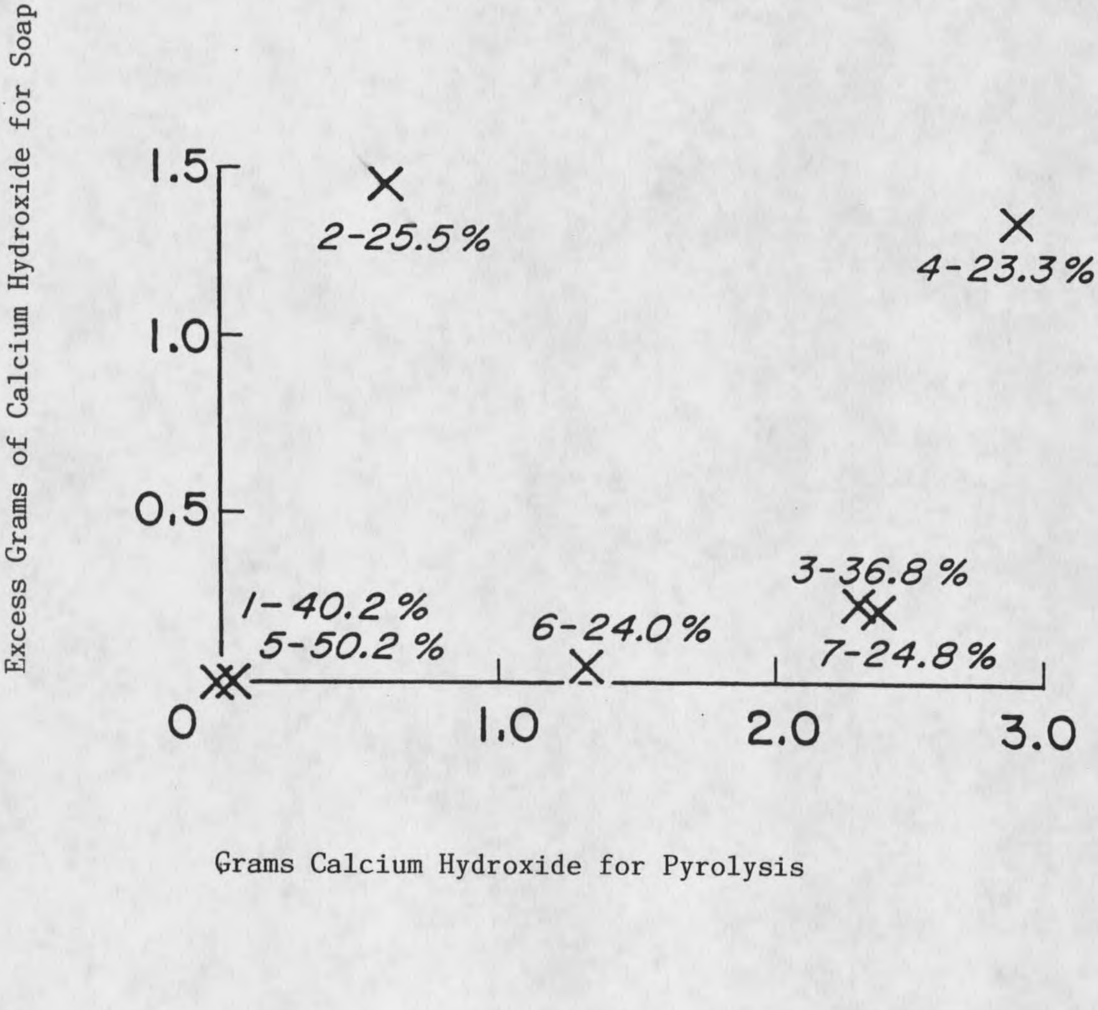


Figure 7. Variable Levels for Complex Method of Box Optimization Technique

all the experiments were good. Run 3 and 7 are duplicates of each other. Run 7 was performed since the Run 3 yield looked suspicious. The duplicate Run 7 showed that Run 3 was out of line and probably in error.

Table 14. Results for the Complex Method of Box

Run	x_1(g)	x_2(g)	%Yield	Viscosity (HS) (cSt) Initial	Viscosity (HS) (cSt) Final	Viscosity (MS) (cSt) Initial	Viscosity (MS) (cSt) Final
1	0.0	0.00	40.2	79.2	125.6	138.9	189.8
2	1.45	0.78	25.5	82.3	131.7	133.6	198.8
3	0.39	2.90	36.8	81.7	110.5	143.9	212.5
4	1.50	3.00	23.3	76.9	109.1	119.3	200.6
5	0.03	0.00	50.2	79.8	115.3	126.3	207.5
6	0.03	1.26	24.0	80.1	122.7	136.2	202.2
7	0.39	2.90	24.8	77.3	112.1	136.8	184.8

yield is calculated per 100 grams of safflower oil

x_1=excess of $Ca(OH)_2$ used to make the soap
x_2=$Ca(OH)_2$ added prior to pyrolysis

HS=high speed lubrication oil
MS=medium speed lubrication oil

Once the optimum appeared to be found, a factorial experimental design was used to fit an equation to the surface of the yield as a function of the two variables [30]. The reason for obtaining this equation was to represent all the possible yields over the ranges of the two variables rather than just the yields for the particular experimental runs. An optimization technique could then be used to find the maximum yield on the surface; this would then be verified with an experimental run at optimum conditions. This factorial required nine experimental runs of which three of the previous runs were used and six new experiments were made (See Figure 8). The order of the new experiments was determined randomly. Table 15 shows the experiments for the 3^2 factorial and the corresponding yields and kinematic viscosities at each level.

Table 15. Results from the 3^2 Factorial

			Viscosity (HS) (cSt)		Viscosity (MS) (cSt)	
x_1	x_2	%Yield	Initial	Final	Initial	Final
0.015*$	0.00	45.2*@	79.5*@	120.5*@	132.6*@	198.7*@
0.000	1.45	24.0@	80.1@	122.7@	138.2@	202.2@
0.000	2.90	23.5	78.1	114.2	126.5	190.2
0.195	0.00	37.7	77.8	114.2	132.7	188.6
0.195	1.45	26.5	79.0	108.6	133.1	188.8
0.195	2.90	26.8	79.2	115.8	130.0	185.0
0.368	0.00	29.8	82.0	116.2	129.0	184.3
0.368	1.45	14.7	73.2	119.3	108.0	199.4
0.390&	2.90	24.8@	77.3@	112.1@	136.8@	184.8@

* averages of duplicate runs

@ taken from previous work in this study

$ although this number should have been 0.0, it was close enough and could be used in the factorial experimental design

& although this number should have been 0.368, it was close enough and could be used in the factorial experimental design

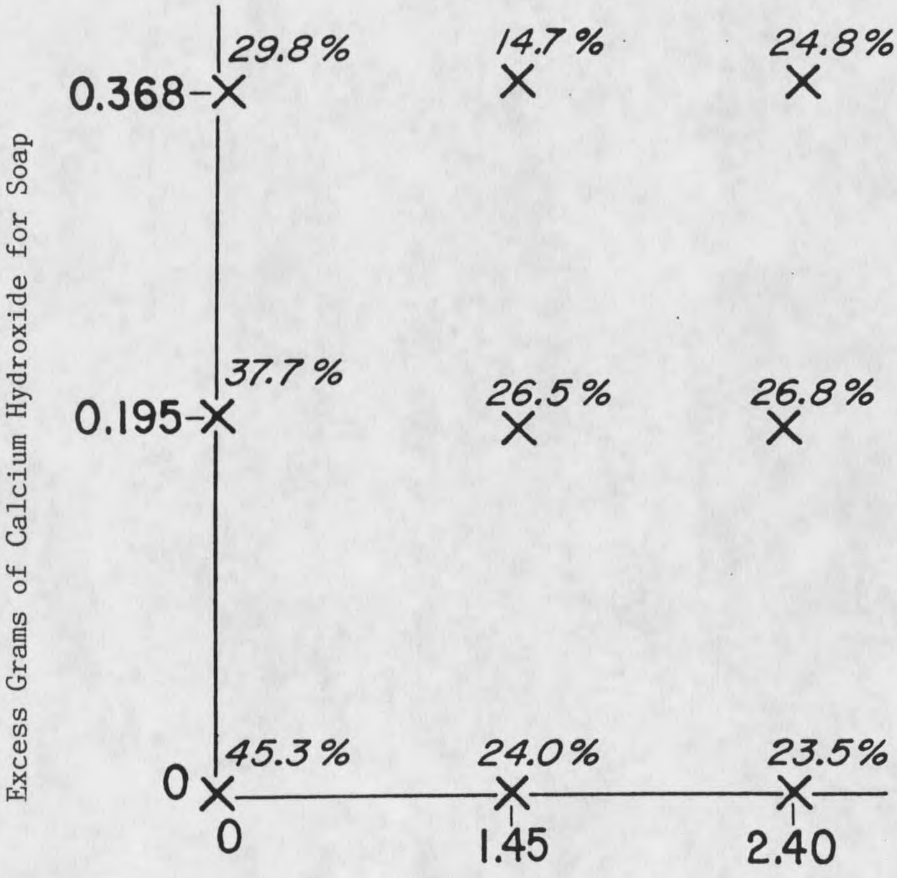
The mathematical equation that describes the yield surface was:

$$y = B_0x_0 + B_1x_1 + B_2x_2 + B_{11}x_1^2 + B_{22}x_2^2 + B_{12}x_1x_2$$

where: y = yield per 100 grams of safflower oil

x_1 = excess grams of $Ca(OH)_2$ in soap

x_2 = grams of $Ca(OH)_2$ added prior to pyrolysis



Grams Calcium Hydroxide for Pyrolysis

Figure 8. Variable Levels for the Factorial Experimental Design

The procedure used to find the constants is described by Davies [31]. A more complete discussion for finding the constants is given in Appendix A. As outlined by Davies, the variables were coded and later decoded to simplify calculations. The levels of the variables are given in Table 16.

Table 16. Variable Levels Used for Optimization

Variable	Level (grams)
x_1	0.000
	0.195
	0.368
x_2	0.000
	1.450
	2.900

The equation was calculated to be:

$$y = 44.6 - 7.8x_1 - 20.4x_2 - 98.2x_1^2 + 4.6x_2^2 + 15.7x_1x_2$$

All the constants were determined to be significant.

There are many optimization techniques that can be used with an equation such as this one for the surface representing possible fuel yields. The Complex Method of Box is reliable and a computer program was written to use this technique. The program is given in Appendix B. The program includes several subroutines unique to this problem. These are a subroutine for the objective to be maximized and a subroutine for the constraints. The objective to be maximized was the equation for the yield surface. The constraints were: $0<x_1<2$ and $0<x_2<5$, all in grams. The purpose of the constraints was to limit the search for the optimum yield ranges of the variable levels. The values for x_1 and x_2 again correspond to the amount of excess calcium hydroxide used to make the soap and the amount of calcium hydroxide added prior to pyrolysis. The last part of the program uses a subroutine that maximizes the objective function. This subroutine uses the Complex Method of Box and is already programmed in the computer. This program determined the maximum yield occurred at values of 0.315735577E-6 for x_1 and 0.151638811E-6 for x_2. Therefore, the maximum yield can be said to occur at the point $x_1=0$ and $x_2=0$. This was used as a check on the optimum value of the objective function.

One last run was done at the optimum using a stoichiometric amount of calcium hydroxide for soap production (0 grams excess) and no calcium hydroxide (0 grams) added to the soap prior to pyrolysis. In addition, duplicate polymerization tests were done along with an acid number and iodine value for this fuel. Table 17 gives the results for this final run. The data on this table does indeed indicate this was the point for maximum yield. This yield of 39.8% can be compared to a value of 44.6% predicted by the equation. This shows there is experimental variability present. The variability is further evidenced by runs 1 and 5 in Table 14. Performed at almost identical conditions the yield differed from 40.2% to 50.2%.

Table 17. Final Run Results

%Yield	Iodine Val.	Acid No.
39.8	158	1.7

Viscosities (HS) (cSt)		Viscosities (MS) (cSt)	
Initial	Final	Initial	Final
76.9	113.3	120.0	210.7
77.3	114.7	120.6	207.2

The thickening characteristics are all similar to previous results in the Optimization Study. The kinematic viscosities for the fuels in the final run increased different percentages with the high speed and medium speed lubrication oil. Fuel used with the high speed lubrication oil increased an average of 47.6% while fuel used with the medium speed lubrication oil increased an average of 73.7% in 48 hours in the polymerization apparatus. The failure point given earlier in this thesis was a 375% increase in kinematic viscosity in 64 hours. Also, the acid number of 1.7 shows there is little free fatty acid content and an iodine value of 158 displays significant unsaturation.

Several things were learned from the optimization studies. First, yield was effective for evaluating the differences between the fuels since changes in thickening properties were not as significant. Second, the optimum values for the variables tested occurred with (1) a stoichiometric amount of calcium hydroxide added to the safflower oil for soap production and with (2) no amount of calcium hydroxide added to the soap prior to pyrolysis since the yield was a maximum here. The kinematic viscosity increased less after 48 hours in the polymerization apparatus when the high speed lubrication oil was used compared to the medium speed lubrication oil. However, in reference to the results in the Pyrolysis With/Without Calcium Hydroxide Reactant results section, the high speed lubrication oil is more resistant to polymerization than the medium speed lubrication oil. The control polymerization tests that were run with lubrication oil without any added soap-pyrolysis fuel showed after 48 hours in the polymerization apparatus the high speed lubrication oil experienced a 3.7% increase in kinematic viscosity while the medium speed had a 32.0% increase. Therefore, the differences in viscosity increases were probably due to the characteristics of the two lubricating oils rather than due to the addition of soap-pyrolysis fuels.

A final comparison is made between safflower oil and the soap-pyrolysis fuel. In previous work done in this lab for the soap-pyrolysis technique, straight safflower oil was tested [32]. The previous lubricating oil used for the polymerization tests was Phillips 66 HD II SAE 30W (similar to the present high speed lubrication oil) and a 5.0 weight percent concentration of safflower oil was used. The safflower oil experienced a 110% increase in kinematic viscosity in 48 hours in the polymerization apparatus from about 95 to 200 centistokes. In addition, the iodine value for the safflower oil was 149 and a typical acid number was 170. These results in comparison to the soap-pyrolysis fuels in this study indicate safflower oil has a greater tendency to polymerize than the soap-pyrolysis fuels when subjected to conditions of a simulation of a diesel engine. The most apparent chemical difference between safflower oil and soap-pyrolysis fuels is that the safflower oil has a much greater acid number. Iodine values of both the safflower oil and soap-pyrolysis fuels showed significant unsaturation.

CONCLUSIONS

1. An advantage might be gained by using fresh soap as opposed to old or dried soap since the fuel produced from fresh soap would have a lower initial kinematic viscosity than that of the fuel from the old soap.

2. Glycerol is not desirable in the soap prior to pyrolysis since it decreased yield of the fuel in the soap-pyrolysis process.

3. The greater the amount of calcium hydroxide used to produce the soap in the fusion process the less thickening that will occur in the fuel.

4. Calcium soap is superior to magnesium soap since the calcium soap gives a greater yield of fuel in the soap-pyrolysis process.

5. The lighter fraction of product obtained in the soap-pyrolysis process had a lower initial kinematic viscosity. The lighter the fraction of fuel in the soap-pyrolysis process was subject to greater thickening in the polymerization apparatus.

6. The total product obtained by the soap-pyrolysis process is thicker starting out and experiences less thickening in the polymerization apparatus.

7. Aging of soap pyrolysis fuels does not affect their thickening properties.

8. The addition of calcium hydroxide to the soap prior to pyrolysis decreases thickening while limiting yield.

9. The fusion soap-making process with no solvent and the precipitation soap production method give the greatest yield of fuel of the methods investigated. The fusion process with no solvent is recommended since it is easier to perform than the precipitation method.

10. It might be desirable for the safflower oil to contain more oleic acid esters than linoleic or linolenic acid esters since the yields would probably be higher and the thickening not as severe.

11. Optimization of the soap-pyrolysis process indicates that calcium hydroxide used in a stoichiometric quantity for soap production gives the best results.

12. No great advantage will be gained by adding calcium hydroxide to the soap prior to pyrolysis.

13. Soap-pyrolysis fuels are better than straight safflower oil in the regard of tendency to polymerize in the polymerization apparatus at 150°F which simulated a diesel engine.

RECOMMENDATIONS FOR FUTURE RESEARCH

1. Investigate pyrolysis in a stainless steel apparatus with the same dimensions as the glass apparatus used for pyrolysis to determine any effect in yield.
2. Study the relationship between free fatty acid content and unsaturation more thoroughly.
3. Investigate the percentage of soap-pyrolysis fuel that could be added to diesel fuel.
4. Investigate the evaporation of vegetable oil fuel in the polymerization tests.

APPENDICES

APPENDIX A

OPTIMIZATION RESULTS

Table 18 gives the values of the variables used to find the constants for the mathematical model of fuel yield from the soap-pyrolysis process. The variables were coded to simplify the calculations. The variables are expressed in grams of calcium hydroxide. This following procedure is given in Davies [33].

Table 18. Coded and Uncoded Variables for the Mathematical Model of the Soap-Pyrolysis Process

Coded	Uncoded x_1	Uncoded x_2
-1	0	0
0	0.195	1.45
+1	0.368	2.90

Table 19 gives the values of the independent variables needed in the equation for yield. The equation is shown in the Sample Calculations section of this Appendix A.

Table 19. Values for Surface Yield Equation Calculation

Coded Variables						
x_1	x_2	%Yield	$x_1{}^2-2/3$	$x_2{}^2-2/3$	x_1x_2	x_0
-1	-1	45.2	1/3	1/3	+1	1
-1	0	24.0	1/3	-2/3	0	1
-1	+1	23.5	1/3	1/3	-1	1
0	-1	37.7	-2/3	1/3	+1	1
0	0	26.5	-2/3	-2/3	0	1
0	+1	26.8	-2/3	1/3	-1	1
+1	-1	29.8	1/3	1/3	+1	1
+1	0	14.74	1/3	-2/3	0	1
+1	+1	24.8	1/3	1/3	-1	1
		sum y^2=7735.0				

Table 20 gives the estimates of the constants.

Table 20. Constants Estimate

constant estimated	(2) sum x^2	(3) sum yx	(4) estimate 3/2	(5) $3^2/2$
n_0	9	253.1	28.1	7116.6
B_1	6	-23.5	-3.9	91.9
B_2	6	-37.5	-6.3	234.1
B_{11}	2	-6.7	-3.3	22.2
B_{22}	2	19.1	9.6	182.4
B_{12}	4	16.7	4.2	69.9
				sum=7717.1

Sample Calculations

The equation for yield fits form of:
$y = B_0x_0 + B_1x_1 + B_2x_2 + B_{11}x_1^2 + B_{22}x_2^2 + B_{12}x_1x_2$

The above equation when expressed in different form is:
$y = n_0x_0 + B_1x_1 + B_2x_2 + B_{11}(x_1^2-2/3) + B_{22}(x_2^2-2/3) + B_{12}x_1x_2$

The relationship to return to the first equation is:
$b_0 = \acute{Y} - 2/3b_{11} - 2/3b_{22}$
$b_0 = 28.1 + 2/3(3.3) - 2/3(9.6) = 24.0$

The estimated constants with the ranges are:
b_0 = 24.0 +/- 1.8
b_1 = -3.9 +/- 1.0
b_2 = -6.3 +/- 1.0
b_{11} = -3.3 +/- 1.7
b_{22} = 9.6 +/- 1.7
b_{11} = 4.2 +/- 1.2

The numbers needed to calculate the range are:
7735.0 - 7717.1 = 17.9 = deviations from regression
17.9/3 = 6.0

$V(b_0) = V(Y) + (2/3)^2V(b_{11}) + (2/3)^2V(b_{22}) = 0.05555\text{var}^2$

The ranges for the constants are:
b_0: sqrt((0.5555)(6.0)) = 1.8
b_1, b_2: sqrt(6.0/6) = 1.0
b_{11}, b_{22}: sqrt(6.0/2) = 1.7
b_{12}: sqrt(6.0/4) = 1.2

The next step was to decode the equation and this was done by finding the following relationships between the coded and uncoded variables:
x_2(coded) = (x_2(uncoded)−1.45)/1.45
x_1(coded) = (x_1(uncoded)−0.184)/0.184

The final step was to substitute the right side of the above equations into the left and simplify:

$$y = 44.6 - 7.8x_1 - 20.4x_2 - 98.2x_1^2 + 4.6x_2^2 + 15.7x_1x_2$$

APPENDIX B

COMPUTER PROGRAM USED FOR OPTIMIZATION

Figure 9. Computer Program Used For Optimization

```
MILESTONE 5 OPTIMIZATION

IMPLICIT REAL*8(A-H,O-Z)
DIMENSION X(2,4),XL(2),XH(2),XC(2),XX(2),FUNC(4),XP(2,4),
1XXP(2)
1     READ*,M,N,KK,KPRINT,EPSI
READ*,(X(I,1),I=1,N)
READ*,(XL(I),I=1,N)
READ*,(XH(I),I=1,N)
CALL CMBOX(M,N,KK,KPRINT,X,XL,XH,XC,XX,XP,XXP,FUNC,EPSI)
GOTO 1
END

SUBROUTINE OBJ(X,N,XP,OB,KOB)
IMPLICIT REAL*8(A-H,O-Z)
DIMENSION X(N),XP(N)
KOB=KOB+1
Y1=23.97-3.91/0.184*(X(1)-0.184)-6.25/1.45*(X(2)-1.45)
Y2=-3.33*((X(1)-0.184)/0.184)**2+9.55*((X(2)-1.45)/1.45)**2
Y3=4.18/0.184/1.45*(X(1)-0.184)*(X(2)-1.45)
Y=Y1+Y2+Y3
OB=Y
DO 2 I=1,N
XP(I)=X(I)
2     CONTINUE
RETURN
END

SUBROUTINE CONSTR(X,N,IVI)
IMPLICIT REAL*8(A-H,O-Z)
DIMENSION X(N)
IVI=0
G1=X(1)
IF(G1.LT.0.0) THEN
IVI=1
RETURN
ENDIF
IF(G1.GT.2.0) THEN
IVI=1
RETURN
ENDIF
G2=X(2)
IF(G2.LT.0.0) THEN
IVI=1
RETURN
ENDIF
IF(G2.GT.5.0) IVI=1
```

Figure 9--Continued

```
RETURN
END
SUBROUTINE CMBOX(M,N,KK,KPRINT,X,XL,XH,XC,XX,XP,XXP
1FUNC,EPSI)
IMPLICIT REAL*8(A-H,O-Z)
DIMENSION X(N,KK),XL(N),XH(N),XC(N),XX(N),FUNC(KK),
1XP(N,KK),XXP(N)
K=1
KI=1
NUM =7621
KCOUNT=0
KRCOUNT=0
INIT=0
IF(EPSI.LT.1.D-6) EPSI=1.D-6C
KPR = 100
KOB = 0
GO TO 10
4      IF(INIT.EQ.1) GO TO 42
IF(K.EQ.KK) GO TO 30
DO 1 I=1,N
XC(I)=0.
DO 5 J=1,K
5      XC(I)=XC(I)+X(I,J)
1      XC(I)=XC(I)/K
K=K+1
KI=KI+1
DO 2 I=1,N
NUM=241*NUM + 5
NUM=MOD(NUM,65536)
ANUM=NUM/65536.
2      X(I,K)=XL(I)+ANUM*(XH(I)-XL(I))
10     DO 6 I=1,N
6      XX(I)=X(I,K)
IF(M.EQ.0) GO TO 4
CALL CONSTR(XX,N,IVI)
IF((KI.EQ.1).AND.(IVI.EQ.1)) GO TO 80
GO TO 81
80     WRITE(2,400)
WRITE(6,400)
RETURN
81     IF(IVI.EQ.1) GO TO 20
GO TO 4
20     DO 3 I=1, N
3      X(I,K)=(XC(I) + X(I,K))/2.
GO TO 10
30     DO 31 K=1,KK
```

Figure 9--Continued

```
DO 32 I=1,
32    XX(I)=X(I,K)
CALL OBJ(XX,N,XXP,OB,KOB)
DO 29 I=1,N
29    XP(I,K)=XXP(I)
31    FUNC(K)=OB
36    IF((KPRINT.EQ.0).AND.(KCOUNT.NE.KPR)) GO TO 37
35    WRITE(2,200)(FUNC(K),K=1,KK)
WRITE(6,200)(FUNC(K),K=1,KK)
DO 51 I=1,N
WRITE(2,200)(XP(I,K),K=1,KK)
51    WRITE(6,200)(XP(I,K),K=1,KK)
WRITE(2,100)
WRITE(6,100)
IF(KCOUNT.EQ.6) GO TO 70
IF(KPRINT.EQ.1) GO TO 37
IF((KPRINT.EQ.0).AND.(KCOUNT.NE.KPR)) RETURN
KPR=KPR + 100
37    SMALL=FUNC(1)
IR=1
DO 33 K=2,KK
IF(SMALL-FUNC(K))33,33,34
34    SMALL = FUNC(K)
IR=K
33    CONTINUE
BIG=FUNC(1)
DO 38 K=2,KK
IF(BIG-FUNC(K))39,38,38
39    BIG=FUNC(K)
38    CONTINUE
KCOUNT=KCOUNT+1
EPS=DABS((BIG-SMALL)/BIG)
IF(EPS.LT.EPSI) GO TO 60
IF(KCOUNT.GE.999) GO TO 60
DO 40 I=1,N
XC(I)=0.
DO 41 K=1,KK
41    XC(I)=XC(I)+X(I,K)
XC(I)=(XC(I)-X(I,IR))/(KK-1.)
40    X(I,IR)=2.3*XC(I)-1.3*X(I,IR)
K=IR
INIT=1
GO TO 10
42    CALL OBJ(XX,N,XXP,OB,KOB)
KRCOUNT=KRCOUNT+1
DO 45 I=1,N
45    XP(I,K)=XXP(I)
```

Figure 9--Continued

```
FUN=OB
IF (KRCOUNT.GT.49) THEN
WRITE(2,700)KRCOUNT
WRITE(6,200)KRCOUNT
GO TO 60
END IF
IF (FUN.GT.FUNC(K)) THEN
KRCOUNT=0
GO TO 50
END IF
DO 43 I=1,N
43    X(I,K)=(X(I,K)+XC(I))/2.
DO 44 I=1,N
44    XX(I)=X(I,K)
GO TO 42
50    FUNC(K)=FUN
GO TO 36
60    WRITE(2,300)EPS,KCOUNT,KK,KOB
WRITE(6,300)EPS,KCOUNT,KK,KOB
IF(KPRINT.EQ.0) GO TO 35
RETURN
70    WRITE(2,500)
WRITE(6,500)
READ(5,600) KPRINT
GO TO 37
100   FORMAT()
200   FORMAT(4G18.9)
300   FORMAT(' FUNCTIONAL VALUES WITHIN FRACTIONAL
1 DIFFERENCE ='
1,G14.5/,I5,' CYCLES WITH ',I3,' VERTICES HAVE BEEN'
2' COMPUTED'/' OBJECTIVE HAS BEEN EVALUATED',I5,
3' TIMES')
400   FORMAT(' YOUR STARTING POINT DOES NOT SATISFY THE'
1' CONSTRAINTS')
500   FORMAT(' ENTER A VALUE FOR KPRINT')
600   FORMAT(I1)
700   FORMAT(' PROGRESS NOT MADE AFTER ',I2,'CONTRACTIONS.'/
1'START OVER WITH CURRENT BEST X(I)S AND/OR NEW EPSI')
END
```

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