Decarboxylation and hydrogenation of safflower and rapeseed oils and soaps to produce diesel fuels
by Dwight Randall Hiebert

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 decarboxylation and hydrogenation of safflower and rapeseed vegetable oils and their derivatives and evaluate their products' potential use as diesel fuels.

Decarboxylation reactions were carried out on the raw oils and their calcium salts (soaps) in a 500 ml batch reactor. These experiments were run at high temperatures (700-800°F) and at atmospheric pressure, both with and without catalysts. Hydrogenation was done in a 500 ml rocking bomb at 1500 PSI and 300°F using a Raney nickel catalyst. Thickening tests were performed at 150°C in the presence of oxygen and a copper catalyst to determine if small amounts of the fuel substitute would polymerize in crankcase lubricating oil. Feed materials and products were analyzed to determine the following physical characteristics: iodine value, kinematic viscosity, density, water content, distillation ranges, acid number, and elemental analysis.

The most promising safflower oil decarboxylation catalyst was a Harshaw nickel-molybdenum variety which gave liquid product yields of 74%. Even greater yields (over 90%) were obtained using this catalyst to decarboxylate crude rapeseed oil. Decarboxylation of the calcium soap of safflower oil produced its highest yield (55%) without the aid of a catalyst. Thermal decarboxylation of the rapeseed calcium soap without a catalyst produced yields of over 60%. Hydrogenation, both prior to and following decarboxylation, formed solid products.

Both safflower and rapeseed calcium soap decarboxylation products were excellent candidates for diesel fuels based on their low viscosities and tendency not to polymerize. Conversely, decarboxylation products of the raw safflower and rapeseed oils polymerized extensively in the engine lubricating oil and formed a heavy "sludge," which would make them unsuitable as fuel substitutes. The tendency of safflower and rapeseed oil decarboxylation products to polymerize increased with increasing fatty acid content of the cracked products. The tendency of safflower and rapeseed soap decarboxylation products to polymerize increased slightly with increasing unsaturation of the soap product.

DECARBOXYLATION AND HYDROGENATION OF SAFFLOWER AND RAPESEED OILS AND SOAPS TO PRODUCE DIESEL FUELS

by

Dwight Randall Hiebert

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

of

Master of Science

in

Chemical Engineering

MONTANA STATE UNIVERSITY
Bozeman, Montana

May 1985

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TABLE OF CONTENTS

TABLE OF CONTENTS—Continued

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The purpose of this research was to study the decarboxylation and hydrogenation of safflower and rapeseed vegetable oils and their derivatives and evaluate their products' potential use as diesel fuels.

Decarboxylation reactions were carried out on the raw oils and their calcium salts (soaps) in a 500 ml batch reactor. These experiments were run at high temperatures (700-800°F) and at atmospheric pressure, both with and without catalysts. Hydrogenation was done in a 500 ml rocking bomb at 1500 PSI and 300°F using a Raney nickel catalyst. Thickening tests were performed at 150°C in the presence of oxygen and a copper catalyst to determine if small amounts of the fuel substitute would polymerize in crankcase lubricating oil. Feed materials and products were analyzed to determine the following physical characteristics: iodine value, kinematic viscosity, density, water content, distillation ranges, acid number, and elemental analysis.

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INTRODUCTION

Vegetable Oil Fuels

Extensive worldwide research is presently addressing the use of vegetable oils for diesel fuels. These fuels can consist of either the raw vegetable oil or various derivatives of that oil. Crude fuels were produced from many types of plant and animal oils during the first half of the 20th century and the concept is currently experiencing renewed interest. With the constant price rise of petroleum and the continued threat of oil embargoes, the outlook for vegetable oil fuel substitutes gets brighter every day.

Diesel fuels derived from vegetable oils are a very attractive alternative for agricultural machinery. Theoretically, a farmer could plant a fraction of his land in oil-producing crops and use the fuel derived to power his entire operation. In one study, Helgeson and Schaffner [1, pp. 1561-1566] estimated that the agricultural fuel needs of the entire United States could be met by planting 13.4% of the total cropland with sunflower. Other researchers have placed the figure around 10% for various oilseed crops [2, p. 11]. As an added benefit, vegetable oil processing yields a high protein meal suitable for animal feed as a by-product [3, pp. 10-17].

Despite these advantages, the use of vegetable oils as fuels is not economically feasible at this time. Prices for vegetable oils are dependent on their value as foods which has historically put them in a higher price bracket than petroleum products. Collins et al. [4, pp. 138-148] shows that diesel fuel prices would have to double or triple before even the best vegetable oil fuels would become economically competitive.

Two principal problems have been identified with using vegetable oils directly as diesel fuels: (1) vegetable oils form carbon deposits inside direct injection engines and (2) vegetable oils carried into the crankcase polymerize in the lubricating oil leading to eventual engine failure [5, pp. 1927-1933]. Both problems are related to the chemical structure differences between vegetable oils and diesel fuel.

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. It has been found that the carbon deposition problem can be avoided 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 oils is a significant reduction in viscosity compared to unmodified vegetable oils. This lowering of the viscosity appears to prevent the formation of carbon deposits.

Transesterification, however, does not reduce the previously mentioned polymerization problem. Polymerization is caused by either the carbon double bonds or the carboxyl groups (both present in all crude vegetable oils). High unsaturation levels of the unprocessed oil has been reported to be the most likely cause, which transesterification does not eliminate. The oil polymerizes and forms gums which plug filters and lines.

Polymerization problems can therefore presumably be solved by modifying the chemical structure of the vegetable oils to eliminate unsaturated carbon bonds and the carboxyl groups. The double bonds can be removed relatively easily by hydrogenation but this results in a product that is solid at room temperature. Decarboxylation (the removal of the carboxyl group from the fatty acid component) could be accomplished by thermal means with or without the aid of catalysts. Decarboxylation with subsequent hydrogenation would

result in straight-chain, saturated hydrocarbon products with essentially the same chemical structure as the primary constituents of diesel fuel. The term decarboxylation is used interchangeably with decomposition.

Because of the above problems it appears that vegetable oils will require chemical modification before they will be suitable for use as diesel fuels. Most recent research has concentrated on simplified processing oriented toward farm-scale production units. Even though decarboxylation and hydrogenation are relatively simple processes, they do involve high temperatures and pressures; and it is not reasonable to expect that they can be successfully applied on a small-scale basis using part-time personnel. Decarboxylation and hydrogenation of vegetable oils would only be viable if they were done in a commercial processing facility using efficient technology. Identification of economical processes employing relatively moderate operating conditions is desirable.

Early History

Following is a chronological summary of major decarboxylation experiments performed between 1888 and 1951. Data from these early experiments will be presented even though its accuracy is somewhat questionable. Yields are difficult to compare since many different methods were used to calculate product yields and the products themselves are not usually comparable. Temperatures given are the maximum obtained unless otherwise stated.

The thermal or catalytic decarboxylation of vegetable oils has been studied for nearly 100 years starting with the work of Engler in Germany. In 1888 he synthesized hydrocarbons from vegetable oils in order to support the theory that petroleum originated from organic materials [6, p. 1816].

Pictet and Potak reported in 1919 and 1920 that the low pressure (13 to 15 mm Hg), dry distillation of sodium stearate produced a mixture of saturated hydrocarbons. These hydrocarbons ranged from C10 to C34 [7, pp. 501-510; 8, pp. 641-656].

In 1920 Grun and Wirth also pyrolyzed sodium stearate at 1000-1100°F and atmospheric pressure to produce about a 60% yield of mostly unsaturated hydrocarbons [9, pp. 1301-1312].

The French scientist, A. Mailhe, did extensive work on decarboxylation of oils in the early 1920s. He was the first to report using catalysts to decompose oils. Both plant and animal oils were heated to 750-840°F in the presence of various catalysts in liquid-phase and vapor-phase experiments. Liquid products similar to gasoline were obtained that contained linear, cyclic and aromatic hydrocarbons. Mailhe also observed the presence of free fatty acids in all products. From his observation that similar products were obtained from oils of various origins, Mailhe postulated that carboxylic acids were the precursors of the hydrocarbons [10, pp. 358-359; 11, pp. 658-660; 12, pp. 873-874; 13, pp. 249-252; 14, pp. 321-324; 15, pp. 37-39; 16, pp. 202-204; 17, pp. 65-68; 18, pp. 3-5].

Most of the studies done by these European scientists were purely research-oriented since the hydrocarbons produced could not compete with petroleum as fuels. However, due to war-time situations and subsequent fuel shortages, Oriental countries such as Japan and China turned to vegetable oil fuels as petroleum substitutes. Much of the ensuing research was done hastily and many of the details of these studies are incomplete or missing [19, p. 99].

Work was done in Japan in 1921 by both Kobayashi and Inouye. Kobayashi decomposed soybean oil, coconut oil and stearic acid at temperatures of approximately 1300°F to obtain "vegetable petroleum." The best yields resulted from using stearic acid [20, pp. 1-26, 1421-1424; 21, pp. 1399-1420]. Inouye obtained similar results working primarily on thermal cracking of the vegetable oil soaps [22, pp. 1065-1072].

In 1922 Hirose and Yamada, also in Japan, performed pyrolysis of the sodium soaps of herring oil to obtain a 53% yield of a highly unsaturated oil containing no naphthenes. Excess methane was also reported [23, pp. 1428-1438].

Gallo and Corelli in 1923 catalytically decomposed vegetable oils with superheated steam in the presence of alkaline earths and passed the vapors over an FeO catalyst at 1000° F. Their hydrocarbon yields ranged from 60 to 65% with both paraffins and olefins being present in the liquid product [24, p. 257].

In 1923 Zelinski and Levine, working in the USSR, studied the decomposition of some of the higher fatty acids [25, pp. 20-30].

The decomposition of cottonseed oil in a closed vessel at 840° F was studied by Waterman and Perquin in 1924. Liquid products consisted of a hydrocarbon mixture primarily in the gasoline boiling range [26, p. 36].

In the 1920s Sato and his co-workers in Japan investigated the dry distillation of calcium and magnesium soaps of soybean oil both at atmospheric and reduced pressure. At atmospheric pressure the constituents of the resulting liquid products were primarily paraffins, olefins and naphthenes. They found that the magnesium soap decomposed at lower temperatures and also gave heavier products than its calcium counterpart. Sato also pyrolyzed calcium and magnesium stearates and oleates under absolute pressures of 5 to 7 mm Hg at 930° F. A substantial amount of ketones was produced along with various hydrocarbons [27, pp. 13-24; 28, pp. 297-304; 29, pp. 242-245; 30, pp. 109-115; 31, pp. 245-252].

A process patented in Britain by Worsley in 1932 described the decarboxylation of vegetable oils in the presence of activated carbon at 480° F. Hydrocarbon yields of 75% were obtained in the 230-480° F boiling range [32].

Egloff, Morell, and Faragher in 1932 decarboxylated palm oil under pressures of 50 to 135 PSI. Maximum liquid product yields were obtained at the lower pressures [33, pp. 133-141]. In another study, they pressure-cracked fish oil at 570-750° F and 60 to 100

PSI. The gasoline range product yield increased, and the diesel-range products decreased, with increasing pressure [34, pp. 440-441]. In the same year, Egloff and Morell cracked cottonseed oil under high pressure to obtain almost a 60% yield of products in the gasoline boiling range [35, pp. 1426-1427]. In a separate study, Egloff and Nelson obtained similar results from the cracking of seal oil [36, pp. 386-387].

In China during 1935 Ping decomposed nine different vegetable oils of various degrees of unsaturation with an aluminum chloride catalyst. He obtained primarily liquid products distilling above 480°F. The more saturated vegetable oils gave heavier products [37, pp. 95-102, 281-287].

In the same year, Koo and Cheng decarboxylated cottonseed, soybean, tung and rapeseed oils using a sodium hydroxide catalyst at 800°F and no catalyst at 1000°F. Higher product yields were observed at the lower temperature using the catalyst. These researchers were primarily interested in gasoline production [38, pp. 2021-2039; 39, pp. 466-479; 40, pp. 348-353].

In 1939 Dalal and Mehta in India cracked vegetable oils by two different methods; they decomposed the liquid oils in iron and glass tubes and also distilled the oils in the presence of a zinc chloride catalyst. They found that liquid product yields increased with increasing temperature and decreased with increasing unsaturation of the vegetable oil [41, pp. 213-245].

The effect of the addition of lime to the reaction mixture on the cracking of tung oil was studied by Chang, Shiah, and Chan in 1941. They were primarily interested in gasoline product yields and found that the amount of lime had little effect on their yields [42, pp. 100-107].

Ishakawa in a 1943 Japanese patent described the decomposition of stearic acid at 750°F for 3 to 5 hours in the presence of tin and lead. Primary products were heptadecene and heptadecane [43].

A 1944 British patent by Worsley showed how to obtain hydrocarbon fuels by cracking vaporized vegetable oils at 930 to 1200°F [44].

In 1946 Goswami, Chakrabarty, and Modak, working in India, pyrolyzed oleic acid at about 650°F. A 50% hydrocarbon yield was obtained using a copper catalyst [45, pp. 135-136].

Prior to and during World War II, decomposition of tung, soybean, peanut, cottonseed, and rapeseed oils was carried out in China by Chang and Wan. Various methods were used, including vapor-phase cracking, liquid-phase high pressure cracking, liquid-phase catalytic cracking, and soap pyrolysis. The best yields of liquid products were obtained with the liquid-phase catalytic process at temperatures of 570 to 660°F using aluminum chloride catalysts [46, pp. 1543-1548].

A 1947 Japanese patent by Tokunaga described the catalytic pyrolysis of saturated fatty acids to olefins at temperatures of approximately 570°F. He used granular catalysts consisting of binary mixtures of silica gel, alumina, activated acidic clay, or bentonite with various metal oxides or hydroxides [47].

Mandlekar and co-workers in 1947 pressure distilled a number of vegetable oils in India. Diesel range products were found to decrease with increasing pressure with the highest yields obtained by cracking coconut oil at 45 PSI. Also, diesel-range products decreased with increasing zinc chloride catalyst [48, pp. 1-16].

Petroff and Prats patented a process in 1948 for producing hydrocarbon fuels from the pyrolysis of the calcium soaps of coconut oil. Excess powdered slaked lime was added to the reaction mixture as a catalyst and temperatures up to 930°F were used. They claimed liquid product yields up to 97% with some gasoline, but the majority of the products being heavier oils [49].

In 1948 Ishakawa and co-workers pyrolyzed stearic acid for 20 hours to obtain about a 70% yield of C10 to C15 olefins [50, pp. 239-243].

Hsu, Osburn, and Grove in 1950 decarboxylated the calcium salts of both stearic acid and tung oil. Both soaps decomposed to give paraffinic and olefinic products. The liquid product yields were substantially higher for the calcium stearate [51, pp. 2141-2145].

Tokunaga in 1950 studied the decarboxylation of palm, coconut and chrysalis fatty acids using various mixed clay-metal oxide catalysts. He found that decomposition of fatty acids with higher degrees of unsaturation produced lower molecular weight hydrocarbons [52, pp. 37-48].

In 1950 Toyoda obtained primarily a saturated hydrocarbon product by pyrolyzing the sodium salts of various fatty acids in the presence of a sodium hydroxide catalyst [53, pp. 11-15].

Products from the decomposition of tung oil pyrolyzed in the presence of aluminum chloride at 840°F were separated into four fractions by Huang in 1951. These were a gasoline fraction, 140-400°F; a kerosene fraction, 400-530°F; a gas oil fraction, 530-660°F; and a lubricating oil fraction, above 660°F [54, pp. 95-102].

Recent History

From the early 1950s until the late 1970s, very little was done in the field of decarboxylation research. This was probably due to the fact that petroleum was plentiful and relatively inexpensive and there was little incentive to produce fuels by alternative means. Rapid petroleum price increases and shortages in the 1970s motivated most of the new research. Following is a chronological summary of major decarboxylation experiments performed between 1978 and 1983.

A 1978 U.S. patent by Rao of India described the production of hydrocarbons by thermolysis of vegetable oils at atmospheric pressure. The process involved liquid-phase decarboxylation in the presence of a silica-alumina catalyst impregnated with oxides of the transition metals. Reaction temperatures ranged from 570 to 1300°F with a maximum

yield of 70% reported at 790°F. An increase in the liquid hourly space velocity of the vegetable oil feed also increased the liquid product yield to some extent [55].

Weisz, Haag, and Rodewald in 1979 transformed various vegetable oils into a hydrocarbon fuel using shape selective catalysis. They used a ZSM-5 zeolite catalyst to produce a high grade fuel in the gasoline range. The process involved initial thermal decomposition of the vegetable oils to smaller hydrocarbons followed by zeolite restructuring to the desired product [56, pp. 57-58].

In 1982 Alencar, Alves, and Craveiro pyrolyzed native Brazilian vegetable oils without a catalyst at 570 F for four hours. The liquid product yield was about 50% and contained mostly paraffins and olefins [57].

Another recent study in Brazil by Anjos, Gonzalez, Lam, and Frety was concerned with the production of diesel fuels from decomposition of soybean oil. Both crude and hydrogenated oils were vaporized and passed over either acidic or basic catalysts in a glass tubular reactor at 570 to 930°F. The products from these experiments were analyzed by infrared spectroscopy and gas chromatography. Results from these experiments were compared with catalytic decomposition of stearic and oleic acids under similar conditions. It was found that the best liquid-product yields were obtained from the pyrolysis of the saturated oils. Decarboxylation of hydrogenated soybean oil gave fewer oxygen-containing products than decomposition of stearic acid [58, pp. 299-308].

Numerous others have investigated the thermal or catalytic cracking of vegetable oils or their salts. Their experiments are similar to others mentioned previously and will not be described in detail here. The names, years of principal work, and appropriate references are as follows: Melis—1924 [59, pp. 238-240], Oberhausen—1929 [60], Petrov—1931 [61, pp. 1827-1834], Delaby and Charonnat—1930 [62, pp. 1011-1012], Beuer and Weinmann —1935 [63, pp. 42-50], Lo and Tsai—1936 [64, pp. 57-71; 65, pp. 44-50], Bouffort—

1939 [66], Lo—1940 [67, pp. 127-138], Arnoux—1941 [68, pp. 1-13], and Gomez—1942 [69, pp. 197-205].

Process Details

A major problem with decarboxylation reactions has been to find a "form" of the fatty acid suitable for cracking which involves the mildest (and presumably most economic) reaction conditions. Temperatures great enough to cause spontaneous decarboxylation of long chain fatty acids are sometimes above their boiling points. Therefore, to obtain high yields of hydrocarbons, the cracking of vegetable oils without catalysts must either be done in the vapor phase or under sufficient pressure to cause the oils to remain liquid. Both of these "solutions" have various problems associated with them which will be discussed later. Alternatives such as catalytic cracking or soap cracking can lower the reaction temperature sufficiently to allow it to proceed in the liquid (or solid) state. For these and other reasons, numerous cracking methods have been attempted; some were successful and others were not.

Decarboxylation reactions of vegetable oils can be classified into four general categories based on their respective reaction conditions:

1. Liquid-phase catalytic cracking
2. Liquid-phase high pressure cracking
3. Vapor-phase cracking
4. Soap pyrolysis

For all of the above processes either heat alone, or heat in conjunction with catalysts is used. As would be expected, the addition of catalysts usually allows processing at milder conditions and decreases the time required for reaction. The major differences between these processes is the phase of the substance being cracked (gas, liquid, or solid) and the form of the fatty acid.

Following is a discussion of each of these major processes, giving approximate reaction conditions and typical yields.

Liquid-Phase Catalytic Cracking

More research effort seems to have gone into studying direct decarboxylation of the raw vegetable oils in the liquid state than into studying the other three processes. In this process the vegetable oil is heated to temperatures of 600-800° F at atmospheric pressure in the presence of a catalyst. Certain oils have been cracked in the absence of catalysts, with yields of about 50% [57]. In much of the early work, unsophisticated catalysts were used with surprisingly good results. The most successful catalysts have been silica-alumina impregnated with either molybdenum, magnesium or titanium oxides. With these, liquid product yields of 50% to 70% were common with most of that in the diesel fuel range [58, pp. 299-308].

Pyrolysis of highly saturated vegetable oils was reported to give more liquid products than decomposition of unsaturated oils. In one study liquid cottonseed oil and tung oil were decarboxylated using identical conditions. The more highly unsaturated tung oil had liquid-product yields of 75% compared with 82% for the cottonseed oil [46, pp. 1543-1548].

Table 1 summarizes reaction temperatures and liquid-product yields for some of the liquid-phase catalytic cracking studies which have been done.

Liquid-Phase High Pressure Cracking

In liquid-phase high pressure cracking the vegetable oil is heated to approximately 750 to 900° F under pressures of 50 to 300 PSIG. High pressures are necessary to keep the oil in the liquid phase for a sufficient time to allow cracking without the aid of catalysts. High pressure cracking usually results in lighter products than the other processes. Liquid product yields have typically ranged from 25-75%. This process has not been studied

Table 1. Liquid-Phase Catalytic Decarboxylation Studies.

Year	Catalyst	Max. Temp. (°F)	Wt. % Yield	Ref.	Page
1932	Activated carbon	660	—	32	
1935	Aluminum carbon	—	75	37	95-102, 281-287
1935	Sodium hydroxide	800	53	38	2021-2039
				39	466-479
				40	348-353
1943	Tin, Lead	750	—	43	
1945	Aluminum chloride	—	—	19	99
1946	Copper	725	50	45	135-136
1947	Various	660	72-83	46	1543-1548
1947	Various	570	—	47	
1950	Clay metal oxides	—	—	52	37-48
1951	Aluminum chloride	840	—	54	95-102
1978	Various	900	20-72	55	

extensively because of the obvious problems associated with high pressure equipment. In addition, overall liquid product yields are usually lower for this process than for the others [26, p. 36; 33, pp. 133-141; 34, pp. 440-441; 35, pp. 1426-1427; 36, pp. 386-387; 46, pp. 1543-1548; 48, pp. 1-16].

Vapor-Phase Cracking

For vapor-phase cracking the liquid vegetable oil is heated to a sufficiently high temperature (600-1100°F) to cause it to partially decompose. The vapors produced are passed over a catalyst where they are further decarboxylated. The cracked products are then condensed by cooling. This process has not been used as much as some of the others for a number of reasons. The processing equipment is somewhat more expensive and the yields are usually lower than for the other processes. Typical yields for this process range from 30-65%.

Table 2 shows the results from several vapor-phase cracking experiments, including catalyst used, reaction temperature and liquid-product yields obtained.

Table 2. Vapor-Phase Decarboxylation Studies.

Year	Catalyst	Max. Temp. (°F)	Wt. % Yield	Ref.	Page
1923	FeO	1020	60-65	24	257
1944	—	1200	—	44	
1947	None	840	55-56	46	1543-1548
1983	Silica-alumina	930	32-55	58	299-308

Soap Pyrolysis

In soap pyrolysis the fatty acids of the vegetable oils are converted into metal salts (soaps) prior to cracking at atmospheric pressure. Utilization of the soaps allows processing at reduced temperatures, usually under 750° F. According to Chang and Wan [46, p. 1547], this process has historically occupied the leading position in total output of vegetable oil fuels. Soap cracking, however, has not experienced the recent resurgence of popularity that liquid-phase catalytic cracking has.

In a patent describing the pyrolysis of calcium soaps, calcium hydroxide is recommended for use as a catalyst. In that study, liquid-product yields of up to 97% are claimed with about 70% of that being in the diesel range. The maximum temperature used for that particular reaction was 630° F [49].

Again, as with liquid-phase cracking, the types of products formed by soap pyrolysis are reported to depend on the degree of unsaturation of the original oil used to make the soap. In a 1950 study, the soaps of saturated oils gave liquid-product yields of 76% compared with 42% for pyrolysis of unsaturated oil soaps [51, pp. 2141-2145].

The type of metal used to fabricate the soap is also important in the cracking operation. Because of their availability and low expense, calcium soaps have been used to a greater extent than other types. Magnesium soaps, however, have been reported to decompose more rapidly and at lower temperatures than their calcium counterparts [70, p. 1014]. Sodium and potassium soaps have been avoided because of extensive foaming [19, p. 99].

In Table 3 are several representative soap-pyrolysis experiments, complete with reaction temperatures and liquid-product yields.

Table 3. Soap Pyrolysis Studies.

Year	Max. Temp. (°F)	Wt. % Yield	Ref.	Page
1920	1100	60	9	1301-1312
1922	—	53	23	1428-1438
1926	930	—	27	13-24
1945	—	55	19	99
1947	—	72-74	46	1543-1548
1948	930	97	49	
1950	1000	42-76	51	2141-2145

Decarboxylation Mechanisms

Decarboxylation is a very complex process about which very little is understood. The situation is further complicated by the fact that the actual mechanism is dependent on many factors, including reaction temperatures and pressures, whether or not catalysts are used, and the type, form and degree of unsaturation of the vegetable oil used.

To date, mechanisms of vegetable oil decarboxylation have not been studied extensively, but instead research has concentrated on fatty acids. It has been presumed that since triglycerides are easily decomposed into fatty acids and glycerol, the mechanisms would be similar for both.

The thermal decomposition of saturated fatty acids has been presumed to proceed via the following mechanism: (1) dehydration to anhydrides, (2) decarboxylation to ketones, and (3) decarbonylation to paraffins and olefins. This mechanism is supported by the fact that ketones are often produced by pyrolyzing fatty acids using milder conditions (temperature and pressure) than those used for hydrocarbon synthesis [70, p. 1020].

Unsaturated fatty acids having, or being capable of forming, alpha-beta or beta-gamma unsaturation may decarboxylate by an intermolecular process. Pyrolysis of these fatty

acids usually gives terminal olefins at lower temperatures than is generally required for fatty acid decarboxylation. A number of investigations have indicated that the thermal decarboxylation of certain alpha-beta unsaturated fatty acids may proceed by the beta-gamma isomer as an intermediate. These beta-gamma unsaturated fatty acids are thermally unstable and decarboxylate easily. Therefore, it appears that any unsaturated fatty acid whose double bond system is able to migrate to the beta-gamma position at high temperature will preferentially decarboxylate to a terminal olefin rather than undergo ketonic decarboxylation [71, pp. 616-624; 72, pp. 2153-2165; 73, pp. 1603-1609].

The thermal migration of double bonds during the pyrolysis of unsaturated fatty acids appears to be quite common. This helps explain the many different olefins formed by the decarboxylation of a single fatty acid. The decarboxylation of fatty acid soaps has also been shown to proceed via ketone intermediates. This was first demonstrated by Sato in Japan working with calcium and magnesium stearates and oleates [74, pp. 252-260]. Hsu, Osburn, and Grove postulated a similar mechanism for the pyrolysis of calcium stearate and tungate [51, pp. 2141-2145].

As stated previously, the degree of unsaturation of the vegetable oil or associated soap has been shown to have an effect on decarboxylation products. The carbon-carbon double bond is a more active reaction site than the single bond. When this reaction site is eliminated by prehydrogenation, the reactivity of the molecule shifts to other positions such as to the carboxyl group. Since the carboxyl group is at the end of the carbon chain, the decomposition of an oil without double bonds will result in a hydrocarbon of greater molecular weight than decomposition of an unsaturated oil.

The reason that the thermal decomposition of the free fatty acids produced more oxygen-containing liquids than decarboxylation of the pre-hydrogenated vegetable oils is not clear. This particular finding has only been documented clearly in one study. The

researchers speculated that the size of the triglyceride molecule compared to the smaller fatty acid molecules might be influencing the reaction mechanism [58, pp. 299-308].

Literature Summary

All of these decarboxylation processes had results that were similar. The liquid-phase catalytic process and soap pyrolysis appear to have definite advantages over both the vapor-phase cracking and pressure cracking processes. They allow processing at lower temperatures and pressures which is beneficial both in terms of equipment and operating costs and, of course, safety. The most important factor, however, is that these two processes have been shown to consistently give higher yields of diesel-range products than the other two methods.

As stated previously, according to data from some of the studies done, the degree of unsaturation of the raw vegetable oil used had an effect on the quantity and type of products formed, no matter which process was used. Decarboxylation of saturated oils reportedly produced more liquid products (less gaseous and solid) and the products that were formed had a higher average molecular weight than those from unsaturated oils. The exact reason for this is unknown, but possibly has something to do with the decarboxylation mechanisms which change with increasing unsaturation. Lighter products are apparently formed as the oils "crack" at the double bonds rather than at the carboxyl groups. This area was not explored by many of the researchers because they were usually attempting to maximize the gasoline-range products and extra cracking was desirable to some extent. In most studies, paraffins and olefins were always produced, no matter which process or which initial reactants were used. The cracking mixture also usually contained a mixture of a few naphthenes and aromatics.

In studies where high pressure and atmospheric pressure cracking were compared, the high pressure process invariably gave lower yields of diesel-range products. In one study,

cottonseed oil was cracked by both methods. At 840° F and 280 PSIG with no catalyst, liquid-product yields were about 65%. At atmospheric pressure and 570° F using an aluminum chloride catalyst, yields were over 80% [46, pp. 1543-1548].

In general, higher processing temperatures also resulted in fewer diesel-range products. In a Brazilian study, soybean oil was cracked at various temperatures from 570 to 930° F, holding other conditions constant. The liquid products decreased approximately 4-5% for every 180 degree F rise in temperature [58, pp. 299-308].

According to the same Brazilian study, cracking of the pre-hydrogenated vegetable oils produced fewer oxygen-containing liquids than cracking of the free fatty acids [58, pp. 299-308].

Most of the research on decarboxylation of vegetable oils was done many years ago under less than ideal conditions. For this and other reasons, data and results from these studies are not as accurate or complete as it could be and some inconsistencies exist. Nevertheless, it is felt that a feasible method for relatively simple decarboxylation can be found for use on an industrial scale. This research attempts to accomplish that by exploring decarboxylation and hydrogenation of both vegetable oils and their soaps.

EXPERIMENTAL PROCEDURES AND EQUIPMENT

Apparatus and Reaction Parameters

Safflower mill oil, refined in Montana, was selected as the primary vegetable oil feedstock for these experiments. Safflower oil was chosen because it is an important Montana oilseed crop and also because of its availability to the researcher. Another positive aspect is that safflower and sunflower oils, which are chemically similar, have both been the subjects of extensive fuels research.

Rapeseed oil, also from plants grown extensively in Montana, was used to verify the results obtained with the safflower oil. Only the experimental procedures which gave the highest yields and best results with safflower oil were performed on the rapeseed oil. Rapeseed oil was chosen for the same reasons as the safflower oil.

Hydrogenation of the raw safflower oil and other materials was accomplished in a Parr Instrument Co. series 4000 pressure reaction apparatus. This equipment consisted of a 500 ml stainless steel bomb, rocker assembly, thermocouple, pressure gauge, hydrogen tank, pressure lines and valves. A Pyrex glass liner was used inside the bomb to keep the bomb clean and to prevent the metal from interfering with the reaction. Between 100 and 150 ml of raw oil was processed at a time in a batch reaction. Smaller amounts of other materials were used.

Two different hydrogenation catalysts were used. For the first few runs, a Harshaw nickel catalyst (Ni-1430, EI/8) was used. This catalyst turned out to be very ineffective at the required operating conditions and was replaced with a Raney nickel catalyst (42% Ni,

58% Al) from W. R. Grace & Co. The Raney nickel proved to be a very active hydrogenation catalyst and was subsequently used to produce most of the saturated oil. The Harshaw catalyst could be used without modification, but the Raney nickel required a preparation procedure to activate it. A method outlined in the Journal of the American Chemical Society [86, p. 1471] was slightly modified to prepare the Raney nickel. This procedure consisted of leaching out the aluminum with a 20% sodium hydroxide solution for about one hour. The catalyst particles were then washed with distilled water to remove all traces of sodium hydroxide. Washing with ethanol was used to remove the water and the catalyst was dried and immediately stored under oil. The final product, a pure, high surface area nickel, was subject to rapid deactivation with time or exposure to air.

Hydrogenation reaction conditions were based on standard industrial operating procedures for edible vegetable oils and fatty acids [75, pp. 14-17]. Since a batch system was used, the approximate degree of hydrogenation could be calculated from the decrease in the bomb hydrogen pressure. Initial hydrogen pressure was varied between 150 and 1500 PSI. After the first few experiments, pressures of 1500 PSI were used exclusively. The system was re-pressurized periodically to the initial hydrogen pressure following pressure drops due to hydrogen consumption. Reaction temperatures averaged 300°F and did not exceed 350°F because decomposition or discoloration was reported to take place at temperatures near 400°F [75, p. 15]. The reaction time varied between two and ten hours depending on the catalyst used and the average hydrogen pressure.

After the hydrogenation rate started decreasing substantially, the reaction bomb was allowed to cool. Later the solid product was heated until liquid and filtered to remove the catalyst. Rather than trying to characterize each product separately, a uniform material was made by combining the products from all the hydrogenation experiments.

Following the establishment of a general hydrogenation procedure, pressure and temperature data were recorded only as often as necessary to monitor the extent of the reaction and to assure that oil decomposition did not occur.

Decarboxylation reactions were performed in a 500 ml glass batch reactor at atmospheric pressure with a water-cooled condenser. Heat was supplied by a high temperature heating mantle and both liquid and vapor temperatures were measured.

The quantity of raw oil used in the vegetable oil decarboxylation reactions was 150 grams. Various amounts of the soap were used in the soap decomposition experiments with the quantity being kept as constant as possible. This was difficult due to the highly variable water contents of the raw soaps. The reactions were performed both with and without the aid of catalysts. For a description of the various catalysts used, see Appendix A. Enough catalyst was used in the catalytic reactions to avoid mass transfer resistance. This was verified several times in the duplicated runs by varying the catalyst concentration. Vigorous stirring by a magnetic stirrer was also used to counteract resistance to mass transfer.

Heat was continually supplied to the various decarboxylation experiments to keep the liquid distillate rate fairly high. The reaction was considered complete when no further liquid could be distilled from the reaction mixture at reasonable temperatures or when the condenser became completely plugged with solid products.

Saponification reactions were also performed in a glass batch reactor. About 200 grams of raw vegetable oil were reacted with at least 50% excess of the stoichiometric amount of a 25% sodium hydroxide solution. This mixture was heated at its boiling temperature until the reaction appeared complete. The sodium soap was separated from the mixture by dissolving in hot water. A saturated solution of calcium chloride was then added to replace the sodium ions with calcium which precipitated the soap. The resulting calcium soaps were filtered, washed, and dried for use in subsequent experiments.

Hydrogenated soaps were made by saponifying partially saturated oils by the above procedure. This sequence was used rather than trying to hydrogenate unsaturated soaps because of reports of catalyst poisoning by the soap [75, p. 117].

The polymerization reactions were carried out in a glass batch reactor using approximately 500 ml of Phillips 66 Super HD II SAE 30W lubricating oil as the base stock. The decarboxylation product to be analyzed was mixed with this base stock to make a 5% solution. The polymerization procedure used was developed by C. Rewolinski who is currently pursuing vegetable oil research at Montana State University.

The safflower oil product with the best yield from each of the following groups of decarboxylation reactions was selected for the polymerization study: (1) thermal decarboxylation of raw oil, (2) catalytic decarboxylation of raw oil, (3) thermal decarboxylation of calcium soap, and (4) catalytic decarboxylation of calcium soap. Also, polymerization studies were done on the decarboxylation products of rapeseed oil and its calcium soap. It was planned to perform polymerization tests on the decarboxylation products of the partially hydrogenated safflower oil and soaps. Polymerization tests of post-hydrogenated decarboxylation products were also planned.

The purpose of the polymerization experiments was to simulate crankcase oil conditions in a diesel engine and to determine the thickening effects of the proposed fuel substitute with the engine lubricating oil. To accomplish this, the experiments were run for 60 or 70 hours at a constant temperature of 150°C. Pure oxygen was bubbled through the oil mixture at a rate of approximately 2 ml/sec. A 20 cm^2 strip of copper was used as a catalyst. The kinematic viscosity at 40°C was measured every ten hours and plotted to show thickening characteristics versus time. According to one source [76, p. 31], a similar test was considered a success if the oil had less than a 375% increase in kinematic viscosity in 64 hours.

Analytical Procedures

Numerous tests were performed to characterize the various feed materials and products formed in this research project. They included: iodine value, kinematic viscosity, moisture content, density, distillation ranges, elemental analysis, and acid number. In the interest of consistency and reproducibility of results, an ASTM test procedure was used whenever possible. Some of these same tests are part of the standard specification for diesel fuel oils—ASTM D 975-81 [77, p. 466]. Thus it was felt that results from these tests in combination with the polymerization data would give a good indication how the decarboxylation products would perform as fuels. Some of the physical properties for diesel fuel from this specification are shown in Table 4.

Table 4. Properties of No. 2 Diesel Fuel.

Distillation Temperature (90 vol. % point) Maximum — 640°F
Kinematic Viscosity, cSt, 40°C Minimum — 1.9 Maximum — 4.1

The iodine value of an oil is the measure of its unsaturation, i.e., relative number of carbon-carbon double bonds. The method used to measure iodine values was the common Wijs Procedure performed according to ASTM D 1959-69 [78, pp. 283-286]. According to Eckey [79, p. 231], this method has been shown to give accurate results for oils with nonconjugated double bonds, which are the only type present in crude safflower and rapeseed oils and their derivatives. Iodine value is expressed as centigrams of iodine absorbed per gram of sample. If the average molecular weight of the sample and its iodine value are known the average number of double bonds per molecule can be calculated.

The kinematic viscosities of all liquid polymerization and decarboxylation products were measured using the Cannon-Fenske routine. These tests were all run at a constant temperature of 40°C per ASTM D 445-79 [80, pp. 244-249].

Moisture contents of all feed materials were measured using the distillation procedure detailed in ASTM D 460-78 [81, pp. 15-16]. The soap or oil was refluxed with toluene and the water collected in a trap after condensing.

Densities of all liquid decarboxylation products at 20°C were calculated by weighing and measuring their volume in a graduated cylinder.

The purpose of the distillation tests was to determine the volatility characteristics of the various decarboxylation products. The method used is similar to that specified in ASTM D86-78 [82, pp. 8-26]. It differs in the fact that the distillation is considered complete at 640°F since this is the approximate end point given for diesel fuel in this standard. The liquid distilling above 640°F is considered to be residue. The apparatus used in this experiment was a boiling flask with a vapor temperature thermometer, condenser, and receiving flask.

The Carlo Erba Elemental Analyzer, model 1106, was used to determine the composition of the decarboxylation products. The analyzer automatically processes the samples after they are weighed and inserted into the machine. A high temperature (over 1000°C) furnace was used to pyrolyze the sample with excess oxygen. It was then passed over several highly active catalysts to insure complete combustion. Combustion products were scrubbed for everything except CO_2, H_2O, and NO_2, and then fed to a gas chromatograph. Based on their respective GC peak heights the carbon, hydrogen, and nitrogen percentages were calculated. Excess air with the samples was accounted for by running a few blanks. Calibration of the machine was accomplished each time by running two different standard samples with known percentages of carbon, hydrogen, and nitrogen. Oxygen percentage was calculated by difference after assuming it was the only other element present.

The acid number of an oil or oil product is a relative measure of the free fatty acid content. The procedure used is that described in ASTM D 460-78 [81, p. 23]. This involves dissolving the oil in hot 95% ethanol and titrating with KOH to a phenophthalein end point. Acid number is expressed as centigrams of KOH per gram of sample.

RESULTS AND DISCUSSION

Composition and Characterization of the Crude Oils

Vegetable oils can have wide variations in composition and physical properties within the same species. The data given in the literature are merely typical values and are dependent on a number of variables such as source, treatment, and age of the oil. Fatty acids, primary constituents of all vegetable oils, are straight-chained, monocarboxylic acids which differ only in the length of the carbon chain and the number of double bonds. For example, the structure of the linoleic acid is:

$$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$$

The composition of the crude safflower oil used in this investigation was assumed to be typical, with properties similar to that given in the literature. Safflower oil has been reported to consist of 61-70% linoleic acid, 18-33%, oleic acid, and 6-12% miscellaneous fatty acids [83, pp. D-216-217; 84, p. 144]. Based on the measured iodine value of 149, the safflower oil used in these experiments was probably comprised of 65% linoleic, 25% oleic, and 10% miscellaneous fatty acids. The calculations used to arrive at these figures are shown in Appendix B.

The crude rapeseed oil used, however, was the subject of a detailed analysis shown in Table 5. It had a combined oleic and linoleic acid content of about 80%, which made it very similar to the safflower-sunflower family. The Agriculture Canada Research Station at Saskatoon, Saskatchewan performed the analysis using gas-liquid chromatography, and supplied it to Peterson [85, p. 16].

Table 5. Composition of the Crude Rapeseed Oil Used in This Study.

Fatty Acid		Fatty Acid
Name	No. of C Atoms:No. of Double Bonds	Wt. Percentages
Myristic	14:0	0.6
Palmitic	16:0	5.2
Palmitoleic	16:1	0.4
Stearic	18:0	1.8
Oleic	18:1	42.9
Linoleic	18:2	38.1
Linolenic	18:3	6.6
Arachidic	20:0	1.4
Eicosenoic	20:1	0.3
Behenic	22:0	0.6
Erucic	22:1	1.9
Lignoceric	24:0	0.3

This reported composition is not typical of most literature values given for rapeseed oil. Usually the erucic acid content is much higher; on the order of 50% [83, pp. D-216-217; 84, p. 143]. Table 6 shows the results of various tests performed on both raw oils to characterize them.

As expected, both of the raw vegetable oils had negligible moisture contents. The acid numbers for both were also very low because of the majority of the component fatty acids being tied up in the form of triglycerides.

Table 6. Vegetable Oil Characterization Tests.

Test	Safflower	Rapeseed
Iodine Value	149	57
Acid Number	1.1	1.2
Density (g/ml)	0.919	0.873
Moisture Content	none	none
Kinematic Viscosity at 40 C (cSt)	28.6	8.7

Saponification Results

Because it was not the primary research objective, saponification of vegetable oils was not examined in detail. Some details about saponification which were not found in the literature were discovered by experimentation and are given below. Hereafter, unless otherwise specified, all soaps mentioned are calcium soaps.

A solution of approximately 25% sodium hydroxide seemed to give a faster reaction rate than much weaker or stronger concentrations. Refluxing the reaction mixture at its boiling point was more effective than trying to keep the solution just below the boiling point to prevent boil over. Two to three hours were all that were required to drive the reaction to completion using 50-100% excess NaOH. The calcium soaps produced by ion exchange were insoluble in water and easily separated from their soluble sodium counterparts.

Moisture content determinations were performed on safflower, hydrogenated safflower, and rapeseed soaps. In all cases it was found that the water content varied considerably depending on the length of time between making the soap and performing the test. Moisture contents varied from as high as 47% for week-old soap to as low as 3% for month-old soap.

Hydrogenation Results

This portion of the research was concerned only with saturating raw safflower oil and certain decarboxylation products. Therefore, hydrogenation was not analyzed in detail and few results are reported.

The effects of changes in temperature and pressure on the reaction rate were not studied extensively, but general trends were noted. As expected, it was found that the hydrogenation rate increased with increasing hydrogen pressure. At 1500 PSI the time required for reaction was substantially lower than at 150 PSI.

The crude safflower was hydrogenated from an iodine value of 149 down to an average value of 37. At this level of saturation the product was a hard white solid at room temperature.

Hydrogenation was also performed on a select few of the decarboxylation products. These included products from the thermal and catalytic decomposition of safflower and rapeseed oils and soaps. They were all hydrogenated quite extensively and all turned solid at the resultant low iodine values. These hydrogenated decarboxylation products were solids at room temperature, which would make them unacceptable as fuel substitutes. Therefore, no polymerization tests were performed on them.

Decarboxylation Results

Even though decarboxylation was the primary objective of this research, it was not successfully accomplished in all experiments. The majority of the products retained a fairly high concentration of carboxyl groups, in the form of fatty acids, even after high temperature processing. Some decarboxylation was evident in all experiments, however, and the term is used interchangeably with decomposition of the vegetable oils and their derivatives. Fatty acid content of the products was measured by titration with a base to obtain the acid number. Lower acid numbers indicated products which had been decarboxylated extensively, i.e., more hydrocarbons and fewer fatty acids.

Table 7 shows the detailed results from the successful decarboxylation experiments. Yields for the oil products were calculated on a weight percent of the raw vegetable oil. The soap yields were determined on a water-free basis because of inconsistent moisture contents in the raw soap. Distillate, water, and bottoms percentages did not usually add up to 100 since some products were lost as uncondensible gases. Also, some material was lost due to small leaks and leftover residues in the equipment. An accurate bottoms yield was calculated on only one of the soap decarboxylation products (#30, Table 7). The residue

Table 7. Decarboxylation Results.

Exp. No.	Form	Catalyst	Yields (wt. %)			Max. Temp. (°F)	Distillate			
			Distillate	Water	Bottoms		Viscosity (cSt)	Iodine Value	Acid Number	Density (g/ml)
1	Safflower Oil	None	35.5	1.6	43.5	725	2.85	92	226	0.87
2	Safflower Soap	None	10.1	–	–	700	4.44	90	175	0.85
4	Safflower Soap	None	27.9	–	–	745	–	152	2	0.83
5	Safflower Oil	$Ca(OH)_2$	34.1	3.8	54.1	760	3.31	116	168	0.84
6	Safflower Oil	$Al(Cl)_3$	44.5	3.9	30.2	805	6.61	121	180	0.86
7	Safflower Oil	V-0601	51.3	2.3	35.1	800	3.89	95	186	0.85
8	Safflower Oil	None	68.5	1.5	18.9	825	4.50	101	170	0.85
11	Safflower Oil	Silica-magnesia	70.6	2.2	15.1	825	4.46	112	158	0.85
12†	Safflower Soap	$Ca(OH)_2$	47.9	–	–	840	2.73	135	3	0.83
14	Safflower Oil	Zeolite "B"	72.2	3.5	13.0	825	6.54	111	140	0.85
15	Safflower Oil	HT-500	74.1	2.8	6.9	850	4.34	97	116	0.85
16	Safflower Oil	HT-400	73.9	2.4	–	850	4.21	101	137	0.85
17	Safflower Oil	UOP-S-6	78.0	2.4	–	840	4.69	96	127	0.85

Table 7 (continued).

Exp. No.	Form	Catalyst	Yields (wt. %)			Max. Temp. (°F)	Distillate			
			Distillate	Water	Bottoms		Viscosity (cSt)	Iodine Value	Acid Number	Density (g/ml)
18	Safflower Soap	HT-400	45.4	–	–	890	2.24	155	1	0.81
19	Safflower Soap	Zeolite "B"	24.2	–	–	850	2.50	160	3	0.83
22	Safflower Oil	UOP SPA-2	28.0	2.3	51.1	705	8.56	108	209	0.86
23	Safflower Oil	UOP-S-6	71.7	3.2	10.8	850	4.94	97	122	0.85
24†	Safflower Oil	None	73.4	1.1	14.7	850	6.76	97	163	0.87
25†	Safflower Soap	None	55.6	–	–	800	3.33	160	5	0.83
26	Safflower Soap	$Ca(OH)_2$	45.3	–	–	900*	3.13	143	2	0.85
27	Rapeseed Oil	HT-500	88.3	0.9	6.1	820	4.20	37	55	0.84
28†	Safflower Oil	HT-500	72.8	2.7	7.3	840	4.28	99	98	0.85
29†	Rapeseed Oil	HT-500	91.4	1.1	2.8	830	4.49	40	54	0.85
30†	Rapeseed Soap	None	60.5	–	34.1	825*	3.37	41	60	0.83
31	Safflower Soap	None	47.0	–	–	930*	2.97	147	1	0.83
32	Rapeseed Soap	None	58.4	–	–	820*	3.31	38	53	0.82

*Flask temperature.
†Denotes polymerization study performed.

following these soap reactions was invariably a black, solid mess, which made cleaning the glassware and subsequent calculation of residue yields difficult.

The distillate yield for all decarboxylation reactions was dependent on the maximum temperature obtained. It was necessary to keep the reaction temperature relatively high to decompose the oils into lighter boiling compounds. Higher temperatures, however, caused heavier products to distill over. These additional products usually raised the average boiling point and kinematic viscosity of the mixture above the range for no. 2 diesel fuel (see Table 4).

The maximum reaction temperature measured, as shown in Table 7, was not always consistent among experiments. As the soap decarboxylation experiments neared completion, solid residues effectively insulated the thermometer from the reaction vessel. In many of the soap pyrolysis experiments, the Pyrex reaction vessel softened and, in a few cases, melted at temperatures registered by the thermometer of less than 900° F. Accurate temperature measurements were not difficult during the vegetable oil decarboxylations because the reaction mixture remained liquid.

Decarboxylation of raw safflower oil was accomplished both thermally and with the aid of various catalysts to produce fairly high yields of liquid products. This decomposition lowered the kinematic viscosity of the raw oil by about an order of magnitude. See Appendix A for a description of the catalysts used.

The greatest yields from the catalytic decomposition of safflower oil (SOCD) were obtained by using hydrocracking catalysts—Harshaw HT-500 (Ni-Mo), Harshaw HT-400 (Co-Mo) and a UOP catalyst, UOP-S-6. The liquid product yields using these catalysts were between 70-80%. Seventy percent of the HT-500 products were in the diesel fuel range (distilling under 640° F). Resulting product kinematic viscosities of 3 or 4 centiStokes (cSt) were in the range of no. 2 diesel fuel and were substantially lower than the raw oil viscosity of 28.6 cSt. Unsuccessful catalysts, aluminum chloride, zeolite "B", and phosphoric acid,

not only gave low product yields, but their products all had viscosities greater than 6 cSt. Some catalysts had results intermediate between these two extremes. Vanadia on alumina and silica-magnesia catalyzed the decomposition of crude safflower oil to yields of 50-70% with product kinematic viscosities around 4 cSt.

Markley [70, p. 1013] reported the synthesis of hydrocarbons from calcium soaps by heating with calcium hydroxide. Therefore, an SOCD experiment was performed using calcium hydroxide as the catalyst. It was postulated that by using a metal hydroxide, the decarboxylation mechanism would proceed via a soap intermediate, and would give products similar to soap decarboxylation. However, analysis of the products did not support this hypothesis. The products were very similar to those obtained by using other mediocre SOCD catalysts, both in appearance and physical properties. The most obvious difference, however, between this and the soap decomposition products was the acid number. The SOCD product using the calcium hydroxide catalyst had an acid number of 168 compared to acid numbers of less than 5 for the majority of the soap decarboxylation products. This would indicate that the reaction mechanisms were very different for both species.

The SOCD product with the highest yield and best properties was chosen for polymerization study. Even though the UOP catalyst gave a better yield, the Harshaw HT-500 products were chosen for three reasons: (1) they had the lowest acid number, (2) they had a lower viscosity than the UOP products, and (3) more was known about the composition of the HT-500 catalyst than the UOP catalyst.

The safflower oil thermal decomposition (SOTD) product yields were as high as 73%. This was comparable to catalytic decomposition yields, but the kinematic viscosity of those products was about twice as high as that for the hydrocracking catalysts. Seventy-two per cent of the best SOTD product was in the diesel fuel range. This product was selected for a polymerization study.

The iodine values of the catalytic and thermal decomposition products of safflower oil were in the neighborhood of 100-quite a bit lower than the original oil value of 149.

Decarboxylation of safflower calcium soaps either thermally (SSTD) or catalytically (SSCD) gave essentially the same results. The use of catalysts did not increase the yield, and in one case, the use of a zeolite catalyst actually decreased the yield of liquid products.

Calcium hydroxide was the SSCD catalyst of primary interest. For reactions run until similar temperatures were reached, the calcium hydroxide catalytic products were almost identical to those obtained with no catalyst. For both, yields of approximately 50% were obtained, with about 70% in the diesel fuel range.

Iodine values around 150 were measured for the liquid products of both SSTD and SSCD. This was very similar to the iodine value of crude safflower oil.

Kinematic viscosities of safflower soap decomposition products were usually lower than that for the oil decomposition products. The liquid product yields were also lower, which would partially explain the lower viscosities. Decomposition of raw safflower oil to these same lower yields would also result in a lighter liquid product and its accompanying lower viscosity.

An SSTD product and the SSCD product obtained by using the calcium hydroxide catalyst were both chosen for polymerization studies.

As stated previously, decarboxylation of highly saturated vegetable oils was reported to give higher liquid product yields than decarboxylation of comparable unsaturated oils. For this reason, some of the safflower oil and soaps were partially saturated prior to the decarboxylation process. Decomposition of these hydrogenated materials, however, resulted exclusively in solid products at room temperature. The condenser became plugged with these solids, forcing the end of the experiment. No catalyst was found which would crack these materials into lighter products. Because these products were solids at room temperature they would be poor fuel substitutes. Therefore, the products were not characterized

and no polymerization studies were performed on them. Hydrocracking of these vegetable oils could possibly result in better liquid product yields. This would involve high temperatures in conjunction with high hydrogen pressure.

Because of excellent results with safflower oil, the catalyst chosen for the decomposition of rapeseed oil (ROCD) was the Harshaw HT-500 catalyst. Liquid product yields of about 90% were obtained, with 84% distilling in the diesel fuel range. The kinematic viscosity of the product was about 4 cSt and the iodine value was a little lower than the original crude oil. This product was also selected for study in a polymerization experiment.

Since catalysts did not seem to aid the decomposition of safflower soaps, the soap of rapeseed oil was also decomposed with no catalyst (RSTD). Again, as with the oil, the rapeseed soaps gave substantially higher liquid product yields than their safflower counterparts. Yields of around 60% were obtained, with 76% distilling in the diesel fuel range. Kinematic viscosity was slightly lower than that for the ROCD products. Iodine values were, however, very similar to the values obtained for the ROCD products. A polymerization study was also performed on this product.

Distillation ranges were determined for all the decarboxylation products selected for polymerization study and are listed in Table 8.

Table 8. Distillation Characteristics of Decarboxylation Products.

Product	Total Dist. (Vol. %)	Temperature (°F) at Volume Distilled										
		Initial	5%	10%	20%	30%	40%	50%	60%	70%	80%	90%
SOTD	60	145	165	345	430	453	560	587	620	–	–	–
SOCD	70	131	206	260	390	458	507	562	588	605	–	–
SSTD	76	176	263	295	365	423	470	525	588	635	–	–
SSCD	70	175	260	292	340	402	472	548	604	620	–	–
ROCD	84	150	390	418	435	484	510	536	558	585	614	–
RSTD	92	186	360	418	440	480	503	525	550	573	614	645

The rapeseed oil and soap decarboxylation products had significantly higher percentages of product distill under 640°F than their safflower counterparts.

Water was a small but measurable by-product of the decomposition of raw safflower oil. Between a 1 and 4% yield was obtained, depending on the catalyst used. Decarboxylation of rapeseed oil produced less than half as much water using the same catalyst. According to Chang and Wan [46, p. 1545], water is produced by the decomposition of the fatty acids to form ketones by the following reaction:

$$2RCOOH \longrightarrow CO_2 + H_2O + RCOR$$

This also supports the previously mentioned mechanism of ketonic intermediates during decarboxylation.

Water yields from the decarboxylation of the safflower and rapeseed soaps were not measured because of the high initial water content of the raw soaps.

Elemental Analyses Results

The results of the elemental analyses are shown in Tables 9 and 10. All of the successful decarboxylation products were analyzed along with the crude safflower oil and one of the decarboxylation residues. The entire decarboxylation product was tested, not just that portion in the diesel fuel range. The numbers given are weight percent of the element listed.

Except for three of the soap decarboxylation products, nitrogen content was negligible for all of the samples tested. After the discovery that calcium nitrate, used for ion exchange, was the source of the nitrogen contamination, it was replaced with calcium chloride. In addition, the calcium soaps were washed more thoroughly to remove all trace contaminants.

The acid numbers of the crude safflower oil decomposition products were found to have a linear relationship to percent oxygen between acid numbers of 98 and 226. The two lines on Figure 1 are from two sets of elemental analyses run on separate days. Since these

Table 9. Elemental Analyses of Decarboxylation Products.

Exp. No.	Raw Material	Catalyst	Wt. %C	Wt. %H	Wt. %N
1	Safflower Oil	None	76.0	12.4	0
2	Safflower Soap	None	74.3	12.0	1.2
4	Safflower Soap	None	85.0	13.1	0.4
5	Safflower Oil	$Ca(OH)_2$	79.3	13.0	0
6	Safflower Oil	$Al(Cl)_3$	79.4	12.9	0
7	Safflower Oil	V-0601	78.6	12.9	0
8	Safflower Oil	None	79.5	12.8	0
11	Safflower Oil	Silica-magnesia	80.5	12.9	0
12	Safflower Soap	$Ca(OH)_2$	83.5	12.7	0.8
14	Safflower Oil	Zeolite	82.1	12.9	0
15	Safflower Oil	HT-500	83.5	13.3	0
16	Safflower Oil	HT-400	80.5	12.5	0
17	Safflower Oil	UOP-S-6	81.0	12.7	0
18	Safflower Soap	HT-400	85.2	13.1	0
19	Safflower Soap	Zeolite	78.8	12.0	0
22	Safflower Oil	UOP SPA-2	76.0	12.2	0
23	Safflower Oil	UOP-S-6	82.0	12.8	0
24	Safflower Oil	None	77.9	12.3	0
25	Safflower Soap	None	84.1	12.9	0
26	Safflower Soap	$Ca(OH)_2$	82.8	12.4	0
27	Rapeseed Oil	HT-500	84.9	13.2	0
28	Safflower Oil	HT-500	82.9	12.8	0
29	Rapeseed Oil	HT-500	84.5	13.1	0
30	Rapeseed Soap	None	85.8	13.3	0
31	Safflower Soap	None	85.4	13.0	0
32	Rapeseed Soap	None	84.9	13.2	0

Table 10. Elemental Analyses of Other Materials.

Material	Wt. %C	Wt. %H	Wt. %N
Crude Safflower Oil	77.5	12.1	0
Decarboxylation Residue (from exp. #1)	85.3	12.3	0

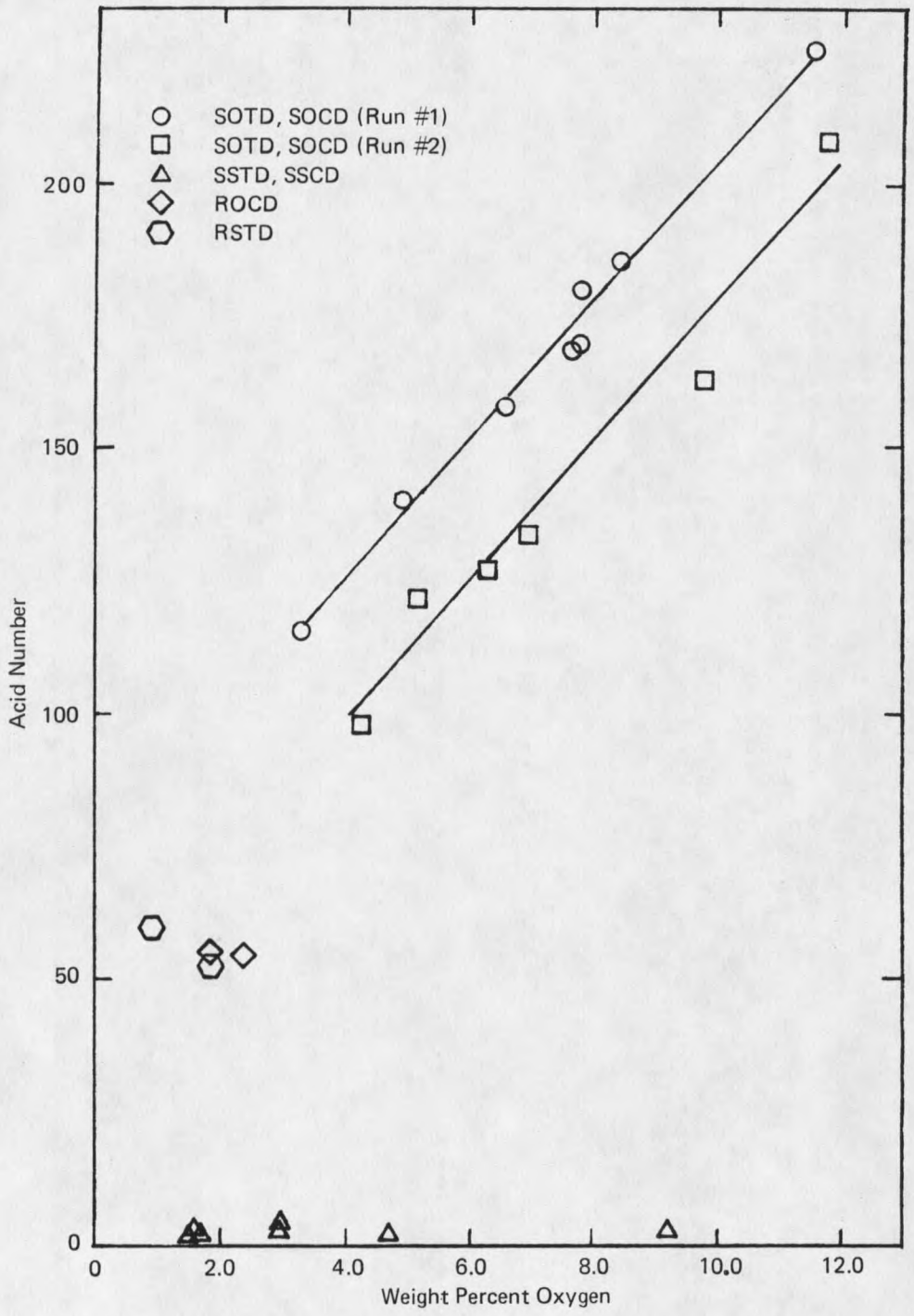

Figure 1. Acid number vs. percent oxygen for decarboxylation products.

relatively low oxygen percentages have been calculated by difference, some inaccuracy probably exists, but the percentages are consistent within the same set of data. An estimation of the oxygen percentage error, as calculated from the elemental analyses, is shown in Appendix C. This estimation accounts for most of the difference between the two sets of data. Not enough data was available from the rapeseed decomposition products to determine if a similar correlation existed.

The SSTD and SSCD products had very low fatty acid content. This was due to the removal of the carboxyl groups leaving principally hydrocarbons. The elemental analyses showed small amounts of oxygen in these products, but apparently most of it was contained in miscellaneous oxygenated compounds other than fatty acids.

Polymerization Results

The polymerization or thickening tests were designed to show the compatability of the proposed diesel fuel substitute with crankcase oil at high temperatures in the presence of oxygen and a copper catalyst. Some of the decarboxylation products with viscosities similar to no. 2 diesel fuel were selected for these studies. The samples for polymerization study were taken from the entire decarboxylation product, not merely the portion in the diesel fuel range. Products with the highest yields in combination with the best physical properties were chosen from each of the following categories:

1. Safflower oil thermal decomposition (SOTD) – Exp. No. 24
2. Safflower oil catalytic decomposition (SOCD) – Exp. No. 28
3. Safflower soap thermal decomposition (SSTD) – Exp. No. 25
4. Safflower soap catalytic decomposition (SSCD) – Exp. No. 12
5. Rapeseed oil catalytic decomposition (ROCD) – Exp. No. 29
6. Rapeseed soap thermal decomposition (RSTD) – Exp. No. 30

The results were documented on Table 11 and plotted on Figures 2 and 3 as kinematic viscosity of the lube oil versus time. In order to compare the graphs more easily, they were also plotted as percent increase in the initial viscosity versus time in Figures 4 and 5 (the soap decarboxylation product plots were separated from those for the raw oils).

Table 11. Polymerization Results.

Exp. No.	Decarboxylation Product	Kinematic Viscosity (cSt) at Time							
		Initial	10 hr	20 hr	30 hr	40 hr	50 hr	60 hr	70 hr
24	SOTD	89.8	104.6	116.6	210.5	296*	363.8	405.4	—
28	SOCD	86.6	98.7	102.3	128.5	187.2	225.4	234.7	—
25	SSTD	78.0	96.2	101.7	111*	118.1	133.8	155.7	176.8
12	SSCD	77.8	97.1	102.1	111.2	117.1	133.2	152.3	172.1
29	ROCD	84.6	91.3	95.6	98.2	121.6	167.4	197.8	236.0
30	RSTD	82.6	87.5	90.2	93.0	96.0	100.9	109.9	121.8

*Interpolated value.

Thickening tests of these products were compared with a baseline test done with crude safflower oil. As shown in Figures 2 and 3, the kinematic viscosity of the lube oil with 5% safflower oil increases with time in an exponential curve.

The polymerization test results of the SOTD products are shown in Figures 2 and 4. The kinematic viscosity increases rapidly between 20 and 30 hours and then the rate of thickening increase tapers off somewhat.

The polymerization of the SOCD products showed similar results (Figures 2 and 4). In this case, the kinematic viscosity did not increase quite as rapidly, but the curve is of the same general shape. This S-shape curve has been documented before with a similar polymerization test using soybean oil methyl ester as the analysis product [87, p. 215].

A substantial quantity of very thick, semi-solid material was formed during the polymerization tests of both the SOTD and SOCD products. This "sludge" was much thicker than the remaining oil and did not enter into the viscosity tests. Also, the surface of the copper strip used in both of these tests was covered with a layer of hard black material.

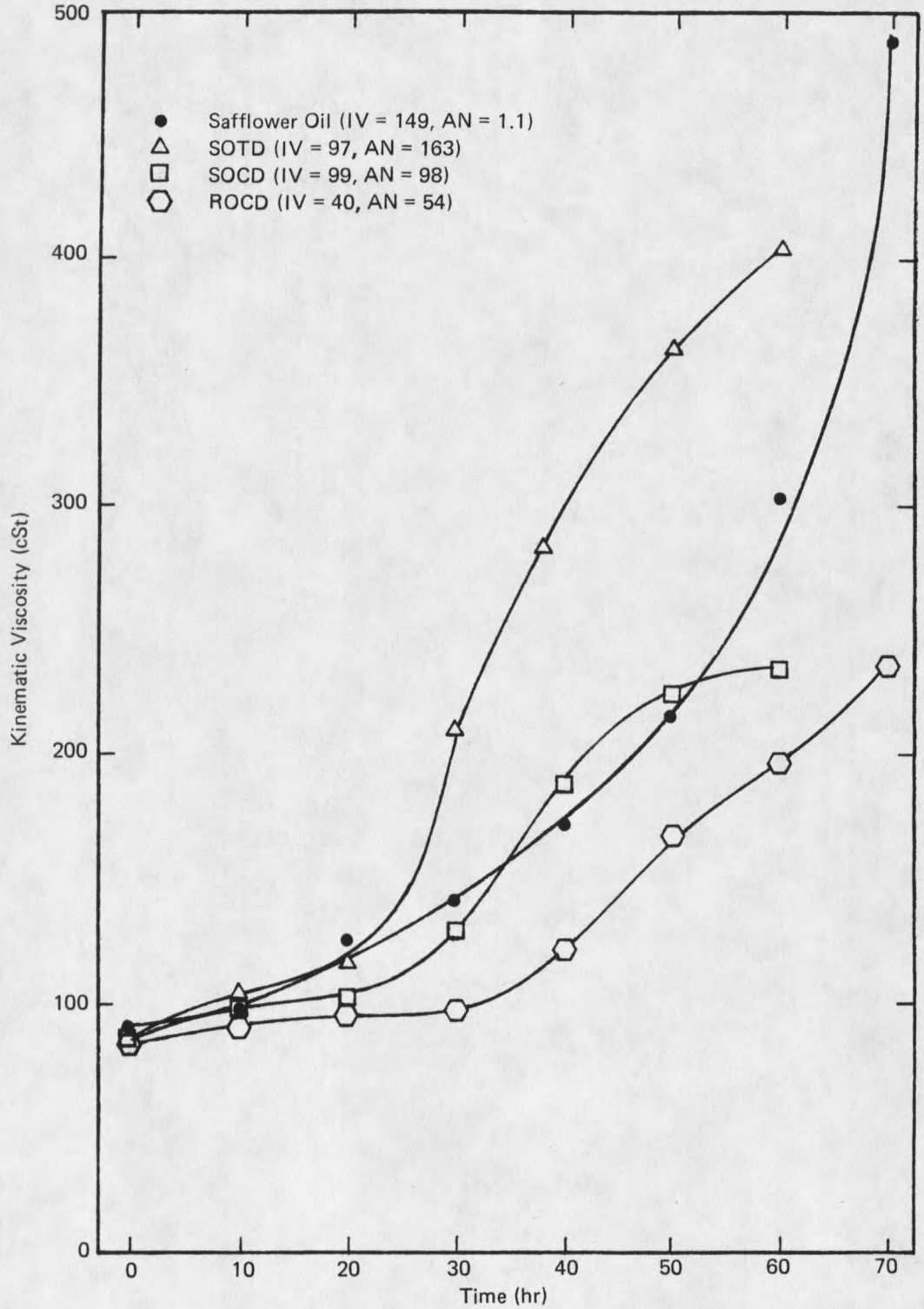

Figure 2. Polymerization characteristics of vegetable oil decarboxylation products and crude safflower oil.

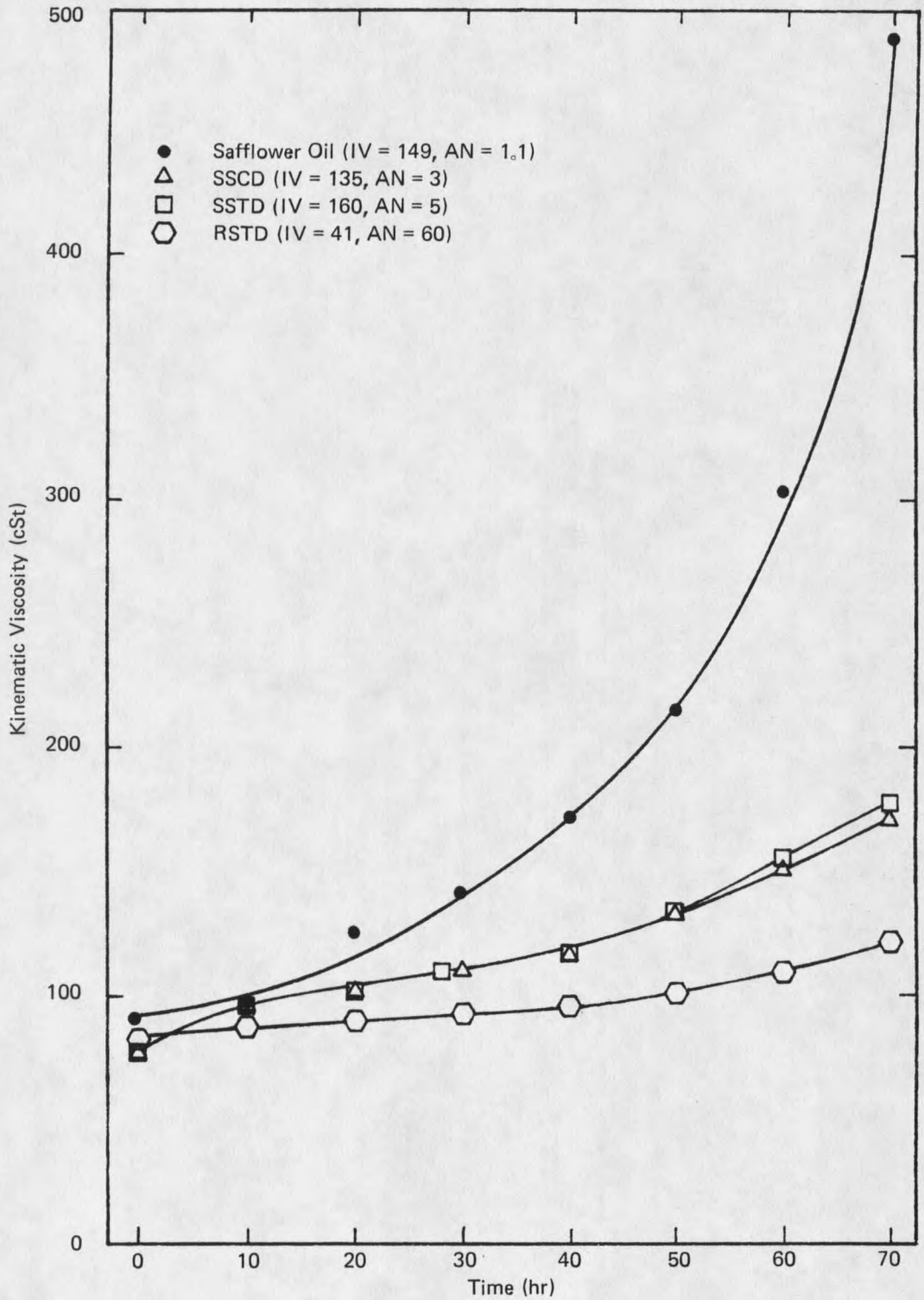

Figure 3. Polymerization characteristics of soap decarboxylation products and crude safflower oil.

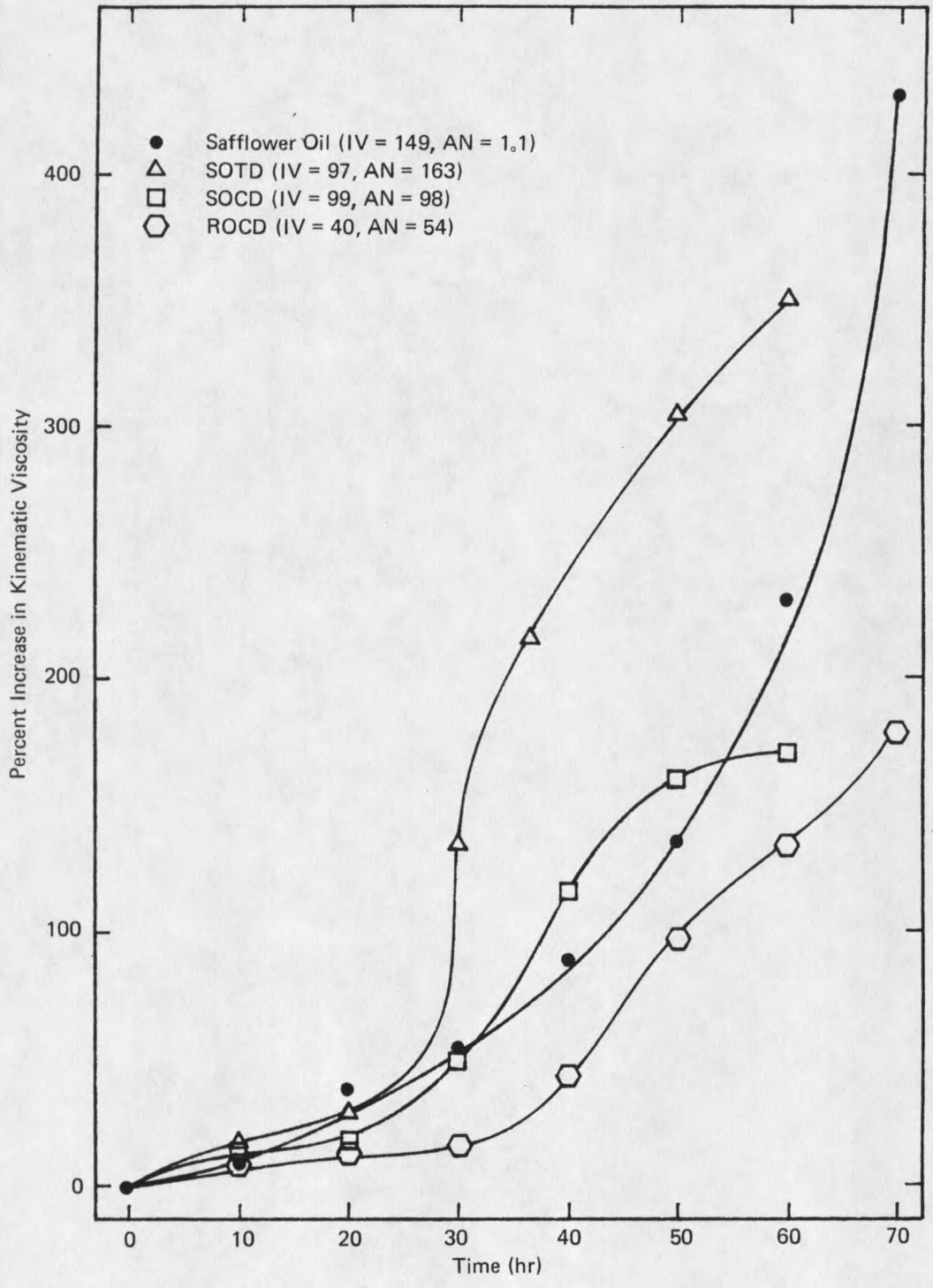

Figure 4. Standardized polymerization characteristics of vegetable oil decarboxylation products and crude safflower oil.

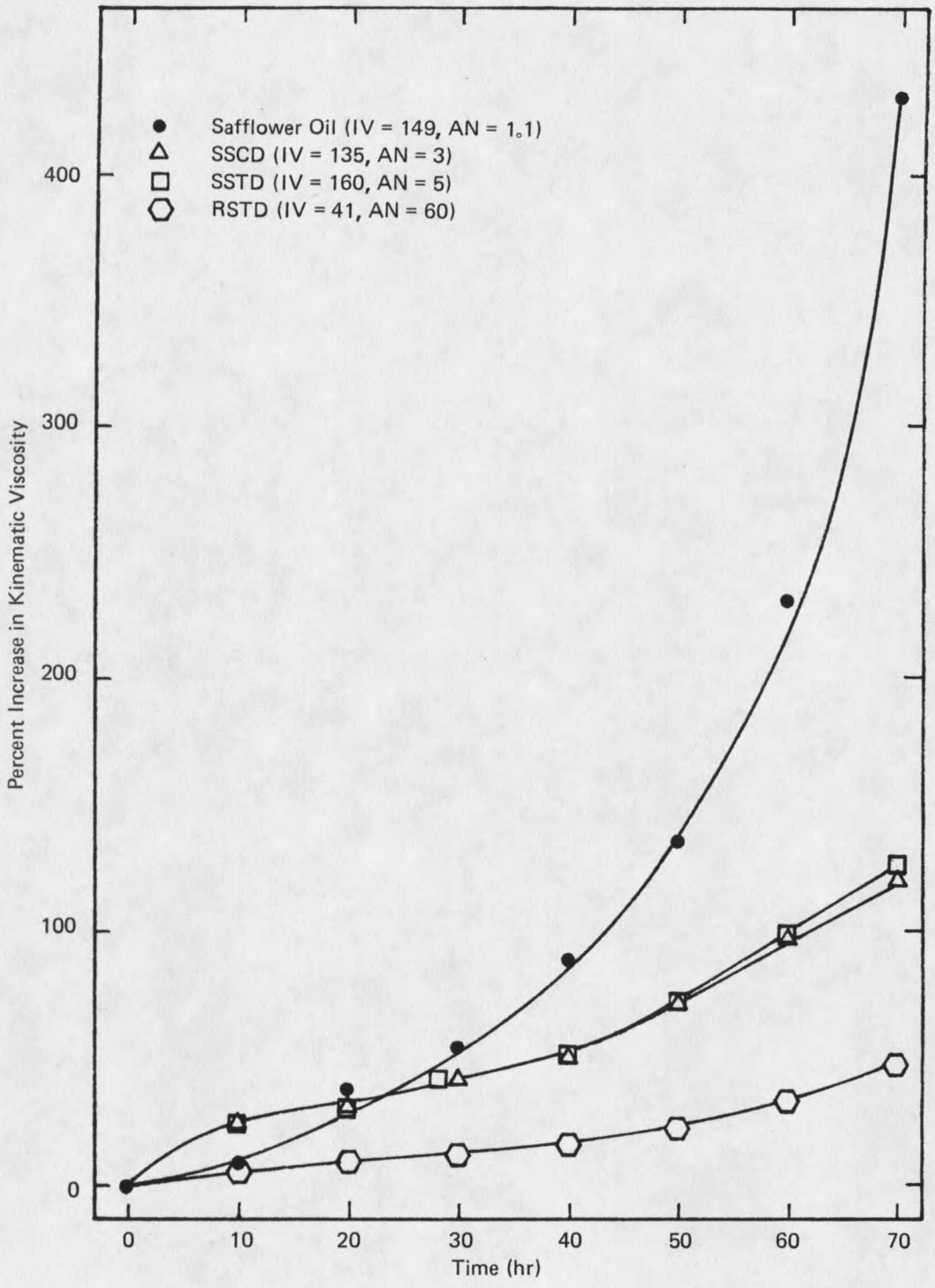

Figure 5. Standardized polymerization characteristics of soap decarboxylation products and crude safflower oil.

The presence of heavy "sludge" in the reaction vessel following polymerization tests is important. It most likely causes the tapering off of the rapid viscosity rise in the graphs. The decarboxylation products are consumed to form "sludge," leaving fewer of them to polymerize. Therefore, Figures 2 and 4 do not represent a true picture of overall viscosity changes with respect to time. This heavy material would also undoubtedly prove extremely detrimental to engine operation should these products be used as diesel fuels.

The thickening test results for both the SSTD and SSCD products were almost identical. Figures 3 and 5 both show the very slow rise of kinematic viscosity with respect to time. Also, no "sludge" was found in the reaction vessels and the surface of the copper strip was clean following the test.

Even though the safflower soap decarboxylation products had significantly higher iodine values than the safflower oil decomposition products (160 and 135 compared to 100) they did not polymerize nearly as much. This seems to refute any theory which states that unsaturation is the only contributor to polymerization of oils. It is certainly a factor because of the high reactivity of the double bond sites.

Other differences between the safflower oil and soap decarboxylation products were their acid numbers and kinematic viscosities. The SOCD and SOTD products have much higher acid numbers and slightly higher viscosities than their soap counterparts. Polymerization differences could be partially attributed to either of these properties.

It is possible that the carboxyl component of the fatty acid could precipitate additional polymerization of the oil. This theory is supported by the fact that raw safflower oil, which is easily decomposed into constituent fatty acids and glycerol, polymerizes very extensively.

Differences in relative viscosity of the decarboxylation products could also account for polymerization disparities. Heavier products would, theoretically, form larger molecules upon polymerizing, thus increasing the thickening rate.

The polymerization test performed on the rapeseed oil decomposition products had results similar to the SOCD test. In Figures 2 and 4 the kinematic viscosity of the lube oil rose at a fairly rapid rate with respect to time. The copper strip was also coated in a similar fashion. Heavy black "sludge" was present in the reaction vessel following the test —although only about half as much was produced by the SOCD product polymerization.

Rapeseed soap decarboxylation products had the least tendency to polymerize of any product tested. The kinematic viscosity versus time curve had the same general shape as the safflower soap curves (Figures 3 and 5). Also, no "sludge" was present in the reaction vessel and the copper strip was very clean.

Iodine values for both the ROCD and RSTD products were about 40. Acid numbers were between 50 and 60 for both. Even with these apparent similarities, their tendencies to polymerize were extremely different, as evidenced by Figures 2 through 5.

The major difference, found by this research, between the rapeseed oil and soap decarboxylation products is that the soap product has about a 33% lower kinematic viscosity. The same reason given previously for safflower oil could account for some of the polymerization differences between the two rapeseed products.

The ROCD products polymerized to a lesser extent than either of the crude safflower oil products. This rapeseed product also had a substantially lower iodine value (40) than either of the safflower products (100). The two safflower oil decomposition products also polymerized to very different degrees but had almost identical iodine values. Because of these two very different results, it is very difficult to correlate polymerization tendencies of vegetable oil decomposition products to their relative degrees of unsaturation.

There does appear to be a correlation, however, between the polymerization of these three vegetable oil decarboxylation products and their acid number. The tendency of these products to polymerize increases with an increasing concentration of fatty acids.

Although neither the safflower nor rapeseed soap decarboxylation products polymerized to any great extent, the polymerization did increase with increasing unsaturation. The rapeseed soap products, with an iodine value of 40, polymerized less than either of the safflower soap products, which had iodine values of 160 and 135. The two safflower soap products showed the same trend in relation to each other. This difference was so small, however, that it is probably within experimental error. It can be inferred from these results that highly unsaturated soap decarboxylation products have a greater tendency to polymerize than those from more saturated soaps.

SUMMARY

1. Hydrocracking catalysts work very well for the decomposition of crude safflower and rapeseed oils.

2. Catalysts have no beneficial effect on the decarboxylation of safflower calcium soaps.

3. Decarboxylation of safflower calcium soaps proceeds via a different mechanism than that of crude safflower oil, as evidenced by their respective products.

4. Hydrogenation of safflower oil, prior to or after decarboxylation, does not seem to be beneficial in terms of increasing liquid product yields.

5. Safflower and rapeseed calcium soap thermal decarboxylation products are the best diesel fuel candidates of all the products tested, based on their low viscosity and tendency not to polymerize.

6. Catalytic and thermal decomposition products of crude rapeseed and safflower oils would not make good diesel fuels because they polymerize extensively and form a heavy "sludge."

7. Decarboxylation products with lower kinematic viscosities do not polymerize as much as those with higher viscosities.

8. The tendency of safflower and rapeseed oil decomposition products to polymerize increases with increasing fatty acid content. Relative unsaturation does not appear to be a primary factor.

9. The tendency of safflower and rapeseed calcium soap decarboxylation products to polymerize increases with increasing unsaturation of the soap products. Fatty acid content does not seem to be a major consideration.

RECOMMENDATIONS FOR FURTHER STUDY

1. Hydrocracking of vegetable oils should be examined thoroughly. This process could potentially result in excellent product yields in the diesel fuel range with a low degree of unsaturation and a low fatty acid content.

2. A realistic mechnism for decarboxylation of both vegetable oils and their soaps needs to be documented.

3. Vapor-phase catalytic cracking of vegetable oils should be explored.

4. Continuous liquid-phase catalytic cracking could be performed on the most promising vegetable oils and catalysts.

5. Actual diesel engine tests of the most successful soap decarboxylation products should be accomplished.

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APPENDICES

APPENDIX A

DECARBOXYLATION CATALYSTS

Table 12. Decarboxylation Catalysts.

Catalyst	Supplier	Composition	Use
$Ca(OH)_2$	—	—	—
$Al(Cl)_3$	—	—	—
V-0601	Harshaw	10% V_2O_5 on high activity alumina	Oxidation
Silica-magnesia	Davison	—	Cracking
Zeolite "B"	Grace	Silica-alumina	Cracking
HT-500	Harshaw	16% MoO_3, 4% NiO on alumina	Hydrocracking
HT-400	Harshaw	15% MoO_3, 3% CoO on alumina	Hydrocracking
UOP-S-6	UOP	Cobalt, nickel, molybdenum	Hydrocracking
UOP SPA-2	UOP	P_2O_5 on kieselguhr	Alkylation

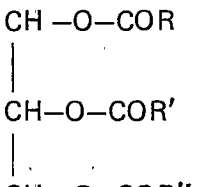
APPENDIX B

SAFFLOWER OIL FATTY ACID CONTENT

SAFFLOWER OIL FATTY ACID CONTENT

Because of similarities to reported values of density, iodine value, and kinematic viscosity, the safflower oil used in this research has been assumed to have a fatty acid content corresponding to literature values. According to these sources [83, pp. D-216-217; 84, p. 144], safflower oil is usually made up of approximately 90% oleic and linoleic acids. Since the remaining 10% are fatty acids of various types, it is assumed, for ease of calculation, that they have the same average carbon chain length and number of double bonds as the oleic/linoleic portion. Calculations can then be performed based on safflower oil composed of 100% oleic and linoleic acids. The resulting ratio of oleic to linoleic acid will then be used to figure a more realistic fatty acid content.

The general chemical structure of a triglyceride is as follows:



Oleic acid, $R=C_{17}H_{33}$ (1 double bond)

Linoleic acid, $R=C_{17}H_{31}$ (2 double bonds)

The average molecular weight (MW) of a triglyceride molecule made up exclusively of these two fatty acids with an oleic acid weight fraction of X is:

$$MW=(57)\ (12.011)+(6)\ (15.999)+\ (104)\ (X)+(98)\ (1-X)\ \ 1.008$$

$$MW=879.4+6.047(X)$$

The iodine value of the safflower oil has been measured to be 149, expressed as centigrams of iodine absorbed per gram of oil sample. The average number of double bonds (DB) per molecule can be calculated as follows:

$$\frac{DB}{molecule} = (1.49 \frac{g\ I}{g\ oil}) (\frac{mole\ \ I}{126.9\ g\ I}) (\frac{mole\ \ DB}{2\ mole\ \ I}) (MW \frac{g\ oil}{mole\ oil})$$

$$\frac{DB}{molecule} = 0.00587\ (MW)$$

If the safflower oil triglyceride molecule was 100% oleic acid it would contain 3 double bonds; 6 double bonds if 100% linoleic. Therefore:

$$DB/molecule = 3(X) + 6(1-X) = 6-3(X)$$

Finally, combining all the previous equations:

$$6-3(X) = 0.00587(MW) = 0.00587\ \ 879.4+6.047(X)$$

$$X=0.276 \quad or \quad 27.6\%\ oleic\ acid$$

But since only 90% of the total fatty acids are of the oleic/linoleic variety:

$$Oleic = (0.9)(0.276) = 0.248$$

Or approximately:

25% Oleic Acid

65% Linoleic Acid

10% Other Fatty Acids

APPENDIX C

ELEMENTAL ANALYSES OXYGEN PERCENTAGE ERROR

ELEMENTAL ANALYSES OXYGEN PERCENTAGE ERROR

The correlation between fatty acid content and oxygen percentage was approximately linear for the safflower oil decarboxylation products (Figure 1). Two sets of data were generated by running elemental analyses samples on separate days. The difference in oxygen percentages between these two runs was consistently 2 wt. % for the same acid number. This apparent error was probably due to the method used to calculate oxygen content. The elemental analysis gave only carbon, hydrogen, and nitrogen percentages, so the oxygen was calculated by difference after assuming it was the only other substance present.

During each elemental analysis, a sample with known values of C, H, and N was run as an unknown. The results for this compound were then compared to the actual values as a check on the machine's accuracy. The unknown used for these two runs was sulfanilamide with results shown in Table 13.

Table 13. Sulfanilamide Elemental Analysis.

Element	Actual Wt. %	Run #1 Wt. %	Run #2 Wt. %
C	41.84	41.67	41.59
H	4.68	4.77	4.56
N	16.27	16.15	15.82
Total	62.79	62.59	61.97

It has been assumed, for calculation purposes, that this sulfanilamide sample contained only these three elements and 5 wt. % oxygen. A value of 5% was the approximate average for samples in this research. Using Table 13 percentages as a basis, a total sample weight of 66.09 g is used. This includes 3.30 g oxygen and 62.79 g others.

Calculation of oxygen content by difference gives:

Run #1 — 3.50 g oxygen or 5.30 wt. %

Run #2 — 4.12 g oxygen or 6.23 wt. %

This relatively simple calculation shows how the percentage of oxygen could easily be in error by almost 1%.

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