"in case piloting of the process is being planned, it is suggested that a fluidized bed reactor be used,"

Pyrolytic Conversion of Coconut Oil Fatty Acids Into Industrial Solvents*

by Renato M. David

Abstract

Using a factorial experimental design, the effects of catalyst type and catalyst concentration on the pyrolytic conversion of coconut oil fatty acids into industrial solvents were studied. Results of the pyrolysis of fatty acids at 345°C and 200 psig for 21 hours using each of the following compounds as catalysts in quantities amounting to 1%, 5% and 10% of the total charge: $FeCl_3$, lava, $AlCl_3$ and $Al_2 0_3$, indicated that the type of catalyst that was used affected the solvent yield significantly while the catalyst concentrations that were used did not. Further statistical analysis using Duncan's multiple range test revealed that $FeCl_3$ was the best catalyst, being significantly different from $Al_2 0_3$, lava and $AlCl_3$ which were not significantly different from one another. Duncan's test likewise confirmed the result that the catalyst concentrations that were used had no significant effect on the solvent yields. The mechanism for converting coconut oil fatty acids into industrial solvents has been postulated to involve the conversion of fatty acids to hydrocarbons followed by the latter's subsequent cracking. This mechanism satisfactorily accounts for the gases and distillate products that were obtained during the study.

Introduction

The Problem

Through the years, coconut oil has been slowly replaced by other vegetable oils in its traditional applications or uses. In the future, the Philippines is expected to treble its coconut production and consequently its coconut oil output because of the replanting program. With the present unfavorable posi-

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*MSChE Thesis, University of the Philippines, 1981.

tion of coconut oil in the world fats and oils market, such a development warrants efforts directed towards increasing the number of uses of the said oil.

Studies have been conducted which resulted in the production of diesel oil, gasoline and kerosene from vegetable oils and animal fats. However, there has never been any reported production of solvents like hexane and/or heptane from such starting materials. This study, therefore, seeks to investigate the feasibility of producing these petroleum-based solvents from a renewable source—the coconut.

Outline of Research

1. Liquid-phase pyrolysis of coconut oil fatty acids using each of the following substances as catalyst in quantities corresponding to 1%, 5% and 10% by weight of the charge: Al_2O_3, $FeCl_3$, lava and $AlCl_3$.
2. Separation of the liquid products of pyrolysis into their various components by distillation.
3. Identification of the "best" catalyst by comparing the amounts of products produced and the yields of fractions corresponding to hexane and heptane.
4. Gas chromatographic analysis of the hexane and heptane fractions to confirm the presence of these substances.
5. Pyrolysis of pure lauric acid at various reaction times using the "best" catalyst identified in step (3).
6. Presentation of a. possible mechanism for the pyrolytic conversion of coconut oil fatty acids into hexane and/or heptane.

Literature Review

Several studies have been conducted on the pyrolysis of vegetable oils and fats or their fatty acids. The major reasons for these studies were either to determine the feasibility of producing petroleum products from renewable resources or to trace the origin of petroleum. The first reason was very popular among countries with no known domestic petroleum sources, especially during the Second World War.

The first group to report on the pyrolysis of fatty materials was that of *Engler* and *Hoffer* (1897-1909). In trying to trace the origin of petroleum, they heated various oils, especially fish oils, under pressure and obtained petroleum-like liquids. *Stadnikov* and *Ivanovskii* (1925), for the same reason, heated linseed oil fatty acids to 400°C in a hydrogen atmosphere using iron as catalyst. The analyses of the products of the reactions showed that mostly paraffinic hydrocarbons and an insignificant admixture of cyclic hydrocarbons were obtained. Carbon dioxide and carbon monoxide were likewise formed during the process.

At about the same time that *Engler* and *Hoffer* were conducting their experiments, *Mailhe* (1909-1923) catalytically pyrolyzed a number of oils by first heating them to 380°C at atmospheric pressure, with catalysts amounting to 5-10% by weight and then by stages to 450°C. He reportedly obtained hydrocarbons, gases and liquids resembling petroleum and a variety of other compounds. The oils that were used included linseed, palm, cottonseed and peanut oils; while copper, zinc, nickel, cadmium, kaolin, the chlorides of zinc, calcium, magnesium, barium, strontium and sodium as well as the oxides of manganese, magnesium, aluminum, titanium, zinc and cadmium were among the materials that were used as catalysts. With the results that he obtained, *Mailhe* explained how vegetable oils could be transformed easily by catalytic means into gaseous and liquid hydrocarbons with the production of small amounts of carbon dioxide and carbon monoxide.

Simultaneous with *Mailhe, Kobayashi* (1921), *Inouye* (19217 and *Shimizu* (1921) independently developed different methods of producing petroleum-like products from oils and/or their fatty acids, *Kobayashi* distilled a mixture of powdered Japanese acid clay and fatty oils (fish oils and vegetable oils, including coconut) at a temperature of 500-700°C under ordinary pressure. The product had a greenish flouorescence and a pungent odor. Coconut oil yielded a distillate amounting to 54.7% of the charge. The distillate was composed of 9.6% light oil, 34.7% illuminating oil and 10.4% neutral and heavy oil. *Inouye,* on the other hand, first converted the fatty acids of sardine oil to ketones and then decomposed the ketones using copper as catalyst. *Shimizu* used both thermal and catalytic cracking of fats or their fatty acids at 450-550°C and ordinary pressure. He used tellurium, nickel, aluminum chloride, ferric oxide and nickel oxide as catalysts. The products that he obtained were light hydrocarbons, fuel gas, carbon and carbonates. The light hydrocarbons amounted to 70-80% of the fatty acids charged. The use of catalysts increased the gasoline content of the product to more than 30%.

In 1924, *Melis* made the first attempt to develop an economic method of producing hydrocarbons from vegetable oils or animal fats on a commercial scale. He first saponified the oil/fat with potassium hydroxide, calcium oxide and water and then distilled the resulting soap. The distillates that were collected were transparent yellowish-brown liquids with a green flourescence and petroleum odor.

A decade later, *Banzon* (1935) catalytically pyrolyzed coconut oil at an average temperature of 300°C and atmospheric pressure and arrived at the following conclusions:

a. of the different catalyses (about 4% of the charge) that he used, ferric oxide was the best for producing liquid products, followed by sodium hydroxide and aluminum chloride, and
b. about 20-50% of the products of pyrolysis were within the kerosene range.

Several years later, *Venkatamaran* and *Parekh* (1940-1941) thermally cracked coconut oil under a pressure of 45 psi. The different products of such cracking and the analysis of the gaseous products are presented in Tables 1 and 2, respectively.

Mandlekar, et. al. (1946-1947), also Indians, likewise thermally cracked vegetable oils, including coconut oil at a pressure of 45 psi. They used a temperature range of 326-379°C and obtained motor (C_5-C_{10}) and diesel fuels (C_{12} and higher). They noted that an increase in pressure favored an increase in overall yield but decreased the diesel fuel content of the product. The diesel fraction could be cracked further to increase the yield of motor fuel. The results of their study are presented in Table 3.

Ishikawa (1943) and *Tokunaga* (1947) reported the production of olefins from fatty materials by catalytically pyrolyzing fatty acids. *Ishikawa* heated stearic acid for 3-5 hours at 400°C and 1 atmosphere and obtained a light yellow, transparent fluorescent oil, the largest fraction of which contained heptadecene mixed with heptadecane. *Tokunaga,* on the other hand, decomposed saturated fatty acids or their methyl or ethyl esters at 300°C with a granular catalyst composed of one or a combination of activated acid clay, silica gal. Al_2O_3 or bentonite in combination with one or a mixture of thorium, vanadium, cesium, nickel, cobalt, ferric oxide or hydroxide. In 1950, *Tokunaga* revealed that:

Table 1. Cracking of Coconut Oil

Product	*Quantity (unit/li of oil)*
Coke	31 g
Pressure Distillate	0.92 1
Water	0.0028
Gas	64 1

Table 2. Composition of the Gaseous Product

Component	*Percentage*
Carbon Dioxide (CO_2)	17.69
Carbon Monoxide (CO)	22.73
Hydrogen (H_2)	22.82
Olefins	9.99
Saturated Hydrocarbons	21.77

Source: Vankatamaran, K. and Parekh, J. M. (1943) "Cracking of Coconut Oil". *Rept. Tech. Work Board Sci. Ind. Research,* 1940-41, 6.

Table 3. Motor Fuels from Pressure Cracking of Vegetable Oils

Vegetable Oil Cracked	*Yield of Refined Motor Fuels*
Coconut Oil	46.2
Sesame Oil	41.4
Cottonseed Oil	37.1
Castor Oil	50.0

Source: Mandlekar, M. R.; Mehta, T. W.; Parekh, V. M. and Thosar, V. P. (1947). "Cracking of Vegetable Oils. XXI. Coconut Oil, Sesame Oil, Cottonseed Oil and Castor Oil." *J. Indian Chem. Soc., Ind. & News Ed.* 10, 1-16.

a. decarboxylation, dehydration and dehydrogenation (which yield alkanes and alkanes) of coconut oil were effected least readily when acid clay was used; while bauxite gave the best result.

b. kaolin and bentonite were good dehydrogenation and dehydration agents but were poor in decarboxylating coconut oil.

c. the greatest extent of decomposition was achieved by heating coconut oil to 450-500°C for 40-80 minutes. Below 450°C, dehydrogenation and dehydration (which result in alkenes) were not effected, while above 500°C, larger amounts of gaseous products were obtained.

d. formation of alkenes was best when a catalyst composed of 75% acid clay and 25% calcium oxide was used.

During the Second World War, *Cheng* (1945) and *Chang* and *Wan* (1947) like their Japanese neighbors, experimented on producing fuels from vegetable oils. *Cheng* employed both high pressure thermal cracking of the oil and atmospheric pressure catalytic cracking of its lime soaps. High pressure thermal cracking at 400-500°C and 50-150 psi gave a product of two equal portions: a light spirit and a mixture of kerosene, diesel oil and lubricating oil. The optimum temperature was found to be 450°C. In the atmospheric catalytic cracking process, $AlCl_3$ was found to be a good catalyst. The yield of crude oil was higher in the pressure cracking process (75% by weight of the charge) than in the catalytic atmospheric process (55% by weight of the charge). *Chang* and *Wan* cracked the soap of tung oil thermally and tung oil itself catalytically under normal pressure or thermally under a pressure of 280 psi. In all cases, temperatures of 300-350°C were used during the course of the runs which lasted 120 minutes. $AlCl_3$, lime magnesia and caustic soda in quantities equivalent to 1% and 10% of the charge were used as catalysts. They obtained average yields of crude oil amounting to 70% by volume of the charge. The gasoline content of the crude oil was about 25% by volume.

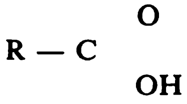
Otto (1945), in the same period, reportedly produced gasoline from vegetable oils. Much later, *Pustilnikova, et. al.* (1962-1968) also produced hydrocarbons from fatty substances. *Pustilnikova, et. al.* pyrolyzed fatty acids for 50 hours at 250°C and 1 atmosphere in a stainless steel reactor using commercial aluminum silicate as catalyst. Kerosene, gasoline and lube oil were recovered.

Just several years ago, *Almon* and *Johns* (1975) studied the kinetics and mechanism of clay-catalyzed fatty acid decarboxylation under conditions simulating burial diagenesis. The mechanism involved electron transfer from the fatty acid to the catalyst acceptor sites which resulted in acyl free radicals. The acyl from radicals then decomposed to alkyl free radicals which were hydrogenated to alkanes.

Recently, *Arida* (1980) tried 32 catalysts which included the salts of transition metals in trying to produce petroleum products from coconut oil. She pyrolyzed coconut oil at 310-400°C and 1 atmosphere from 11 to 20 hours and obtained gasoline-like and diesel-like products. The best catalysts for producing crude products in their decreasing order of effectivity were: $AlCl_3$, CaO, NaCN, Fe_2O_3 and Fe. However, in terms of saturated hydrocarbon yield, NaCN was the best, followed by Fe as a poor second and Fe_2O_3, third. Of the various catalyst concentrations that were used—2%, 4% and 6%—4% gave the best saturated hydrocarbon yield. This is because at concentrations of 6% and above, violent reactions occurred.

Theoretical Considerations

Fatty acids are organic compounds that are made up of a long non-polar hydrocarbon chain and a strongly polar carboxylic group. They are obtained ordinarily from the triglycerides of fats and oils which are comprised of three molecules of fatty acids, usually varying in compositions, and one molecule of glycerine. Chemically, they can be represented by the formula:



$$R - C\begin{matrix} O \\ \\ OH \end{matrix}$$

where R = saturated or unsaturated alkyl group

Coconut oil, the only major source of fatty acids in the Philippines at present, was analyzed by *Banzon* and *Resurreccion* (1979). Its composition is shown in Table 4.

Table 4. Fatty Acid Distribution in Coconut Oil Prepared by Four Methods.

Fatty Acid	Methods Used				Average
	Solvent	Ferment	Freeze	Heat	
C_6	0.57	0.59	0.59	0.63	0.60
C_8	8.51	9.29	9.24	10.03	9.26
C_{10}	5.62	5.97	5.94	6.32	5.96
C_{12}	52.10	49.53	49.65	49.10	50.10
C_{14}	18.01	18.03	16.94	17.58	17.64
C_{16}	7.16	7.55	7.72	7.64	7.52
C_{18}	3.40	3.81	4.20	3.75	3.79
$C_{18:1}$	3.99	4.53	4.91	4.25	4.42
$C_{18:2}$	0.63	0.69	0.81	0.70	0.71

Source: Julian A. Banzon and A. P. Resurreccion. "Fatty Acid Distribution in Coconut Oil Obtained by Four Processing Methods and Secured from Four Philippine Types of Coconuts." *Philippine Journal of Coconut Studies.* Vol. IV, No. 2, p. 5 (1979).

3.2 *Preparation of Hydrocarbons from Fatty Acids*

Chang and *Wan* (1947) gave the different methods for converting vegetable oils or their fatty acids to hydrocarbons as:

1. destructive distillation of the vegetable oil and the subsequent or simultaneous cracking of its vapors. The reactions involved in this method were postulated by *Banzon* (1970) to be:

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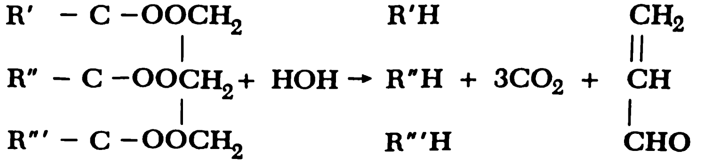
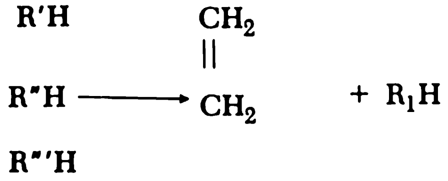


$$\begin{array}{llllll} \mathrm{R'} - \mathrm{C} - \mathrm{OOCH_2} & & \mathrm{R'H} & & \mathrm{CH_2} & \\ \qquad\; | & & & & \; \| & \\ \mathrm{R''} - \mathrm{C} - \mathrm{OOCH_2} + & \mathrm{HOH} \rightarrow & \mathrm{R''H} & + \; 3\mathrm{CO_2} \; + & \mathrm{CH} & (3.01) \\ \qquad\; | & & & & \; | & \\ \mathrm{R'''} - \mathrm{C} - \mathrm{OOCH_2} & & \mathrm{R'''H} & & \mathrm{CHO} & \end{array}$$

carbon dioxide

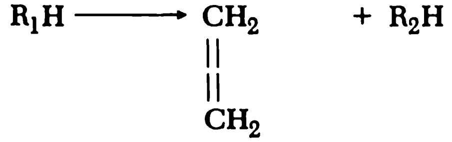
Trigylcarida WaterHydrocarbons Acrolein

where R', R'' and R''' represent hydrocarbon chains of the same or varying lengths.



$$\begin{matrix} R'H \\ R''H \\ R'''H \end{matrix} \longrightarrow \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + R_1H \tag{3.02}$$

where R_1 is a 2-carbon atom less than R', R'' or R'''.



$$R_1H \longrightarrow \begin{matrix} CH_2 \\ \| \\ \| \\ CH_2 \end{matrix} + R_2H \tag{3.03}$$

Again, R_2 is 2-carbon atom less than the parent molecule, R_1.

2. Liquid-phase cracking of the vegetable oil or its fatty acids with or without catalysts under elevated or normal pressure:

$$RCOOH \xrightarrow{\Delta} RH + CO_2 \tag{3.04}$$

$$RH \xrightarrow{\Delta} \text{shorter chain hydrocarbons.} \tag{3.05}$$

3. pyrolysis of the soap of the vegetable oil:

$$RCOO^-Na^+ + NaOH \xrightarrow{\Delta} RH + Na_2CO_3 \tag{3.06}$$

$$RH \xrightarrow{\Delta} \text{shorter hydrocarbons} \tag{3.07}$$

Regardless of the method that is used, the main reactions that are involved in the conversion of vegetable oils or their fatty acids into hydrocarbons of medium lengths are: decarboxylation of the oil or fatty acids resulting in a hydrocarbon that is 1-carbon atom shorter than the parent material and cracking of this hydrocarbon into shorter-chain hydrocarbons. The second step is no different from petroleum cracking reactions.

3.2.1 *Decarboxylation* When fatty acids are subjected to high temperatures, decarboxylation may result yielding carbon dioxide and a hydrocarbon. *Shirley* (1964) gave the reaction as:

$$RCOOH \xrightarrow{\Delta} RH + CO_2 \qquad (3.08)$$

However, at high temperatures, this may not be the only reaction that takes place. *March* (1968) indicated that the following reaction takes place likewise:

$$RCOOH \xrightarrow{\Delta} R'CH = C = O + H_2O \qquad (3.09)$$

The ketene product can then undergo a decomposition reaction and yield a hydrocarbon product.

$$2R'CH = C = O \longrightarrow 2CO + R'HC = CHR' \qquad (3.10)$$

3.2.2 *Cracking.* Cracking is the conversion of large hydrocarbon molecules into smaller ones. It involves the rupture of carbon-carbon bonds and because of its endothermic nature, it is themodynamically favored by high temperatures. It can be carried out with catalysts as in catalytic cracking or without catalysts as in thermal cracking. *Gates, et. al.* (1979) gave the primary reactions involved during cracking as:

$$C_nH_{2n+2} \longrightarrow C_mH_{2m} + C_pH_{2p+2} \qquad (3.11)$$

where $n = m + p$; and

$$C_nH_{2n} \longrightarrow C_nH_{2m} + C_pH_{2p} \qquad (3.12)$$

where $n = m + p$

They also gave the secondary reactions that may occur after the initial cracking steps and which can affect the final product composition. These are:

(1) Isomerization:

$$\text{Olefin} \longrightarrow \text{Isoolefin} \qquad (3.13)$$

(2) Disproportionation of low molecular weight olefins:

$$2H_2C = CH\,CH_2\,CH_3 \longrightarrow H_2C = CH\,CH_3 + H_2C = CH\,CH_2\,CH_2\,CH_3 \qquad (3.14)$$

Thermal Cracking — Thermal cracking is carried out in the absence of air. When a temperature of around 400-500°C is reached, the energy input is sufficient to break a few C-C and C-H bonds, with the C-C rupture much more probable because of its lower energy requirement. The breaking of these bonds have been pointed out by *Shirley* (1964) and *Gates, et. al.* (1979) to be a homolytic rupture into free radicals and free hydrogen atoms inasmuch as this route requires less energy than does the dissociation into ions. At higher temperatures, bond breaking becomes faster and temperature ranges of 600-800°C at pressures as high as 250 psi are used. The free radicals that are formed then start a series of chain-type reactions which result in extensive changes on the molecules involved.

To illustrate the mechanisms of thermal cracking, an example—cracking of butane—is lifted from *Shirley* (1954):

1. Initiation Reactions

$$CH_3\,CH_2\,CH_2\,CH_3 \longrightarrow CH_3\,CH_2\,\overset{\bullet}{C}H\,CH_3 + H\bullet \tag{3.15}$$

$$CH_3\,CH_2\,CH_2\,CH_3 \longrightarrow \bullet CH_3 + CH_3\,CH_2\,\overset{\bullet}{C}H_2 \tag{3.16}$$

2 .

2. Propagation Reactions

$$CH_3\,CH_2\,\overset{\bullet}{C}H_2 \longrightarrow CH_2 = CH_2 + \overset{\bullet}{C}H_3 \tag{3.17}$$

$$CH_3\,\overset{\bullet}{C}H_2 \longrightarrow CH_2 = CH_2 + H\bullet \tag{3.18}$$

$$CH_3\,\overset{\bullet}{C}H_2 + CH_3\,CH_2\,CH_2\,CH_3 \longrightarrow CH_3\,CH_3 + CH_3\,CH_2\overset{\bullet}{C}H\,CH_3 \tag{3.19}$$

3. Termination Reactions

$$\bullet CH_3 + CH_3\,\overset{\bullet}{C}H_2 \longrightarrow CH_3\,CH_2\,CH_3 \tag{3.20}$$

$$CH_3\,\overset{\bullet}{C}H_2 + H\cdot \longrightarrow CH_3CH_3 \tag{3.21}$$

$$H\cdot + H\cdot \longrightarrow H_2 \tag{3.22}$$

Catalytic Cracking — Catalytic cracking is the decomposition of large hydrocarbon molecules into smaller units through the aid of a catalyst. *Ashmore* (1953) defined a catalyst as a substance which alters the velocity of a chemical reaction without appearing in the end product. Its properties or behavior according the *Berkman, et. al.* (1940), *Stevens* (1971) and *Perry* and *Chilton* (1973) are:

1. A catalyst remains chemically unchanged at the end of the reaction.
2. A catalyst does not alter the position of chemical equilibrium.
3. A catalyst increases the rates of both forward and reverse reactions to the same extent—in short, it is a substance that accelerates the approach to chemical equilibrium.
4. A small amount of catalyst promotes a large amount of chemical change and the rate of reaction is generally proportional to the catalyst concentration.
5. When more than one mechanism is feasible for a reaction, a catalyst may exhibit selectivity favoring one mechanism over others, resulting in a product distribution different from those by other mechanisms. Proper application of catalyst selectivity enables the desired reaction to be accelerated and the undesirable reactions, retarded.

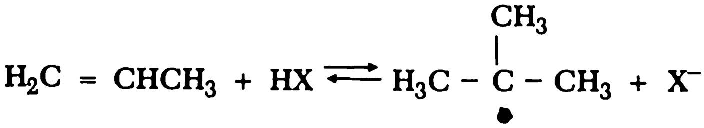
Courberry (1976) and *Rase* (1977) classified catalyst into the following three broad groups:

1. Metallic catalysts — these are generally found as oxides capable of reduction. These metals effectively chemisorb hydrogen and oxygen and function effectively as oxidation and hydrogenation—dehydrogenation agents. Metals under this classification are found in the transition- and noble-metal groups.
2. Insulators — The absence of conductivity in these catalysts excludes the conductor mechanism of chemisorption and catalysts. Characterized by acidity which renders them effective in reaction requiring a carbonium ion mechanism, these catalysts find application in cracking, polymerization, alkylation, isomerization and hydration-dehydration reactions.
3. Semiconductors — These are substances that exhibit low or negligible conductivity at low temperatures but show dramatic conductivity with temperature increase. Capable of electron exchange with adsorbed species, these catalysts function effectively in reaction of the same type catalyzed by the transition and noble metals.

Because of the catalyst, this type of cracking involves a mechanism very much different from that of thermal cracking and requires lower temperatures, usually 500-580°C.

Hansford (1952), *Haensel* (1951), *Shirley* (1964), *Voge* (1958), *Ashmore* (1963) and *Gates, et. al.* (1979) all point to the formation of carbonium ions as the governing mechanism for this type of cracking. *Gates, et. al.* (1979) gave the following reactions as the steps involved in catalytic cracking:

1. Formation of a carbonium ion:
   (a) interaction of an acid with an unsaturated hydrocarbon acting as a weak base.



$$H_2C = CHCH_3 + HX \rightleftharpoons H_3C - \overset{CH_3}{\underset{\bullet}{C}} - CH_3 + X^- \qquad (3.23)$$

   (b) abstraction of a hydride ion from a paraffin

$$RH + HX \rightleftharpoons R^+ + X^- + H_2 \qquad (3.24)$$

or

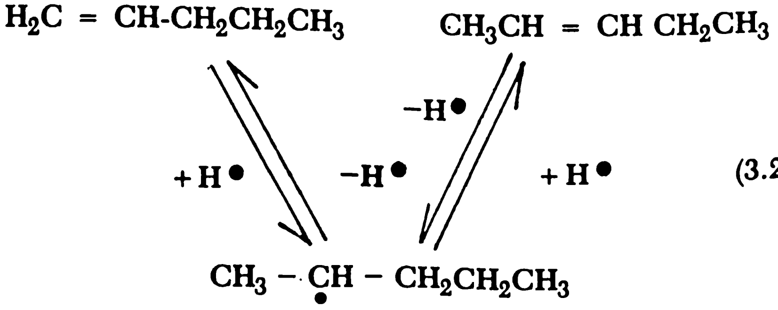
$$RH + L\ (\text{Lewis Acid}) \rightleftharpoons LH^- + R^+ \qquad (3.24.1)$$

   (c) interaction of a carbonium ion with a saturated hydrocarbon to form a new carbonium ion.

$$R_1^+ + R_2H \rightleftharpoons R_1H + R_2^+ \qquad (3.25)$$

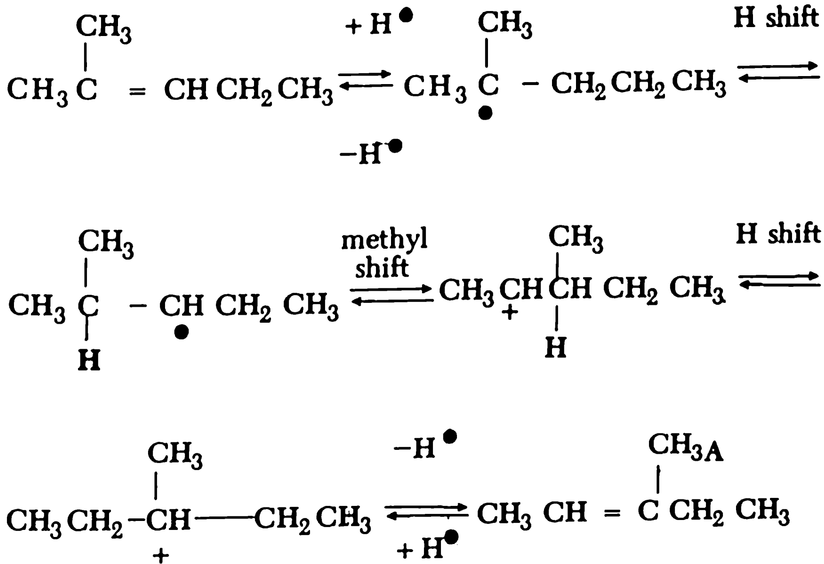
3° > 2° > 1° carbonium ion instability.

2. Reactions of carbonium ions:
   (a) rearrangement by H-atom shifts leading to a double bond isomerization of an olefin.



(3.26)

(b) carbon-atom shifts



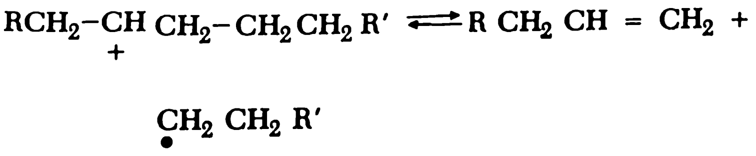
$$\overset{\displaystyle CH_3}{\overset{|}{CH_3C}} = CH\,CH_2CH_3 \underset{-H^\bullet}{\overset{+H^\bullet}{\rightleftharpoons}} CH_3\underset{\bullet}{\overset{\displaystyle CH_3}{\overset{|}{C}}} - CH_2CH_2CH_3 \overset{\text{H shift}}{\rightleftharpoons}$$

$$CH_3\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} - \underset{\bullet}{CH}\,CH_2\,CH_3 \overset{\text{methyl shift}}{\rightleftharpoons} CH_3\underset{+}{CH}\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{CH}}}}\,CH_2\,CH_3 \overset{\text{H shift}}{\rightleftharpoons}$$

$$CH_3CH_2-\underset{+}{\overset{\displaystyle CH_3}{\overset{|}{CH}}}-\!\!\!-CH_2CH_3 \underset{+H^\bullet}{\overset{-H^\bullet}{\rightleftharpoons}} CH_3\,CH = \overset{\displaystyle CH_3A}{\overset{|}{C}}\,CH_2\,CH_3$$

(3.27)

3. Scission at the bond located β to the carbon atom bearing the positive charge:

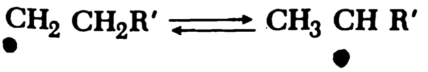


$$RCH_2-\underset{+}{CH}\,CH_2-CH_2CH_2\,R' \rightleftharpoons R\,CH_2\,CH = CH_2 + \underset{\bullet}{CH_2}\,CH_2\,R'$$

(3.28)

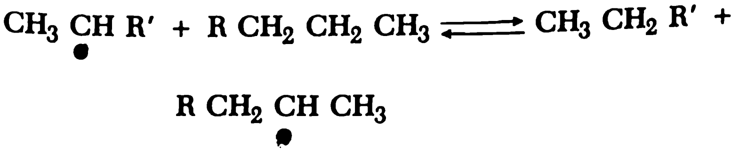
This reaction accounts for the decrease in the carbon-chain length of the original feed material.

4. Formation of saturated hydrocarbons:



$$\underset{\bullet}{CH_2}\,CH_2R' \rightleftharpoons CH_3\,\underset{\bullet}{CH}\,R'$$

(3.29)



$$CH_3\,\underset{\bullet}{CH}\,R' + R\,CH_2\,CH_2\,CH_3 \rightleftharpoons CH_3\,CH_2\,R' + R\,CH_2\,\underset{\bullet}{CH}\,CH_3$$

(3.29.1)

Voge (1958) gave the principal modes of cracking of different important hydrocarbon classes and these are presented in Table 5.

The difference in the mechanisms of the two types of cracking obviously yield differing products. This is easily confirmed by experimental studies. *Greensfelder, et. al.* (1949) gave a comparison of the types of products that can be obtained from both types of cracking. This is shown in Table 6.

Table 5. Modes of Cracking of Different Important Hydrocarbon Classes

Hydrocarbon Type	*Mode of Cracking*	*Products*
n—Paraffin	chain rupture in several places	olefins and paraffins
1—Paraffin	as above	as above, little methane
Naphthene	ring and chain rupture	as above, some aromatics
Naphthene-Aromatic	naphthene ring opened or split from the aromatic ring	mixed aromatic materials and and olefins and paraffins
Pure Aromatic	little or no cracking	— — —
Alkyl Aromatic	alkyl group sheared off	olefins and bare aromatic
N—Olefin	chain rupture in several places	olefins with some paraffins

Source: Hervey H. Voge, "Catalytic Cracking", Vol. VI: *Catalysis*. Edited by Paul H. Emmett. 1958, p. 421.

Table 6. Comparison of Catalytic and Thermal Cracking Products

Hydrocarbon	*Thermal Cracking*	*Catalytic Cracking*
n—Hexadecane (cetane)	Major product is C_2 with much C_1 and C_3. Much C_4 to C_5 n–olefins. Few branched aliphatics.	Major product is C_3–C_6, Few n–α olefins above C_4. Aliphatics mostly branched
Aliphatics	Small amounts of aromatic formed at 500°C.	Large amounts of aromatics formed at 500°C.
Alkylaromatics	Crack within side chain.	Crack next to ring.
n–Olefins	Double bond shifts slowly. Little skeletal isomerization.	Double bond shifts rapidly. Extensive skeletal isomerization.
Olefins	H_2 transfer is a minor reaction and is non-selective for 3° olefins. Crack at about same rate as corresponding paraffins.	H_2 transfer is an important reaction and is selective for 3° olefins. Crack at much higher rate than corresponding paraffins.

Naphthenes	Crack at lower rate than paraffins.	Crack at about same rate as paraffins with equivalent structural groups.

Source: Greensfelder, B. S., Voge, H. H. and Good, G. M., IEC 41, 2573 (1949).

Investigation

Design and Experiments

This study makes use of a two-factor experiment with a completely randomized design. The effects of catalyst type and catalyst concentration on the amount of distillate produced during the liquid phase pyrolytic conversion of coconut oil fatty acids into industrial solvents (hexane and/or heptane) have been considered. The data on these two factors are presented at four and three levels, respectively.

Materials and Equipment Utilized

The crude fatty acid mixture that served as the source of the fatty acid charge in the various runs in this study was obtained from a local soap and oil manufacturing plant.

The substance that were used as starting material or catalysts were the following:

A. Starting Material
   1. Lauric Acid, Biochemical Grade, Merck and Co.

B. Catalysts
   1. Aluminum chloride, anhydrous, BGH
   2. Ferric Chloride, C.P. Baker's Analyzed
   3. Harshaw activated alumina catalyst, AI-0101P
   4. Lava from the Commission on Volcanology (CONVOL)

The reactor that was used in the experiments was a Parr-bench-mounted, high-pressure reactor, Model 4521.

Procedures and Analytical Methods

The crude fatty acid mixture was distilled to remove the impurities present.

To 450 ml of this distilled mixture was added the catalyst amounting to 1% of the total charge's weight (fatty acid mixture including the catalyst). The resulting mixture was then placed inside the bomb of the reactor and pyrolyzed for 21 hours at 345°C and 200 psig. Any pressure in excess of 200 psig was released and passed through a steel condenser that could withstand high pressures. A water-displacement set-up was attached to the outlet of the condenser to measure the volume of the gas that was released with the release of the excess pressure. The complete set-up is shown in Figure 1.

Gas samples were collected and analyzed using an Orsat apparatus after 5, 10, 15 and 20 hours of the reaction. Each run was duplicated to ensure the reliability of results.

The same procedure was followed for runs using catalysts amounting to 5% and 10% by weight of the total charge.

All the distillate products were fractionated into portions corresponding to hydrocarbons with chain lengths of 5-10 carbons. All the fractions corresponding to hexane were mixed and analyzed using a gas chromatograph. The same procedure was carried out on the heptane fractions.

The catalyst that gave the highest distillate and hexane-heptane yields was used in the pyrolysis of pure lauric acid. Pure lauric acid was pyrolyzed for 5.7 and 10 hours in order to follow the course of the reaction and come up with a possible mechanism for the conversion of fatty acids into hexane and/or heptane. All the distillates that were obtained in these runs were likewise analyzed using a gas chromatograph.

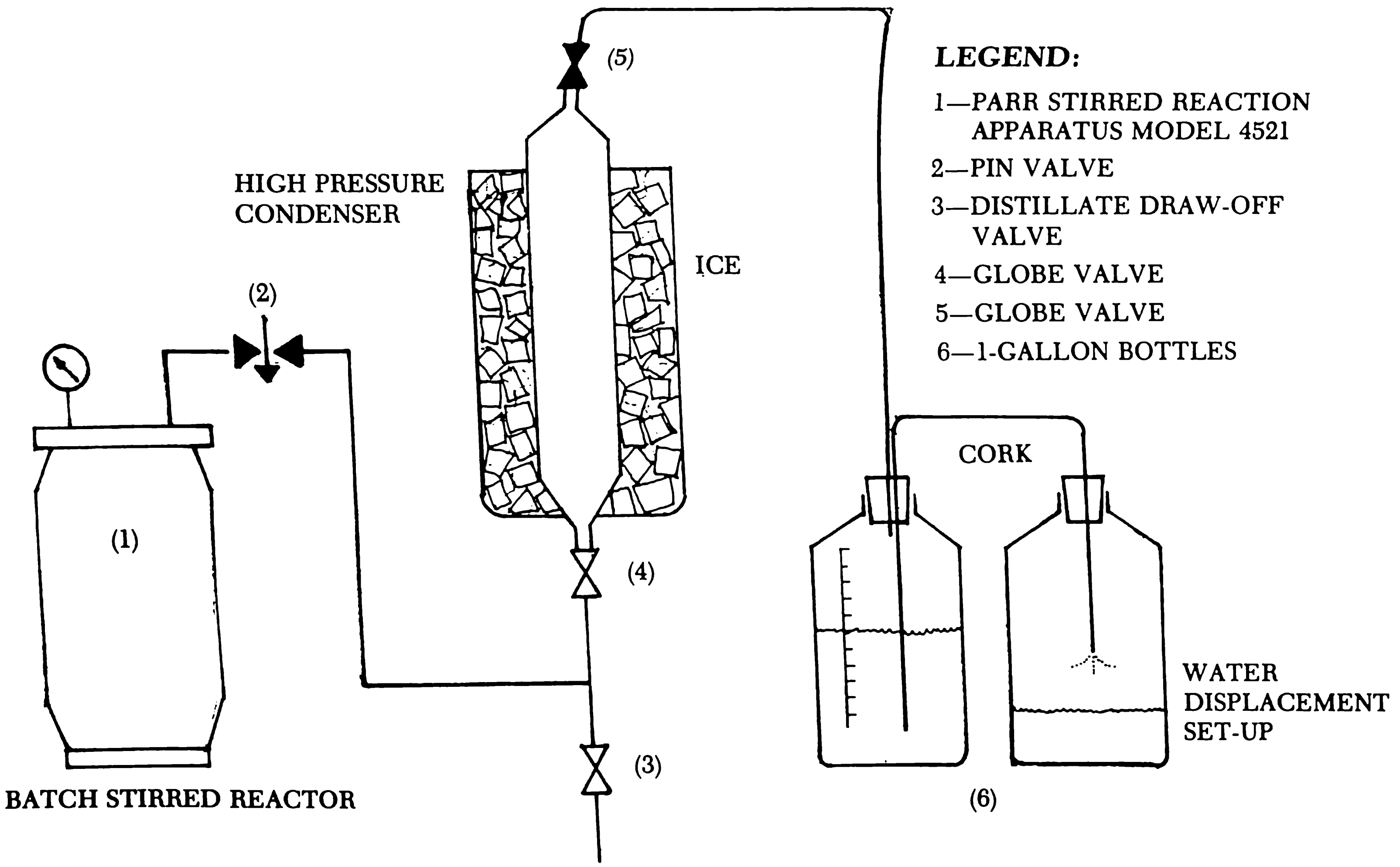


Figure 1. EXPERIMENTAL SET-UP

TABLE 7. Liquid-Phase Catalytic Cracking of Coconut Oil Fatty Acids

	CATALYST USED											
	None	*1%* Al_2O_3	*1%* $AlCl_3$	*1%* $FeCl_3$	*1% Lava*	*5%* Al_2O_3	*5%* $AlCl_3$	*5%* $FeCl_3$	*5% Lava*	*10%* Al_2O_3	*10%* $FeCl_3$	*10% Lava*
Amount of Fatty Acids, ml	450	450	450	450	450	450	450	450	450	450	450	450
Reactor Gage Pressure, psig	200	200	200	200	200	200	200	200	200	200	200	200
Temperature, °C	345	345	345	345	345	345	345	345	345	345	345	345
Reaction Time, hours	21	21	21	21	21	21	21	21	21	21	21	21
Products												
Gas, ml	18,588	21,194	51,637	52,255	34,136	17,523	54,453	67,718	33,572	17,452	72,605	35,548
Distillate, g	245.16	138.41	131.09	241.31	168.95	185.82	85.92	213.29	198.94	110.30	203	169.63
Residue, g	90.42	188.41	83.11	44.82	129.96	137.28	105.80	41.08	88.67	178.40	34.65	87.41

Note: The values presented here are the average of two hours.

TABLE 8. Effect of Catalyst on Composition of Gaseous Product Obtained During the Liquid-Phase Pyrolysis of Coconut Oil Fatty Acids.

		AVERAGE ORSAT ANALYSIS*				
Run Number	*Catalyst*	CO_2	O_2	CO	CH_4	H_2
11-2729-79 NC	None	24.84	1.14	38.37	11.87	0.0
12-35-79 NC	None	24.22	1.22	45.53	8.17	0.0
12-1214-79 A1	Al_2O_3, 1%	29.58	1.91	34.19	3.95	0.0
1-911-80 A1	Al_2O_3, 1%	33.66	1.75	45.90	7.35	0.0
12-1719-79 A5	Al_2O_3, 5%	54.43	1.59	30.08	3.65	0.0
1-1416-80 A5	Al_2O_3, 5%	56.31	1.31	19.06	10.51	0.0
1-24-80 A10	Al_2O_3, 10%	74.73	1.00	11.35	0.70	0.0
3-1719-80 A10	Al_2O_3, 10%	53.84	2.41	18.66	10.65	0.18
5-1620-80 AC1	$AlCl_3$, 1%	17.16	1.00	45.18	6.82	2.99
6-24-80 AC1	$AlCl_3$, 1%	18.31	1.00	45.51	9.37	2.15
5-2830-80 AC5	$AlCl_3$, 5%	9.12	1.73	48.66	5.93	6.18
2-1113-80 FC1	$FeCl_3$, 1%	14.26	1.27	37.81	4.60	9.01
3-35-80 FC1	$FeCl_3$, 1%	14.34	2.52	37.19	3.79	6.82
3-2527-80 FC5	$FeCl_3$, 5%	9.13	2.55	27.51	6.77	14.01
3-28/4-1-80 FC5	$FeCl_3$, 5%	8.53	1.77	29.85	13.98	15.73
5-1215-80 FC10	$FeCl_3$, 10%	8.35	1.00	33.81	14.74	16.13
3-1012-80 LA1	lava, 1%	22.39	1.50	48.10	9.14	2.36
3-2024-80 LA1	lava, 1%	17.57	1.48	63.34	10.51	1.92
4-1822-80 LA5	lava, 5%	34.01	2.20	44.69	9.67	1.42
4-2529-80 LA5	lava, 5%	30.80	1.97	45.72	8.59	1.67
4-30/5-5-80 LA10	lava, 10%	28.70	1.40	46.36	13.60	0.0
5-79-80 LA10	lava, 10%	29.69	1.43	51.79	10.30	0.14

*Weighted Average.

TABLE 9. Liquid Phase Pyrolysis of Coconut Oil Fatty Acids: Effect of Catalyst on Product Distribution.

Date of Run	*Charge*	*Operating Conditions*	*Catalyst*	% *Recovery*			*% Loss*
				Distillate	*Gas*	*Residue*	
11/27-29/79	fatty acids	345°C 200 psig	None	65.89	5.06	13.56	15.49
12/3-5/79	fatty acids	345°C 200 psig	None	58.64	4.86	32.37	4.13
12/12-14/79	fatty acids	345°C 200 psig	1% Al_20_3	35.31	4.82	50.84	9.03
1/9-11/80	fatty acids	345°C 200 psig	1% Al_20_3	34.99	7.95	44.86	12.20
12/17-19/79	fatty acids	345°C 200 psig	5% Al_2O_3	46.49	6.54	34.61	12.36
1/14-16/80	fatty acids	345°C 200 psig	5% Al_2O_3	47.90	5.98	35.12	11.00
1/2-4/80	fatty acids	345°C 200 psig	10% Al_2O_3	5.97	5.97	48.32	18.17
3/17-19/80	fatty acids	345°C 200 psig	10% Al_2O_3	28.49	6.91	42.30	22.30
5/16-20/80	fatty acids	345°C 200 psig	1% $AlCl_3$	41.73	11.21	11.64	35.52
6/2-4/80	fatty acids	345°C 200 psig	1% $AlCl_3$	24.86	13.75	30.67	30.72
5/28-30/80	fatty acids	345°C 200 psig	5% $AlCl_3$	21.82	11.93	26.87	39.38

Date of Run	Charge	Operating Conditions	Catalyst	% Recovery			% Loss
				Distillate	Gas	Residue	
2/11-13/80	fatty acids	345°C 200 psig	1% $FeCl_3$	65.05	11.22	10.14	13.59
3/3-5/80	fatty acids	345°C 200 psig	1% $FeCl_3$	57.52	10.70	12.63	19.15
3/25-27/80	fatty acids	345°C 200 psig	5% $FeCl_3$	54.64	11.76	11.12	22.58
3/28-4/1/80	fatty acids	345°C 200 psig	5% $FeCl_3$	53.79	11.95	9.75	24.51
5/12-15/80	fatty acids	345°C 200 psig	10% $FeCl_3$	51.56	12.97	8.80	26.67
2/25-27/80	fatty acids	345°C 200 psig	19 lava (unreactivated)	44.67	12.47	32.90	9.96
3/10-12/80	fatty acids	345°C 200 psig	1% lava (reactivated)	46.79	9.63	27.24	16.34
3/30-24/80	fatty acids	345°C 200 psig	1% lava (reactivated)	39.02	10.45	38.77	11.76
4/16-22/80	fatty acids	345°C 200 psig	5% lava (reactivated)	49.90	11.54	25.62	12.94
4/25-29/80	fatty acids	345°C 200 psig	5% lava (reactivated)	51.16	10.30	19.42	19.12
4/30-5/80	fatty acids	345°C 200 psig	10% lava (reactivated)	44.75	11.32	2	22.47
5/7-9/80	fatty acids	345°C 200 psig	10% lava (reactivated)	41.62	11.20	23.04	24.14

NOTE: Percentage computed here are based on weight.

TABLE 10. Simple Distillation of the Distillate* Products into Various Fractions

Run Number	*Catalyst*	*Percentage of Fractions (Volume %)*					*Residue*
		C_5 0-50°C	C_6 50-80°C	C_7 80-110°C	C_8 110-140°C	C_9 160-185°C	
11-2729-79 NC	None	34.90	0.20	13.30	35.40	—	16.20
12-1214-79 A1	Al_2O_3, 1%	10.11	0.54	37.27	40.13	3.71	8.24
1-1416-80 A5	Al_2O_3, 5%	14.55	0.80	42.95	25.95	—	15.75
3-1719-80 A10	Al_2O_3, 10%	15.60	0.30	29.30	29.00	—	25.80
5-1620-80 AC1	$AlCl_3$, 1%	7.70	8.00	61.60	12.00	—	10.70
5-2830-80 AC5	$AlCl_3$, 5%	2.22	11.33	55.56	19.33	—	11.56
3-35-80 FC1	$FeCl_3$, 1%	11.10	17.65	42.75	17.65	—	10.85
3-2527-80 FC5	$FeCl_3$, 5%	18.20	19.80	40.90	12.10	—	9.00
4-79-80 FC10	$FeCl_3$, 10%	37.59	3.80	45.19	2.28	—	11.14
3-1012-80 LA1	Lava, 1%	10.91	6.57	55.11	10.35	7.97	9.09
4-2529-80 LA5	Lava, 5%	2.60	6.50	41.60	30.90	—	18.40
5-79-80 LA10	Lava, 10%	4.00	11.30	65.80	9.50	—	9.40

*Distillate product refers to the liquid product of the pyrolysis of coconut oil fatty acids.

TABLE 11. Effect of Catalyst on Hexane and Heptane Yields.

Catalyst			*Hexane Yield*			*Heptane Yield*		
Type	%	*Distillate, ml*	*ml*	*% in distillate*	*% in orig. charge*	*ml*	*% in distillate*	*% in orig. charge*
None	—	318	0.10	0.033	0.023	0.65	0.20	0.14
Al_2O_3	1	176	0.15	0.09	0.03	0.99	0.56	0.22
$AlCl_3$	1	232	2.15	0.93	0.48	7.10	3.06	1.58
$FeCl_3$	1	302	5.94	1.97	1.32	17.35	5.75	3.86
Lava	1	235	1.80	0.77	0.40	6.03	2.57	1.34
Al_2O_3	5	224	0.28	0.13	0.05	1.58	0.71	0.35
$AlCl_3$	5	154	1.98	1.29	0.44	6.15	3.99	1.37
$FeCl_3$	5	291	6.40	2.20	1.42	18.53	6.37	4.12
Lava	5	254	1.90	0.75	0.42	6.09	2.40	1.35
Al_2O_3	10	134	0.07	0.05	0.02	0.55	0.41	0.12
$FeCl_3$	10	278	1.26	0.45	0.28	4.52	1.63	1.00
Lava	10	212	2.73	1.29	0.61	8.68	4.09	1.93

NOTE: The original fatty acid charge is 450 ml for all runs.

TABLE 12. Pyrolysis of Pure Lauric Acid: Effect of Reaction Time on Product Distribution

Run Number	Lauric Acid Used (g)	Reaction Time (hrs)	Products: Gas (ml)	Products: Distillate (g)	Products: Residue (g)
7-9-80C12-5	50	5	11,113	13.60	18.60
7-18-80C12-7	50	7	11,585	20.10	11.09
7-1415-80C12-10	50	10	13,034	24.50	8.90

NOTE: The catalyst that was used in all the runs reported here was 5% $FeCl_3$.

TABLE 13. Pyrolysis of Pure Lauric Acid: Effect of Reaction Time on Composition of the Gaseous Product Formed

Run Number	Reaction Time (hrs)	Orsat Analysis: CO_2	Orsat Analysis: O_2	Orsat Analysis: CO	Orsat Analysis: CH_4	Orsat Analysis: H_2
7-9-80C12-5	5	8.50	2.69	19.16	3.53	0.28
7-18-80C12-7	7	9.60	4.00	22.80	2.60	2.70
7-1415-80C12-10	10	6.31	4.20	10.61	10.46	8.74

TABLE 14. Pyrolysis of Pure Lauric Acid: Effect of Reaction Time on Hexane and Heptane Yields

Reaction Time (hrs)	Percentage Yield (Volume)			
	Hexane		Heptane	
	in Distillate	in Original Charge	in Distillate	in Original Charge
5	0.089	0.02	1.21	0.29
7	1.01	0.35	2.54	0.89
10	1.33	0.57	2.53	1.08

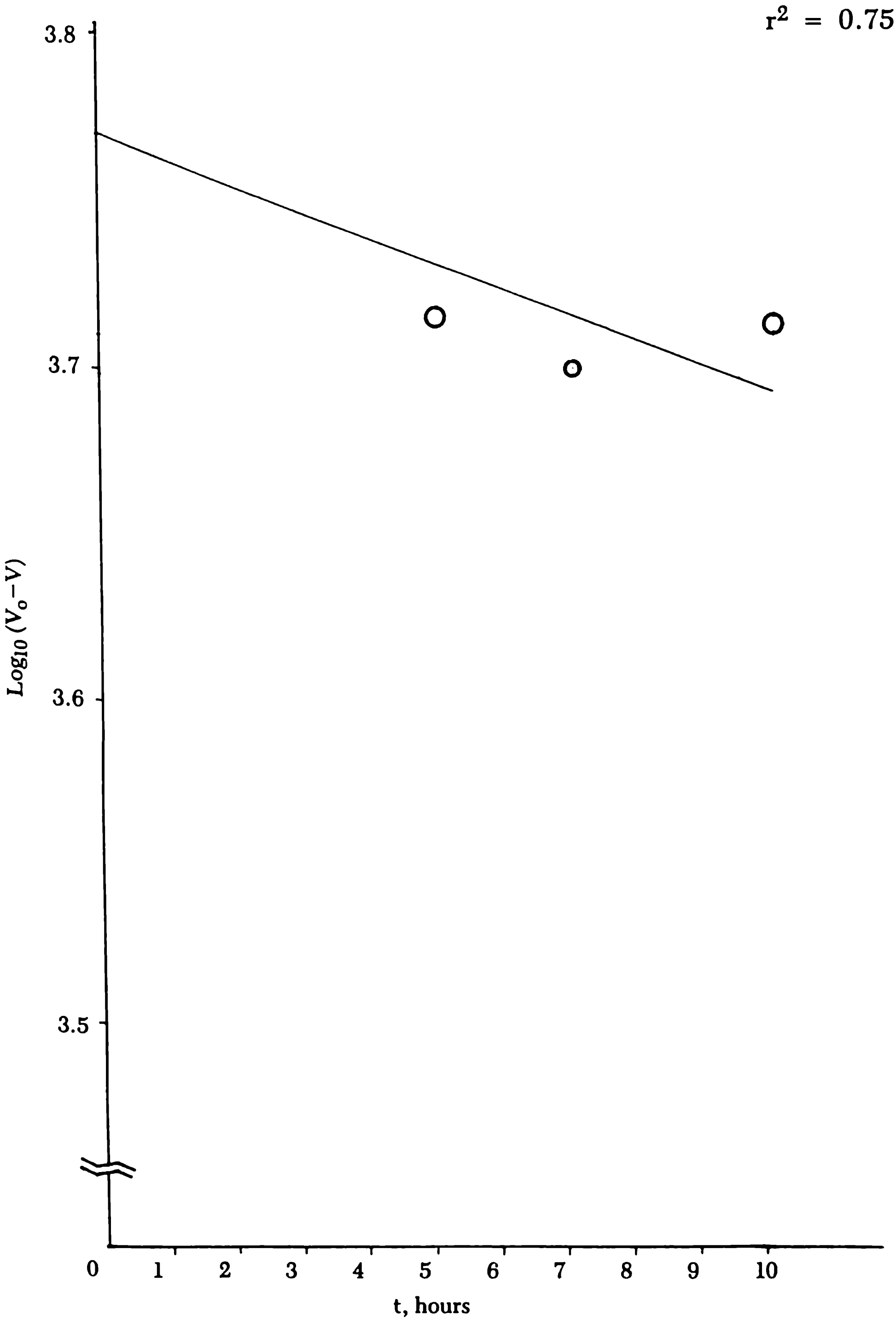


FIGURE 2. Plot of Log_{10} (V_o−V) vs t for the Decomposition of Lauric Acid ($RCOOH \longrightarrow RH + CO_2$)

Discussion of Results

A summary of this whole study is presented in Table 7. This table shows the quantities of products that were obtained in each run as well as the operating conditions and other pertinent data. The operating pressure and temperature that were used during the experimental runs were the maximum that the equipment could withstand—345°C is the maximum temperature at which the reactor should be operated while 200 psig is the maximum pressure at which the maximum temperature will not be exceeded.

The four catalysts that were used are either (1) a component of kaolin or bentonite which, according to the literature survey, gave good hydrocarbon yields when used in the pyrolysis of animal or vegetable oils, (2) good catalysts and have been used in industrial cracking operations or (3) simply being tested to determine their catalytic activity.

Of the four catalysts that were used in this study, the best catalyst is $FeCl_3$ as shown in Table 7. $FeCl_3$ gave the largest amount of gaseous product which served as a measure of the extent of conversion of the oil into hydrocarbons. The main components of this gaseous product were CO_2 and CO as reflected in Table 8. These gases were produced by hydrocarbon-forming reactions as will be seen later.

In Table 9 are presented the percentage distribution of the different types of products that were obtained during the experiment. The high percentage of losses that are likewise shown in this table were due to improper handling, inaccurate measuring devices and leaks that were not detected.

Table 10 shows the various fractions of the distillates that were obtained in the different runs. The values reported in this table were the results of the simple distillation of the distillates products. The chromatographic analyses of the same products are presented in Table 11 which gives the hexane and heptane yields of each run. From this table, we easily see that the best runs in terms of distillate yield were those which made use of no catalyst and $FeCl_3$ as catalyst. However, in terms of solvent yield—hexane and heptane—the best runs were those which made use of $FeCl_3$ as catalyst.

The results of the pyrolysis of pure lauric acid are presented in Tables 12 and 13. $FeCl_3$ (5%) was used as catalyst because it had the highest mean rank as will be shown later in the statistical analysis portion of this study. However, its high mean rank does not mean it was the best concentration since it will also be revealed by the analysis, any of the concentrations that were used would have yielded the same results.

The summary of the experimental runs using pure lauric acid is given in Table 12 while the analyses of the gaseous and liquid products are presented in Tables 13 and 14, respectively. The amounts of hexane and heptane that are reported in Table 14 were determined by graphically integrating the curves of the chromatographs corresponding to the different hydrocarbons present in the distillate and then computing for the amounts of these solvents.

In all the runs, the residue that was left in the reactor was either a dark solid or a thick brown-to-black liquid. No analysis were made to determine the composition of these tar-like substances which according to Grant (1969) is a mixture of hydrocarbons and their derivatives.

Effect of Catalyst Type and Catalyst Concentration

The effect of the type of catalyst and catalyst concentration on the distillate yield was analyzed using the method found in Kempthorne (1952) which is a 2-way classification with unequal numbers and no interaction. The analysis of variance (Anova) table (Table 15) which is shown on the next page indicates that the amount of catalyst that was used has no effect on the distillate yield while the type of catalyst affects the distillate yield significantly.

Further analysis of the data using Duncan's (1955) method is presented in Tables 16 and 17. The catalyst concentrations which were well within the catalyst concentration ranges encountered in the available literature—turned out to be really not significantly different from each other (Table 16). There was no way by which higher concentrations could have been tested due to a major and crucial constraint—insufficiency of funds, both project and personal. It is expected that catalyst concentration should amount to about 86% of the charge inasmuch as according to Gates, et al. (1979) or Unzelman and Wolf (1967), the catalyst-oil ratio in commercial catalytic cracking processes, which were similar to the process described here, is about 6/1.

Through Duncan's (1955) multiple range test, the best catalyst was identified to be $FeCl_3$. This substance was significantly different from the other three which were not significantly different from one another.

$FeCl_3$ was the best catalyst because of its acidic properties. It should be noted that catalytic cracking requires acidic substances as catalyst. The insignificance of $AlCl_3$ was unexpected since according to *Condon* (1958), together with $FeCl_3$, it belongs to a group called acidic halides. This result could be due to lack of replication. Statistically, unreplicated results may result in a higher percentage of error than replicated ones. The replicate for $AlCl_3$ was discarded because of a very large deviation from the trend result. Again, here no further run was possible due to budgetary constraints.

The lava that was used in this study contains significant amounts of SiO_2 (57.17%) and Al_2O_3 (23.24%), the components of commercial cracking catalysts. This is very clear from Table 13. SiO_2 and Al_2O_3 are both acidic and in fact belong to the classification acid chalcides. However, *Gates, et al.* (1979) pointed out that their mere mechanical mixture is not an active cracking catalyst—a possible explanation for its poor performances.

Al_2O_3 gave the lowest ranking mean because, even though it is acidic, *Gates, et al* (1979) mentioned that it deactivates easily. Thus, only a small amount of carbonium ions may have been formed during the process which consequently resulted in very low solvent yields.

TABLE 15. Effect of Catalyst Type and Catalyst Concentration on Distillate Yields Analysis of Variance *(ANOVA)*

		Sum of Squares	*Mean Squares*	*Computed F*	*F* *O.95*
Blocks Ignoring Treatments	2	5,579.84	2,789.92	2.0016	F(2,14) = 3.74
Treatments Eliminating Blocks	3	41,573.35	13,857.78	9.9422	F(3,14) = 3.34
Error	14	19,513.81	1,393.84		
Total	19	66,667			

NOTE: Blocks refer to catalyst concentration while treatments refer to catalyst type.

TABLE 16. Multiple Range Test of the Distillate Yields—Computed Data

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A. Catalyst Concentration Means Ranked in Order

10%	1%	5%
196.2	223.75	239.86

B. Catalyst Type Means Ranked in Order

$AlCl_3$	Al_2O_3	Lava	$FeCl_3$
175.0	176.17	228.83	299.0

C. Standard Errors

1. Catalyst Concentration Mean

$$S_m = \sqrt{\frac{MSE}{df\ (\text{catalyst concentration})}}$$

$$= \sqrt{\frac{1393.84}{2}} = 26.399\ (n_2 = 14)$$

2. Catalyst Type Mean

$$S_m = \sqrt{\frac{MSE}{df\ (\text{catalyst type})}}$$

$$= \sqrt{\frac{1393.84}{3}} = 21.555\ (n_2 = 14)$$

TABLE 17. Multiple Range Test of Distillate Yields Results (at 5% level)

A. Shortest Significant Ranges:

1. Catalyst Concentration	(2)	(3)
Significant Studentized Ranges:	3.03	3.18
Shortest Significant Range (Rp):	79.989	83.949

2. Catalyst Type

Sample Size (p)	(2)	(3)	(4)
Significant Studentized Range:	3.03	3.18	3.27
Shortest Significant Range (Rp)	65.312	68.545	70.485

B. Results

1. Catalyst Concentrations

Concentrations	10%	1%	5%
Means	196.2	223.75	239.86

2. Catalyst Types

Types	$AlCl_3$	Al_2O_3	Lava	$FeCl_3$
Means	175.0	176.17	238.83	299.0

NOTE: Any two means not underscored by the same line are significantly different.
Any two means underscored by the same line are not significantly different.

TABLE 18. Chemical Analysis of Lava
(weight percent, dry basis)

Component	*Percentage*
SiO_2	57.17
FeO	3.44
Fe_2O_3	2.87
Al_2O_3	23.24
TiO_2	1.29
P_2O_5	nil
CaO	10.18
MnO	3.22
MgO	3.22
MnO	0.01
Na_2O	3.26
K_2O	1.19
S	0.52
H_2O + 110°C	— 0 —
H_2O — 110°C	0.0

Source: Commission on Volcanology
Sample No. CVS—80-8

Thus, only a small amount of carbonium ions may have been formed during the process which consequently resulted in very low solvent yields.

Mechanism of Hexane and Heptane Formation

The pyrolytic conversion of coconut oil fatty acids into hexane and/or heptane involves a two-step process:

a. formation of hydrocarbon from the fatty acids and
b. catalytic cracking of the resulting hydrocarbons.

Formation of Hydrocarbons. Hydrocarbons can be obtained from fatty acids by subjecting the latter to high temperatures, usually 450-500°C. The transformation is effected via two routes: direct decarboxylation which results in paraffins and formation of a ketene intermediate which further decomposes into alkenes. Direct decarboxylation, the first route, explains the CO_2 component of the gaseous products produced during the reaction while the second route, the decomposition of the ketene intermediate accounts for the CO component (see Table 8). The reactions involved are:

General

$$C_nH_{2n+1}\,COOH \longrightarrow CO_2 + C_nH_{2n+2} \qquad (6.1)$$

$$2\,C_nH_{2n+1}\,COOH \longrightarrow 2\,CO + 2H_2O + C_{2n}H_{4n} \qquad (6.2)$$

These general equations, when applied to lauric acid, the main fatty acid component of coconut oil, yield:

$$C_{11}H_{23}\,COOH \longrightarrow CO_2 + C_{11}N_{24} \qquad (6.1.1)$$

$$2\,C_{11}H_{23}\,COOH \longrightarrow 2CO + 2H_2O +$$

$$CH_3(CH_2)_9CH = CH(CH_2)_9CH_3 \qquad (6.2.1)$$

The H_2 and CH_4 components of the gaseous products are explained by the catalytic cracking of the resulting hydrocarbons. This will be shown later.

The feasibility of these reactions can be easily established by determining the free energy equation for each reaction and then computing for their free energies at the reaction temperature. The free energy equations are conveniently derived by using the method proposed by *Bruins and Czarnecki* (1941):

a. For C_nH_{2n+1} COOH $CO_2 + C_nH_{2n+2}$

$$\Delta F^\circ = \Delta F^\circ_{CO_2} + \Delta F^\circ_{CO_nH_{2n+2}} - \Delta F^\circ_{C_nH_{2n+1}}\,COOH \qquad (6.3)$$

$$\Delta F^\circ = \Delta F^\circ_{CO_2} \left[(n-1)\,\Delta F_{C-C} + (2n+2)\,\Delta F^\circ_{C-N}\right]$$

$$- \left[(N-1)\,\Delta F^\circ_{C-C} + (2n+1)\,\Delta F^\circ_{C-H} + \right.$$

$$\left. \Delta F^\circ_{C} -COOH \right] \qquad (6.4)$$

$$\Delta F^\circ = \Delta F^\circ_{CO_2} + \Delta F^\circ_{C-H} - \Delta F^\circ_{C-COOH} \qquad (6.5)$$

$\Delta F^\circ_{CO_2}$ can be determined using the method presented by *Smith* and *Van Ness* (1959) while $\Delta F^\circ_{C-H}$and ΔF°_{C-COOH} are given by *Bruine* and *Czarnecki* (1941):

$$\Delta F^\circ_{CO_2} = -94{,}372 - 0.066\,T\ln T - 3.647 \times 10^{-3}\,T^2 + 0.437 \times 10^{-6}\,T^3 + 1.8T \quad (6.6)$$

$$\Delta F^\circ_{C-H} = -3{,}344.5 + 2.97\,T\ln T - 0.0023\,T^2 + 0.01688 \times 10^{-6}\,T^3 - 13.68\,T \quad (6.7)$$

$$\Delta F^\circ_{C-COOH} = -89{,}867 + 6.29\,T\ln T - 0068\,T^2 - 0.0656 \times 10^{-6}\,T^3 - 7.37\,T \quad (6.8)$$

Substituting these expressions into equation 6.5, we have the following free energy equation for the reaction:

$$\Delta F^\circ = -7.849.5 - 3.386\,T\ln T - 8.53 \times 10^{-4}\,T^2 + 0.519 \times 10^{-6}\,T^3 - 4.51\,T \quad (6.9)$$

b. For $2C_nH_{2n+1}COOH \quad 2CO + 2H_2O + C_{2n}H_{4n}$

$$\Delta F^\circ = 2\Delta F^\circ_{CO} + 2\Delta F^\circ_{H_2O} + \Delta F^\circ_{C_{2n}H_{4n}} - 2\Delta F^\circ_{C_nH_{2n+1}}COOH \quad (6.10)$$

$$\Delta F^\circ = 2\Delta F^\circ_{CO} + 2\Delta F^\circ_{H_2O} + [(2n-2)\,\Delta F^\circ_{C-C} + 4n\Delta F^\circ_{C-H} + \Delta F^\circ_{C=C}] - 2\,[\Delta F^\circ_{C-COOH} + (n-1)\,\Delta F^\circ_{C-C} + (2n+1)\,\Delta F^\circ_{C-H}] \quad (6.11)$$

$$\Delta F^\circ = 2\Delta F^\circ_{CO} + 2\Delta F^\circ_{H_2O} + \Delta F^\circ_{C=C} - 2\Delta F^\circ_{C-COOH} - \Delta F^\circ_{C-H} \quad (6.12)$$

Again, ΔF°_{CO} and $\Delta F^\circ_{H_2O}$ are derived using the method of *Smith* and *Van Ness* (1959) while $\Delta F^\circ_{C=C}$, ΔF°_{C-H} and ΔF°_{C-COOH} are taken from *Bruins* and *Czarnecki* (1941):

$$2\Delta F^\circ_{CO} = -54{,}840 - 6.692\,T \ln T - 0.114 \times 10^{-3}\,T^2 - 0.088 \times 10^{-6}\,T^3 + 2.009\,T \qquad (6.13)$$

$$2\Delta F^\circ_{H_2O} = 118{,}168 - 8.364\,T \ln T - 0.747 \times 10^{-3}\,T^2 - 0.248 \times 10^{-6}\,T^3 + 77.78\,T \qquad (6.14)$$

$$\Delta F^\circ_{C=C} = 28{,}000 + 2.75\,T \ln T - 0.00014\,T^2 - 0.0680 \times 10^{-6} T^3 - 24.86\,T \qquad (6.15)$$

$$2\Delta F^\circ_{C-H} = -6689 + 5.94\,T \ln T - 0.0046\,T^2 + 0.03376 \times 10^{-6}\,T^3 - 27.36\,T \qquad (6.16)$$

$$2\Delta F^\circ_{C-COOH} = -179{,}734 + 12.58\,T \ln T - 0.0136\,T^2 - 0.1312 \times 10^{-6}\,T^3 - 14.74\,T \qquad (6.17)$$

The resulting equation after these expressions are substituted for the terms in equation 6.12 is:

$$\Delta F^\circ = 41{,}439 - 30.826\,T \ln T + 0.016\,T^2 - 0.307 \times 10^{-6}\,T^3 + 97.029\,T \qquad (6.18)$$

Solving for the free energies of the two hydrocarbon-forming routes, we get at T = 618°K (345°C), the pyrolysis temperatures; the following:

a) direct decarboxylation route

$\Delta F^\circ_{618} = -24{,}288$ calories

b) ketene-intermediate route

$\Delta F^\circ_{618} = -14{,}986$ calories

These high negative values are clear indications of the feasibility of the hydrocarbon-forming reactions at 618°K (345°C).

Reaction Order. The order of each of the two hydrocarbon-forming reactions can be determined by applying the method presented by *Prutton* and *Marron* (1965) or *Stevens* (1971), using pure lauric acid as the starting material.

This equation can be rearranged to yield the following equation of a line:

$$\log (V_o - V) = -\frac{k_1 t}{2.303} + \log V_o \tag{6.20}$$

which corresponds to the general form:

$$y = mx + b$$

Equation 6.20 shows that a linear plot of log $(V_o - V)$ vs. t will indicate that the reaction is first order. Since the graph in Figure 2 is linear and this linearity is supported by the coefficient of determination r^2 in Table 20, it means that the direct-decarboxylation route is a first-order reaction. However, it is recommended that further studies be conducted to confirm this finding since only 3 data points were used. It was not possible to measure V more than three times as was done in this study because of insufficient funds and lack of adequate supply of pure lauric acid.

The specific reaction rate constant for this reaction can be computed using the information from the graph or the regression coefficient in Table 20 in combination with Equation 6.20.

Using the appropriate data, we get:

$$k_1 = -2.303 \text{ (slope)}$$

$$k_1 = -2.303\ (-0.01)$$

$$k_1 = 0.02303 \text{ hr}^{-1} \text{ or } 1.382 \text{ min}^{-1}$$

This is a rather significant value and leads to the conclusion that the direct decarboxylation route is a fast reaction.

Ketene-intermediate route. Since CO also comes only from pure lauric acid, the procedure for computing for V_0 and V for this reaction is the same as that for the direct-decarboxylation route.

The regression analysis of the data for this route indicates that the reaction is not first-order since the coefficient of determination, r^2, is not significant (Table 20). An attempt was made to determine the actual order of this route using the procedure suggested by Walas (1959) but to no avail. The results of the regression analyses which are given in Table 21 were likewise not satisfactory. This means that the ketene-intermediate route involves a complex reaction which is actually the case since it is a 2-step and not a single step reaction.

Direct-Decarboxylation Route — Since the carbon dioxide (CO_2) comes only from pure lauric acid, the volume of this gas can be used as a measure of the decrease in the concentration of the starting material.

The course of this reaction was followed by measuring in a water-displacement set-up the volume of the gaseous product formed and then determining the volume V of its CO_2 component at various time intervals by Orsat analysis. To complete the desired data, the initial concentration V_0 expressed as milliliters of CO_2.was calculated from the amount of pure lauric acid originally present. The data are presented in Table 19 and the corresponding graph is shown in Figure 2. This graph was based on the repression coefficients (Table 20) that were obtained using the curve-fitting program of a scientific programmable calculator. It was arrived at by applying the equation for first-order reactions expressed in terms of V and V_0:

$$k_1 \, t = 2.303 \log 10 \frac{V_0}{V_0 - V} \qquad (6.19)$$

TABLE 19. Required Data for the Determination of the Order of Hydrocarbon-Forming Reactions*

	Carbon Dioxide (CO_2)			*Carbon Monoxide*		
Time, hrs	*V*	*V_0-V*	*$\log(V_0-V)$*	*V*	*V_0-V*	*$\log(V_0-V)$*
5	2129.25	5159.08	3.713	944.61	3,974.44	3.599
7	2641.38	4991.53	3.698	1,112.16	3,462.31	3.539
10	1444.03	5128.07	3.710	975.62	4,659.66	3.668

*The hydrocarbon-forming reactions are (1) direct decarboxylation of the fatty acid and (2) formation of a ketone-intermediate that yields alkenes.

TABLE 20. Regression Coefficients for the Hydrocarbon-Forming Reactions

Coefficient/Gas	*Carbon Dioxide (CO_2)*	*Carbon Monoxide (CO)*
r^2	0.75	0.37
a	3.77	3.73
b	−0.01	−0.015

NOTE: Coefficient a is the intercept while b is the slope. This is based on the equation $\log (V_0 - V) = -\frac{kt}{2.303} + \log V_0$.

TABLE 21. Hydrocarbon-Forming Ketene Intermediate Route: Determination of Order

Reaction Time	*Values of* $(\frac{1}{V_o - V})^{n-1}$ for various N'S								
	0.1	*0.2*	*0.4*	*0.8*	*1.1*	*1.2*	*1.4*	*1.6*	*1.8*
5	1735.20	757.57	144.40	5.25	0.437	0.191	0.036	0.007	0.001
7	1532.60	678.41	132.93	5.10	0.443	0.196	0.038	0.008	0.001
10	2002.25	860.37	158.86	5.42	0.430	0.185	0.034	0.006	0.001
Regression Coefficients*	Regression Results for Various Values of N								
r^2	0.532	0.428	0.420	0.406	0.391	0.387	0.379	0.370	0.362
r^2	0.432	0.428	0.420	0.406	0.391	0.387	0.379	0.370	0.362
a	1305.29	591.46	120.86	4.97	0.448	0.201	0.040	0.008	0.002
b	61.55	23.73	3.35	0.04	−0.0016	−0.0014	−0.0005	−0.0001	−0.00004

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* According to Walas, a plot of $(\frac{1}{V_o - V})^{n-1}$ vs. time using the correct value of n, the reaction order, should be linear.

Formation of Solvents. From equations 6.1.1 and 6.2.1, the hydrocarbons that are formed initially from pure lauric acid are $C_{11}H_{24}$ and $CH_3(CH_2)_9CH = CH(CH_2)_9CH_3$. Catalytic cracking proceeds as follows:

Step 1: Formation of Carbonium Ions

Haensel (1951) indicated that the initial step of catalytic cracking is the formation of the carbon-catalyst linkage which essentially involves the simultaneous loss of the hydride ion (H:) from the paraffin molecule and of a proton from the acidic catalyst surface. This produces a carbonium ion in combination with the acid anion and molecular hydrogen:

$$C_{11}C_{24} + H^+A^- \longrightarrow CH_3(CH_2)_8\,\underset{+}{C}H\,CH_3 + A^- + H_2 \qquad (6.21)$$

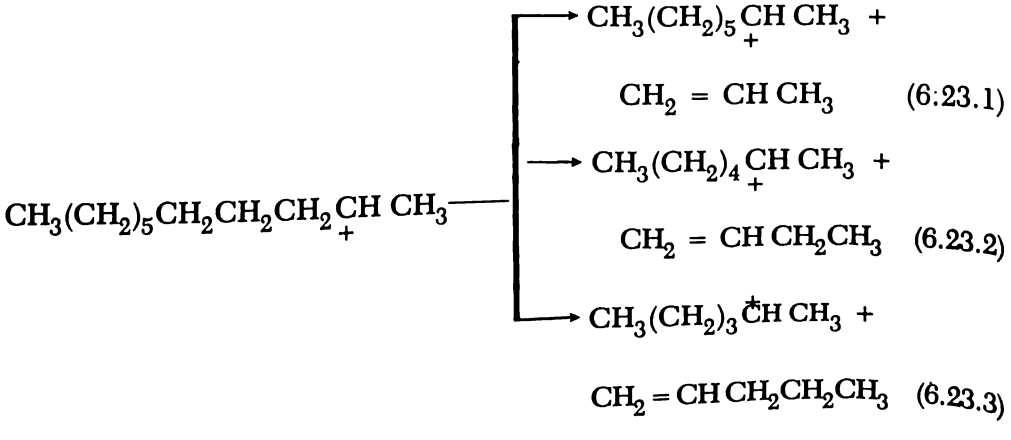
An alternative possibility is the formation of the carbonium ion from the reaction of the olefin with the proton from the catalyst:

$$CH_3(CH_2)_9CH = CH(CH_2)_9CH_3 + H^+A^- \longrightarrow CH_3(CH_2)_9CH{-}\underset{+}{C}H_2(CH_2)_9CH_3 \qquad (6.22)$$

The second reaction (6.22) is more favored to occur since the cracking of olefins occurs at considerably lower temperatures than that of paraffins.

Step 2: β-cracking of Carbonium Ions

Shirley (1964) pointed out that the tendency of β cleavages of carbonium ions is in line with the weakening of this particular bond by hyperconjugation with the carbonium ion center. The bond of the β-hydrogen atom to its carbon atom is likewise weakened favoring the following type of reaction which leads to olefins to occur frequently:



$$CH_3(CH_2)_5CH_2CH_2CH_2\underset{+}{C}H\,CH_3 \longrightarrow CH_3(CH_2)_5\underset{+}{C}H\,CH_3 + CH_2 = CH\,CH_3 \qquad (6:23.1)$$

$$\longrightarrow CH_3(CH_2)_4\underset{+}{C}H\,CH_3 + CH_2 = CH\,CH_2CH_3 \qquad (6.23.2)$$

$$\longrightarrow CH_3(CH_2)_3\overset{+}{C}H\,CH_3 + CH_2 = CH\,CH_2CH_2CH_3 \qquad (6.23.3)$$

$$CH_3(CH_2)_9\underset{+}{C}H_2-CH(CH_2)_9CH_3 \longrightarrow CH_3(CH_2)_7\underset{+}{C}H\,CH_3 + CH_2 = CH(CH_2)_9CH_3 \qquad (6.24)$$

$$CH_3(CH_2)_7\underset{+}{C}H\,CH_3 \longrightarrow CH_3(CH_2)_4\underset{+}{C}HCH_3 + CH_2 = CHCH_3 \qquad (6.25.1)$$

$$CH_3(CH_2)_7\underset{+}{C}H\,CH_3 \longrightarrow CH_3(CH_2)_3\underset{+}{C}HCH_3 + CH_2 = CHCH_2CH_3 \qquad (6.25.2)$$

The above reactions illustrate the possible products that may result from the carbonium ions formed from the starting hydrocarbon materials.

Step 3: Termination/Propagation Step

a. Any one of the carbonium ions formed in Step 2 can remove a hydride ion from a neutral molecule.

$$CH_3(CH_2)_4\underset{+}{C}HCH_3 + C_{11}H_{24} \longrightarrow C_7H_{16} + C_{11}H_{23}^{+} \qquad (6.26)$$

$$CH_3(CH_2)_3\,{}_{+}\,CH\,CH_3 + C_{11}H_{23} \longrightarrow C_6H_{14} + C_{11}H_{23}^{+} \qquad (6.27)$$

b. Any one of the carbonium ions can donate a proton to a base or an olefin and thus be converted to an olefin:

$$CH_3(CH_2)_4\ \underset{+}{C}H\,CH_3 + A^- \longrightarrow CH_3(CH_2)_4CH = CH_2 + HA \qquad (6.28)$$

$$CH_3(CH_2)_4\ \underset{+}{C}H\,CH_3 + CH_2 = CH(CH_2)_9CH_3 \longrightarrow CH_3(CH_2)_4\,CH = CH_2 + CH_3\underset{+}{C}H\,(CH_2)_9CH_3 \qquad (6.29)$$

The mechanism presented above shows that a myriad of hydrocarbons of various chain lengths can be formed from the hydrocarbons produced from pure lauric acid. This is a satisfactory explanation of the different hydrocarbon peaks that appeared in the chromatographs of the distillate products but it does not explain why only a small amount of hexane and heptane were obtained.

Reason for low solvent yields. The chromatographs in Appendix D indicate that hexane and heptane were the shortest-chain hydrocarbons that were produced in significant quantities in this study, while Table 14 gives the amounts of these solvent—that were obtained. The low yields can easily be traced to the temperature (345°C) at which the reaction was carried out. It should be recalled that *Shirley* (1964) stated that catalytic cracking reactions are usually carried out in the range of 450-500°C. Because of the lower temperature that was used, hydrogen transfer became more rapid relative to cracking presumably because of the higher activation energy that was required for cracking. This phenomenon, according to *Gates, et al.* (1979), results in a shift of the product distribution to higher molecular weight:

(1) because of increased hydride ion abstraction by the carbonium ions, converting them to paraffins,

(2) because of H_2 transfer to α-olefins rather than cracking them.

This likewise explains the presence of very little short-chain hydrocarbons in the gaseous product and in the distillate. The higher-molecular-weight ($>C_7$) components of the distillate were not identified because of the inavailability of standards. Only standards for hexane and heptane, the object of this study were available when the analyses were made. The NSRC, PAEC, UP Chemistry laboratory and PCA all did not have the standards needed for identifying the other components of the distillate. It is very possible that the other fractions are likewise saturated, with very little or no unsaturated hydrocarbons despite the fact that alkenes are favored 2 to 1 in cracking as can be deduced from equations 3.11 and 3.12. This can be attributed to the increased H_2 transfer arising from a low cracking temperature and to the long reaction time which allows additional time for H_2 transfer; points raised by *Gates, et. al.* (1979) to explain why product distributions deviate from that predicted by equations 3.11 and 3.12.

Conclusions and Recommendations

The technical feasibility of producing industrial solvents—hexane and heptane—from coconut oil fatty acids has been established. The use of subtances heptane—from coconut oil fatty acids has been established. The use of substances that can act as catalysts increased the solvent yields as expected. Four substances, viz. $FeCl_3$, $AlCl_3$, Al_2O_3 and lava were tried and of these, $FeCl_3$ came out to be the best catalyst. The good performance of $FeCl_3$ can be traced to its acidic nature which is a necessary condition in the mechanism involved in converting fatty acids to industrial solvents.

Hexane and/or heptane can be formed from coconut oil fatty acids via a two-step process:

(1) formation of hydrocarbons (paraffins) by direct decarboxylation of the fatty acids or formation of a ketene intermediate which readily decomposes into hydrocarbons (olefins), CO and H_2O, and

(2) catalytic cracking of the resulting hydrocarbons.

The hydrocarbon-forming reactions readily explain the production of CO_2 and CO during the reaction while the catalytic cracking step accounts for the H_2 and CH_4. Methane, according to *Greensfelder, et. al.* (1949) is probably formed by a less favored type of cracking. The catalytic cracking step is probably the rate-determining step for the whole process. This conclusion is based on the very high value of the specific reaction rate constant for the hydrocarbon-forming step that was obtained in this study and on the mechanism involved in catalytic cracking. *Voge* (1956) mentioned that since carbonium ions are very reactive, the rate of formation of the said ions is the slow step.

The catalyst concentration that were used in this study had no effect on the distillate yield. This could be easily explained by the fact that the concentrations that were used were within the same range. In future studies, therefore, higher concentrations, perhaps amounting to about 86% of the charge which is the concentration being used in commercial cracking operations, should be tried.

If the whole process described here will be studied further in the future, the suggestions given by *Unzelman* and *Wolf* (1967) for increasing the cracking of hydrocarbonic materials may be adopted in order to increase the solvent yield:

(1) increase the reaction temperature
The optimum temperature for catalytic cracking processes is 450°C. However, because of the equipment's limitations, only a temperature of 345°C was used, resulting in limited cracking of the hydrocarbons that were formed during the process and consequently giving very small solvent yields. By using a higher temperature (450°C), significant cracking is expected and thus higher solvent yields may be obtained.

(2) increase the pressure
Mandlecar, et. al. (1946-1947) reported that an increase in pressure during the cracking of vegetable oils results in a decrease in the diesel fuel content of the product. This means that the diesel fuel (C_{12} and higher) and any medium-chain hydrocarbon for that matter cracks further when the pressure is increased.

(3) lower the space velocity or increase the catalyst-to-feed ratio.
These measures are equivalent since space velocity in cracking refers to the weight or volume of feed charged per hour per weight or volume of catalyst in the reaction zone. Higher concentrations of catalyst favors cracking since more protons are made available for the formation of carbonium ions. Higher catalyst concentrations were not tried in this study because of limitations on resource availability.

All the suggestions presented above if adopted alone or in combination with one another are expected to simplify the process by shortening the reaction time since cracking will be enhanced.

In case piloting of the process is being planned, it is suggested that a fluidized bed reactor be used in lieu of the present batch reactor. *Rase* (1977) pointed out that the former type of reactor is more suitable for catalytic cracking reactions which demand the movement of large amounts of solids—the catalyst. Also, the material of construction should be such that it can resist the strong corrosive effects of fatty acids at high temperature and pressures. *Sassoli* (1977) has recommended the use of ASTM A-240 TP 316 instead of the ordinary SS 316 for high temperature and high pressure processes involving fatty acids.

Furthermore, it is likewise suggested that the analyses of the other components of the distillate be made, one thing that we failed to do in this study because of the lack of standards. Based on the mechanism of catalytic cracking, other hydrocarbons like octane, nonane and decane may be formed during the process. If these other hydrocarbons are detected, coconut oil may become a major economic energy source since it can serve as a source not only of solvents but also of motor fuels which are becoming more and more expensive.

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Annex I

Determination of the Free Energy Expressions for CO_2, CO and H_2O.

GAS	α	$\beta \times 10^3$	$\gamma \times 10^6$	$\Delta H_f^\circ(298°C)$	$\Delta F^\circ_{298°}$
CO	6.42	1.665	−0.196	−26,416	−32,808
CO_1	6.214	10.396	−3.545	−94,052	−94,260
O_2	6.148	3.102	−0.923	0.0	0.0
H_2O	7.256	2.298	0.283	−57,798	−54,635

The procedure that is described here is the one presented in Smith and Van Ness. It involves the use of the following equations:

$$\Delta H^\circ = \Delta H_0 + \Delta\alpha T + \frac{\Delta\beta}{2}T^2 + \frac{\Delta\gamma T^3}{3} \qquad (1)$$

$$\Delta F^\circ = \Delta H_0 - \Delta\alpha T - \frac{\Delta\beta}{2}T^2 - \frac{\Delta\gamma T^3}{6} - IT \qquad (2)$$

Using CO as an example, the procedure is illustrated below:

1. Determination of ΔH_0 using equation (1). The governing reaction is:

$$C + 1/2\,O_2 \longrightarrow CO$$

Hence, we have:

$$-26{,}416 = \Delta H_0 + (6.42 - \frac{6.148}{2})T + (\frac{1.665 - 0.5(3.100)}{2}) \times 10^{-3}T^2$$

$$+ (\frac{-0.196 - (-0.923)\ (0.5)}{3}) \times 10^{-6}T^3$$

$\Delta H_0 = -27{,}420.51$ calories.

2. Substitution of this value of ΔH_0 into equation (2) to solve for I at $T = 298°K$:

$$-32{,}808 = -27{,}420.51 - 3.346\ (298)\ \mathrm{In}\ 298 - \frac{0.114}{2}\ (298)^2 \times 10^{-3}$$

$$- \frac{0.2655}{6}\ (298)^3 \times 10^{-6} - I(298)$$

$$I = -1.0046$$

3. Substitution of the values of ΔH_0 and I into equation (2) to get the general expression for ΔF°_{CO} at any temperature T.

$$\Delta F^\circ_{CO} = -27{,}420 - 3.345\ T \ln T - \frac{0.114}{2} \times 10^{-3}T^2 - \frac{0.2655}{6}\ T^3$$

$$+ 1.0046\ T$$

$$\Delta F^\circ_{CO} = -27{,}420 - 3.346\ T \ln T - 0.057\ T^2 - 0.044\ T^3 + 1.0046$$

Using the same procedure, we can get for CO_2 and H_2O the following expressions:

$$\Delta F^\circ_{CO_2} = -94{,}372 - 0.066\ T \ln T - 3.637 \times 10^{-3}T^2 + 0.437$$

$$\times 10^{-6}T^3 + 1{,}80\ T$$

$$\Delta F^\circ_{H_2O} = -59{,}084 - 4.182\ T \ln T - 0.3735 \times 10^{-3}T^2$$

$$- 0.124 \times 10^{-6}T^3 + 38.88\ T$$