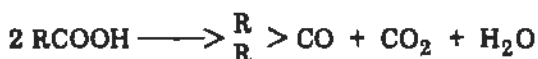


DECARBOXYLATION OF THE FATTY ACIDS OF COCONUT OIL

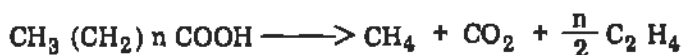
By Julian A. Banzon, Academician

Abstract

At ca 300°C, the fatty acids (FA) of coconut oil (CNO) undergo partial decarboxylation forming high molecular weight ketones in good yield:



At ca. 1000°C the FA of CNO yield by decarboxylation, ethylene, probably according to the equation:



At ambient temperature, ca. 30°C the FA of CNO undergo readily a microbiological decarboxylation yielding methane. For lauric acid, the main FA of CNO, the chemical reaction may be written:



A review of decarboxylation studies in the Philippines is presented.

Theoretically the decarboxylation of fatty acids should yield hydrocarbons of the type $\text{C}_n \text{H}_{2n+2}$. Thus from the acid $\text{C}_{11} \text{H}_{23} \text{COOH}$ (lauric acid, the principal acid in coconut oil), the hydrocarbon undecane would be formed by decarboxylation:



Since gasoline, kerosene and LPG are hydrocarbons, the importance of decarboxylation is obvious. The fatty acid composition of coconut oil is shown in Table I (reference 1). Because of this possibility of producing gasoline from vegetable oils, decarboxylation attracted quite some attention. (ref. 2, 3, 4, 20, 21, 22). During the last China-Japan war, "gasoline" was manufactured by

TABLE I
Fatty Acid Composition of Coconut Oil
(reference I)

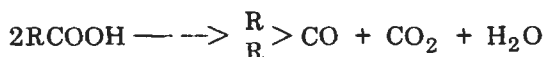
		Possible Hydrocarbon				
100 g CNO	8.34g H ₂ O	FA 94.13g	C ₆ .063 g	C ₅ H ₁₂		
			C ₈ 8.45 g	C ₇ H ₁₆		
			C ₁₀ 5.87 g	C ₉ H ₂₀		
			C ₁₂ 45.32 g	C ₁₁ H ₂₄		
			C ₁₄ 17.85 g	C ₁₃ H ₂₈		
			C ₁₆ 8.28 g	C ₁₅ H ₃₂		
			C ₁₈ 4.24 g	C ₁₇ H ₃₆		
			C _{18'} 2.89 g	—		
			C _{18"} 0.59 g	—		
			Glycerol 14.2 g			

the Chinese from tung oil (ref. 5). The process was further studied in India (ref. 6). In 1946, there was an attempt to make "gasoline" from coconut oil in the Philippines. (ref. 7 & 8). The general method involved in these endeavors is based on the chemistry textbook procedure summarized by the chemical equation:

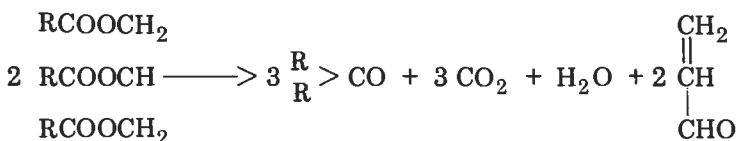


where M may be sodium. In effect the process consists of heating ordinary soap (RCOONa) with sodium hydroxide. To make the process cheaper, the calcium soap is used and heated with slaked lime. (ref. 7 & 8).

Decarboxylation yielding ketones. We tried catalytic decarboxylation using compounds of Al, Zn, Cd, Fe. Small amounts of non-saponifiable liquids were produced, except that Fe catalyst yielded a crystalline solid, melting point 55°C (ref. 9). It proved to be a high molecular weight ketone (ref. 10). We can explain its formation by the following equation:



We found that the formation of ketones proceeded easier with coconut oil itself rather than with the fatty acids probably because with coconut oil the temperature could be raised higher (above 300°C). For coconut oil the decarboxylation reaction can be represented thus:



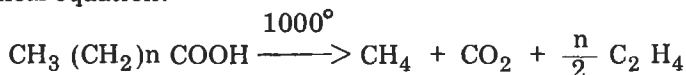
With the formulation of ketones in good yield (64%), we have achieved partial decarboxylation but fell short of getting the desired hydrocarbons. Nevertheless, the ketones present a new chemical derived from coconut oil and open a new area of coconut oil research.

Decarboxylation with transition metal complexes as catalysts.

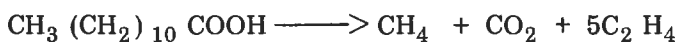
There were reports from the USA of a process for converting tallow (beef fat in large supply in the USA) into gasoline range hydrocarbons, using transition metal complexes as catalysts. It may be recalled that the transition metals proved to be the key to the successful polymerization of ethylene, propylene and styrene.

Anticipating that he can get hold of the tallow-to-gasoline process, a Vietnamese national offered to the NSTA to undertake a coconut oil-to-gasoline conversion. (ref. 11) Nothing further has been heard about this process and there were even denials that the process ever existed.

High temperature decarboxylation. Our studies on decarboxylation of coconut oil indicated the production of another type of hydrocarbon: ethylene. Also during the Occupation, at the U.P. College of Agriculture we generated gas for the laboratories by pyrolysis of coconut oil in lieu of the usual, but no longer available bunker oil. The temperature was estimated at 1000°C because of the dull red color of the heated iron retort. The gas formed was rich in unsaturated hydrocarbons, ethylene mainly. We can explain the formation of ethylene from a fatty acid by the following chemical equation:

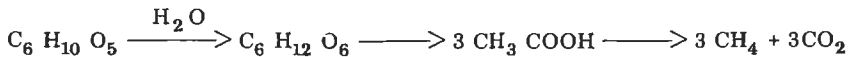


For lauric acid, and calculating for theoretical (and therefore maximum) yield, the conversion percentage would be 70 percent based on the equation:



The standard heat of formation for lauric acid is ca. - 33.6 K cal/mole; the heat of reaction for the above reaction would then be - 15.8 K cal/mole lauric acid.

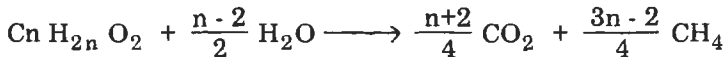
Microbiological decarboxylation. The formation of biogas from organic matter is kind of decarboxylation carried out by microorganisms. The series of biochemical events from organic matter to biogas, appears to be very complex, but may be summarized by the following sequence of reactions (ref. 12).



It is seen that the last step is a decarboxylation reaction of a fatty acid. If this reaction applies to lauric acid then the equation would be:



The formation of hydrocarbons other than methane is now ruled out in "anaerobic digestion" process. (ref. 12). However, simple fatty acids have been known to produce biogas. A general equation for fatty acids undergoing anaerobic decomposition has been proposed (13):



Under a grant from the National Research Council of the Philippines we undertook a study to test if coconut oil (which contains higher fatty acids), does decarboxylate microbiologically (ref. 14). We found the process to take place readily, the "fermentation" time is comparable to that of animal wastes, that is 15 to 20 days. The theoretical methane yield for lauric acid is calculated to be 68% based on the equation:



By comparison, the theoretical methane yield from cellulose is only 30% based on the equation:



Significance of ethylene production from coconut oil. Ethylene is the raw material for the manufacture of many and varied consumer items: polyethelene ware, sheets, pipes; textile fibers like Dacron and Terylene (the "polyesters") ; extremely durable plastic sheets (Mylar); it enters into manufacture of modern detergents. In the USA, ethanol is produced from ethylene on a commercial scale.

The present industrial source of ethylene is petroleum hence the need to locate renewable sources. In India, ethylene is produced from ethanol because of shortage of petroleum. The case of India emphasizes the need to find replacements of petroleum not only for fuel but as raw material for manufactured goods. The urgency of the situation is shown by the following world conferences:

- 1969 Symposium on non-food uses of coconut oil (ref. 15)
- 1976 Report of a study of renewable resources for industrial materials. National Research Council-Academy of Science (USA). (ref. 16).
- 1978 World conference on future sources of organic materials (ref. 17)
- 1979 New crop developments for industrial oils (ref. 18).
- 1979 Fats and oils as chemical intermediates. (ref. 19).

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DISCUSSION ON DECARBOXYLATION OF THE FATTY ACIDS OF COCONUT OIL

Florencio Medina, D. Sc., (*honoris causa*), Discussant

This paper of Dr. Banzon emerged out of scientific investigations of coconut oil which are safely deposited in no less than 22 reference materials. Sometime in the past, coconut was often referred to as the lazy man's crop, and reading 22 research papers, and being able to organize a good paper on the "Decarboxylation of the Fatty Acids of Coconut Oil" is not a lazy man's job. In his paper, Dr. Banzon has objectively pointed out that the fatty acids of coconut oil and therefore the coconut are available and renewable source of energy and an important and versatile source of industrial raw materials. The decarboxylation of fatty acids yields high molecular weight, ketones and saturated as well as unsaturated hydrocarbons.

Of course, it all depends on the nature and the temperature of the reaction and on the catalyst used. The temperature of the reaction can be under ordinary room temperature or can be as high as 1000°C. The catalyst could be compounds of aluminum, cadmium, iron as well as transition metal complexes.

The reaction can be an ordinary simple reaction or a microbiological one. This area of research to my mind is as important and as challenging especially here in the Philippines. I would like to venture and say the NAST can play an important role as a catalyst and have the Ministry of Energy react to the suggestion that it considers. The decarboxylation of fatty acids is one of the several possible sources of energy in the Philippines which is one of the leading countries considered high producers of coconut oil in the world.

The decarboxylation of fatty acids in coconut and other vegetable oils to form hydrocarbons that maybe fractioned into gasoline components should be seriously considered by the Ministry of Energy, by research agencies as well as by industrial organizations in this country.

Industrialists should likewise be interested in the decarboxylation reaction yielding unsaturated hydrocarbons such as ethylene which finds use in the manufacture of polyethelene wares, durable plastics, paper dacrone and terylene and even detergents. Maybe I should not miss to point that in some countries, ethylene is produced from ethanol while in others ethanol is produced from ethylene.

Microbiological decarboxylation has been discussed in the paper of Dr. Banzon. Lauric acid has been made an example in which undecane may be formed but Dr. Banzon points that the formation of hydrocarbons, other than methane is ruled out in anaerobic digestion process.

I would like to inform that alpha articles such as those emitted by plutonium are capable of the decarboxylation process in producing hydrocarbons and in producing methane. Here is another instance of the decarboxylation of fatty acids that has not yet been explored in the Philippines.

The Philippine Atomic Energy Commission, the agency dedicated to the application of nuclear science to agriculture, medicine and basic science and should be in the best position to undertake this kind of research. Funds coming from the Ministry of Energy should be invested in this process. We would like to ask in closing whether any pilot plant has been installed in utilizing any of the processes mentioned in Dr. Banzon's paper and if there is any, have they studied the economics of the processes? Have they also looked into the possible pollution aspects of the process?

Thank you.

Augusto Santos-Ocampo, Ph.D., Discussant

Dr. Banzon's paper has brought attention to the fact that the coconut has other possibilities aside from its use as coconut oil. We all know that these days, coconut oil is blended with diesel as fuel. And coconut oil can be esterified and be used as substitute for diesel fuel. Here, we have all the possibilities of using coconut oil as sources of hydrocarbons and perhaps take the place of gasoline in the future.

Now the only question we should keep in mind, is whether this hydrocarbon from coconut oil will give a favorable energy balance because what we are producing here is an energy product and whether it would be advantageous to produce hydrocarbons out of oil, instead of coconut oil as diesel extender or methyl ester as substitute.

The paper also discusses the possibility of coconut oil as source of ethylene which we know is an important raw material for the plastic industry. I am sure this work is an exploratory and a starting point for what we need is to carry on with this program — that developed this for our future requirements.