



## Investigation of Hydrocarbon Generation Mechanism by Polarizing the Carboxy-group of Fatty Acid Salt with Microwave Radiation

Y.P. WANG<sup>1,2</sup>, Y.H. LIU<sup>1,2,\*</sup>, R. RUAN<sup>1,2</sup>, P.W. WEN<sup>1,2</sup>, Y.Q. WAN<sup>1,2</sup> and J.S. ZHANG<sup>1,2</sup>

<sup>1</sup>Engineering Research Center for Biomass Conversion, Nanchang University, 235 Nanjing Road, Nanchang City 330047, Jiangxi Province, P.R. China

<sup>2</sup>State Key Laboratory of Food Science and Technology, 235 Nanjing Road, Nanchang City 330047, Jiangxi Province, P.R. China

\*Corresponding author: Tel/Fax: +86 791 88333281; Email: liuyuhuan@ncu.edu.cn

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Triglycerides can be converted to renewable hydrocarbons fuel which can be used as engine fuels by alkali pyrolysis decarboxylation and cracking processes. The purpose of present study was to explore decarboxylation mechanism of fatty acid salt with microwave radiation. Sodium stearate, potassium stearate, sodium oleate and sodium laurate was chosen as a model compound. The carboxy-terminal of this dipolar molecule was further polarized with microwave radiation. The Lorentz force of ions of dipolar molecules were moved in accordance with the way of electromagnetic waves, contribute to the formation of carbanion, which effectively promote the decarboxylation reaction. Moreover, the polarity of carboxy-terminal was stronger, more easily decarboxylation. The surface of glycerol formed a "High-Temperature Locus" in microwave radiation reaction system, facilitate the decarboxylation processes, in addition to played a role as the hydrogen donor for this high dielectric value compound. C8-C20 *n*-alkanes and *n*-alk-1-enes were arranged regular in liquid products. It proved the feasibility to derive renewable hydrocarbon fuel from sodium salt of fatty acids by microwave pyrolysis

**Keywords:** Microwave radiation, Fatty acid salt, Decarboxylation, Hydrocarbon.

### INTRODUCTION

Lack of fossil fuels has been a serious threat to the world's energy and economic security, so the popularity of alternative energy and interest in the development of renewable fuels and chemicals are rapidly increasing. On the demand side, interest has been gradually changed to the research of high heat value fuels such as aviation gasoline and kerosene.

People produced biodiesel by transesterification or by pyrolysis method. The main process is the conversion of vegetable oil to diesel<sup>1</sup>. But economic factors and the nature of biodiesel limits its development. For example, the flow of biodiesel is poor at low temperature not suitable for use in cold areas. The molecular structure of functional groups containing oxygen, compared with diesel, its calorific value is lower by 9-13 %. In addition, the thermal stability of biodiesel is relatively poor, prone to deterioration and oxidation<sup>2,3</sup>. It has caused all scholars interest through the pyrolysis of fatty acid to obtain high purity of hydrocarbons. But thermochemical pyrolysis reaction was not easy to control, heating at a slower speed, poor selectivity and existence of many side reactions. Microwave heating has been developed rapidly in recent years, which may preferentially activate the polar partial of the long chain molecule, leading to the high selectivity of decarboxylation<sup>4-6</sup>. Shortcomings of the traditional heating has been

solved, for instance, large temperature gradient, slow heating rate and non-selective decarboxylation<sup>7,8</sup>.

Pyrolysis of the whole triglyceride has been shown to result in oxygenated products<sup>9,10</sup> through complex free-radical reactions<sup>11</sup>. There are little work on the pyrolysis of fatty acid salt, which can be released from triglycerides through various saponification techniques. Many researchers have considered the deoxygenation of fatty acids using different catalysts. However, there are no detailed studies involving the decarboxylation or deoxygenation of fatty acids solely by thermal means. SBA-15/Pd and Pd/C was used to catalyze the decarboxylation or deoxygenation of fatty acids<sup>12,13</sup>, although obtained high-quality hydrocarbon. But it is subject to multiple conditions that can not to be applied. The most recent study examined liquid-phase pyrolysis of stearic acid (C<sub>18</sub>H<sub>36</sub>O<sub>2</sub>) in dodecane using Pd/C catalysts<sup>14</sup>. The main product was *n*-heptadecane and CO<sub>2</sub> was identified in the gas phase, making it likely that the initial reaction is decarboxylation of the fatty acid. The deoxygenated hydrocarbon chain produced through the decarboxylation of fatty acids could be processed further to yield shorter-chain hydrocarbons that could potentially be used as petrochemical replacements. Mechanisms involving thermal decomposition of fatty acids after initial decarboxylation have not been reported.

The main products of stearic acid pyrolysis was series of *n*-alkanes and *n*-alk-1-enes and some undesired oxy-compound. It is associated with the traditional heating that had not strong selectivity<sup>15, 16</sup>. Microwave radiation that can change order and the bonding strength of the chemical bonds of polarity molecules, transform fatty acid into fatty acid salt by saponification, which can increase the polarity of carboxyl terminal, using microwave heating technology, which may preferentially activate the polar molecule and functional groups of the fatty acid salt molecular, leading to the high selectivity of decarboxylation. This research mainly study the decarboxylation and cyclization mechanism of different metal salts of fatty acids, different saturation and length of carbon chain fatty acid salt in the condition of microwave radiation. Sodium stearate, potassium stearate, sodium oleate and sodium laurate were chosen as a model compound, glycerol played a role as the hydrogen donor and microwave absorber for this high dielectric value compound. It was shown that *n*-alkanes and *n*-alk-1-enes had overwhelming superiority by qualitative and semi-quantitative analysis in pyrolysis product, proofed unique advantages that microwave pyrolysis fatty acid salt decarboxylation into the hydrocarbon. Moreover, different fatty acid salt were compared. It was proved that it is feasible to derive renewable hydrocarbon fuel from natural triglyceride by microwave pyrolysis.

## EXPERIMENTAL

Sodium stearate, potassium stearate, sodium oleate and sodium laurate were purchased from Sinopharm Chemical Reagent Co. Ltd in Chinese with > 99 % purity. Others were analytical reagents made in China. Microwave pyrolysis apparatus was manufactured by SinEo in Shanghai. This apparatus is designed by our team. Agilent 6890N/5973 inlet GC-MS (Agilent Technologies); Chromatographic column (HP-5 ms, 30 m × 0.25 mm × 0.25 μm); FT-IR Nicolet 5700 (Thermo Nicolet Corporation); GC 9310 (Chromatography Instrument Co., Ltd. Shanghai).

### General procedure

Pyrolysis device is composed of microwave generators, reactor, condensing system, connecting tubes and liquid collection bottle. The pyrolysis of samples was carried out in a Sinko Bench type Microwave Oven by placing 30 g prepared samples (sodium stearate; potassium stearate; sodium oleate; sodium laurate) mixed with 10 % glycerol (wt. %) in a quartz flask, which in turn was placed inside the cavity of microwave. Oven is supplied with infrared probe to control temperature. Condensing system was composed of condense liquid collecting bottle and series condenser pipe, opening condensed circulatory system until the temperature of condensed water is below 3 °C. The time for microwave treatment was around 10 min. A constant power input of 400 W, 600 W, 800 W was used for each batch, using infrared probe to record the change of temperature. The fraction collected from the bottles connected on the bottom of the condensers is pyrolytic liquid.

The solid char residue was allowed to be cooled down to the room temperature before it was weighed. The condensates adhering to the interior wall of the quartz flask were washed with ethanol into the pyrolytic liquid collection bottle. Collected

liquids were concentrated using a vacuum rotary evaporator (EYELA WATER BATH SB-2000) to a near constant weight and the weight was recorded. The viscosity and density of the collected liquid were determined (SYD-265B and DM-100). The weight of gas product was calculated using the following equation:

$$\text{Weight of gas} = \text{Initial samples} - \text{Pyrolytic liquid mass} - \text{Char residue mass}$$

**Detection method:** Chemical compositions of the liquid products were analyzed using an Agilent 6890N/5973 inlet gas chromatography/mass spectrometer (Santa Clara, CA) with a HP-5ms capillary column. The GC was programmed at 60 °C for 2 min and then increased at 10 °C/min to 280 °C and finally held with an isothermal for 10 min. The injection temperature was 280 °C and the injection size was 0.2 μl. The flow rate of the carrier gas (helium) was 1 mL/min. The ion source temperature was 230 °C for the mass selective detector. The compounds were identified by comparison with the NIST Mass Spectral Database. Only quality matches of above 85 % were recorded.

All experiments were performed in quintuplicate. The data presented in this paper are averaged values. Statistical analysis of the data was conducted using origin 8.0. The standard deviations are presented along with the fractional yield data.

## RESULTS AND DISCUSSION

**Decarboxylation of sodium stearate under different microwave power and glycerol content:** The content of sodium stearate pyrolytic products under different microwave power levels are different as shown in Fig. 1. The content of liquid hydrocarbon is increased with the increase of power, but slight changes (in average 50 to 57 %) take place and the amount of liquid ranged from 63 to 70 %.

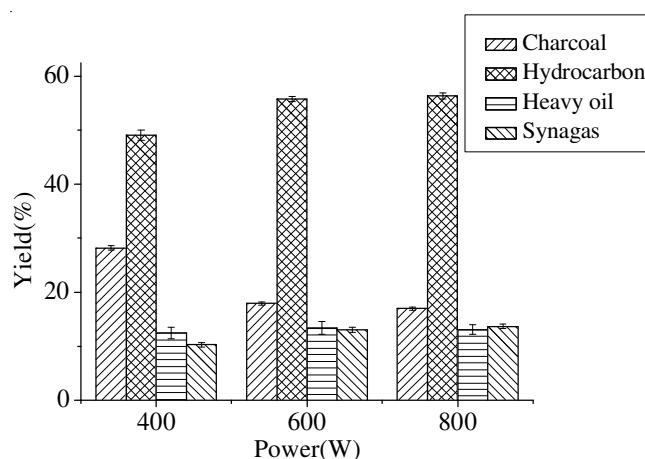


Fig. 1. Decarboxylation of sodium stearate product fractional yields in different microwave radiation (10 min)

The main products of sodium stearate pyrolysis were *n*-alkanes and *n*-alk-1-enes and cyclic hydrocarbons. The peak area of each product can be determined semi-quantitative through the standard of known concentration in the computer. As shown in Fig. 2 and Table-1, *n*-alkanes and *n*-alk-1-enes series were arranged from C<sub>8</sub> to C<sub>20</sub> regularly, which is in line with the law of hydrocarbon pyrolysis; diene series was also

TABLE-1  
MAIN COMPONENTS AND RELATIVE CONTENTS OF LIQUID PRODUCTS BY MICROWAVE  
PYROLYSIS OF SODIUM STEARATE AT DIFFERENT POWERS

Type	Hydrocarbon	M <sup>a</sup>	Retention time (min)					Relative content (%)				
			400W		600W		800W	400W		600W		800W
			10 % glycerol	5 % glycerol	10 % glycerol	20 % glycerol	10 % glycerol	10 % glycerol	5 % glycerol	10 % glycerol	20 % glycerol	10 % glycerol
Alkenes	Octenes	112	3.26	3.25	3.26	3.25	3.26	1.04	1.00	1.21	0.98	1.08
	Dodecenes	168	9.78	9.76	9.75	9.77	9.77	3.62	3.94	3.93	4.17	3.68
	Tridecenes	182	11.27	11.26	11.23	11.26	11.26	4.61	4.88	4.27	4.80	4.67
	Tetradecenes	196	12.74	12.72	12.69	12.72	12.71	6.47	7.55	7.13	7.53	6.84
	Pentadecenes	210	14.09	14.09	14.06	14.10	14.08	8.75	10.26	9.79	10.36	9.39
	Hexadecenes	224	15.23	15.21	15.18	15.21	15.21	5.07	5.41	5.39	5.51	5.03
	Heptadecenes	238	16.45	16.42	16.40	16.43	16.42	6.72	7.31	7.27	7.40	6.83
	Octadecenes	252	17.37	17.37	17.35	17.37	17.36	1.72	1.23	1.44	1.41	1.24
	Nonadecenes	266	18.41	18.40	18.40	18.41	18.40	0.56	0.43	0.48	0.43	0.41
	Eicosylenes	280	19.26	19.26	19.26	19.26	19.26	0.63	0.32	0.48	0.43	0.30
Ring-containing alkenes	Methylcycloheptene	110	3.73	3.72	3.73	3.72	3.72	0.12	0.10	0.13	0.09	0.12
	Cycloheptene	96	5.54	5.54	5.54	5.53	5.53	0.09	0.08	0.08	0.17	0.10
	Cyclodecene	138	4.56	4.56	4.56	4.56	4.56	0.33	0.32	0.40	0.37	0.38
	Cyclododecene	166	-	-	7.01	7.01	7.01	-	-	0.10	0.09	0.08
Dienes	1,4-Octadiene	110	4.24	-	-	-	-	0.03	-	-	-	-
	1,11-Dodecadiene	166	13.63	13.62	13.61	13.62	13.62	0.15	0.13	0.14	0.13	0.12
	1,12-Tridecadiene	180	14.37	14.35	14.34	14.36	14.35	0.17	0.20	0.22	0.21	0.21
	1,13-Tetradecadiene	194	14.91	14.90	14.89	14.90	14.90	0.26	0.17	0.19	0.17	0.15
	1,14-Pentadecadiene	208	15.52	15.51	15.50	15.52	15.52	0.16	0.08	0.10	0.09	0.09
	1,15-Hexadecadiene	222	16.10	16.10	16.08	16.10	16.09	0.30	0.21	0.26	0.19	0.19
Alkanes	1,16-Heptadecadiene	236	16.69	16.68	16.67	16.68	16.68	0.31	0.18	0.23	0.18	0.23
Alkanes	Octanes	114	3.37	3.36	3.36	3.36	3.36	1.00	0.88	1.10	0.88	0.95
	Nonanes	128	4.91	4.89	4.90	4.89	4.90	1.60	1.49	1.80	1.45	1.65
	Decanes	142	6.64	6.62	6.62	6.62	6.63	1.73	1.72	2.01	1.84	1.83
	Undecanes	156	8.33	8.31	8.30	8.31	8.31	1.40	1.68	1.82	1.93	1.61
	Dodecanes	170	9.90	9.88	9.87	9.89	9.88	1.55	1.60	1.93	1.85	1.50
	Tridecanes	184	11.42	11.40	11.38	11.41	11.40	1.25	1.81	2.59	2.01	1.99
	Tetradecanes	198	11.53	11.53	11.52	11.52	11.40	0.12	1.81	2.59	2.01	1.99
	Pentadecane	212	12.90	12.89	12.88	12.89	12.89	0.24	0.19	0.19	0.20	0.18
	Hexadecane	226	14.27	14.25	14.22	14.25	14.25	0.48	0.41	0.43	0.37	0.41
Heptadecane	240	15.40	15.39	15.37	15.39	15.38	0.32	0.19	0.23	0.24	0.19	
Ring-containing alkanes	Ethyl cyclohexane,	112	16.59	16.57	16.56	16.57	16.57	0.56	0.40	0.50	0.40	0.43
	Hexyl cyclopropane	126	3.86	3.86	3.86	3.86	3.86	0.09	0.08	0.10	0.08	0.09
	Proyl cyclohexane	126	4.12	4.12	4.12	3.86	4.12	0.06	0.09	0.12	0.08	0.12
	1,2-Dimethyl cyclooctane	140	4.40	4.40	4.40	4.40	4.40	0.07	0.07	0.10	0.09	0.09
	Pentyl cyclohexane	154	4.76	4.75	4.76	4.75	4.76	1.74	1.71	2.00	1.69	1.87

<sup>a</sup> Relative molecular mass.

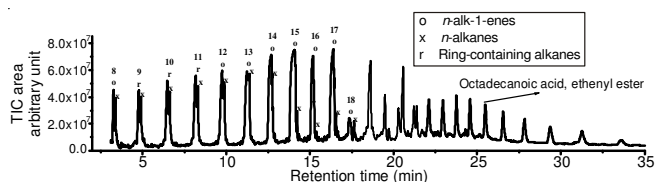


Fig. 2. Main products formed in the microwave pyrolysis experiments (600W and 10 min) on sodium stearate

observed a slight variation, from C<sub>12</sub> to C<sub>17</sub> respectively. The pyrolysis gas of a semi-quantitative analysis of gas phase showed that the existence of CH<sub>4</sub> and proved that the sodium stearate long-chain hydrocarbon of free fracture happened again after the formation of long-chain hydrocarbon.

Pentadecene and heptadecene content were the most important in pyrolysis products, others have a slight difference of peak area in different carbon atoms in the same series of hydrocarbons, compared with the traditional pyrolysis products, which was concerned possibly with microwave radiation<sup>17</sup>. Medium compounds mainly happened while the dipole turning-direction polarization and interface polarization in the microwave field<sup>18,19</sup>. Depending on C-terminus's polarity was the biggest in the long chain fatty acid salt and dipole made desultorily movement and arrangement.

The C-terminus's dipole arranged again and positive charge moved to the negative electrode trend when microwave played role in the polarity along with the change of the

microwave. Lorentz force of ion or polarity molecules forced to move according to the electromagnetic wave function way, which leads to reduce the entropy and molecule collision risk effectively increases billions of times contrast with no catalytic microwave's<sup>20, 21</sup>. In addition, the glycerol (hydrogen donor) was strong microwave absorbing agent added in the reaction system because its dielectric constant is 56.2. Fatty acid salt is strongly activated near glycerin interface leading to decarboxylation reaction. Hydrocarbon products quickly deviate from high-temperature zone. Based on the above analyses, we can infer the possible decarboxylation mechanism of sodium stearate as shown in Fig. 3 in the action of microwave and glycerol.

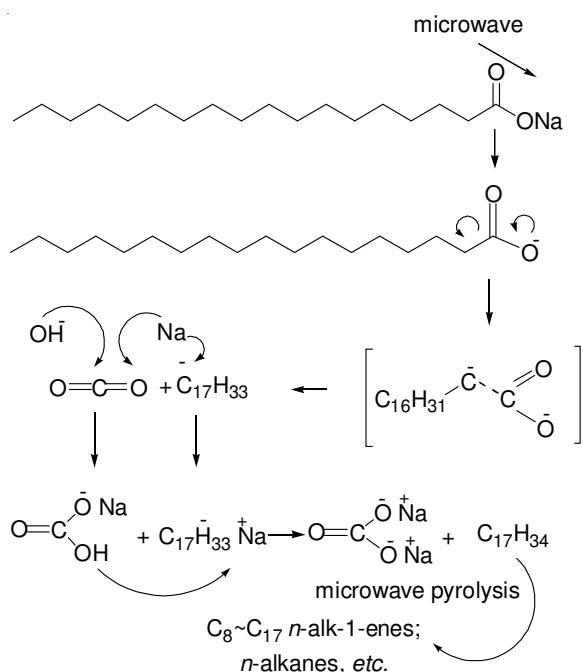


Fig. 3. Decarboxylation reaction mechanism of sodium stearate in microwave radiation

The carboxy-terminal's positive and negative ion migratory direction of sodium stearate formed orderly arrangement under the microwave field, leading to a reduction of activation energy. Carbanion formed under fierce collision with glycerol surface of high-temperature locus under variable microwave frequency, which was relatively stable. The same series of *n*-alk-1-enes and *n*-alkanes were obtained after sodium stearate decarboxylation at relatively stable microwave field. FI-IT showed that large amounts of solid sodium carbonate contained in solid the after pyrolysis, which proved the correctness of the reasoning process. Two reactions may occurred during decarboxylation process, long-chain hydrocarbons were fractured to produce different carbon chain length of *n*-alk-1-enes and *n*-alkanes under high temperature, accompanied by methane, ethane, ethylene and acetylene gases (Fig. 4 and Table-2).

C<sub>9</sub>-C<sub>11</sub> *n*-alk-1-enes was not found in microwave assisted pyrolysis products, but generating same series naphthenic hydrocarbon with the side chain. This is different from traditional pyrolysis. This was also consistent with the microwave cyclization reaction mentioned in the relevant article. However,

TABLE-2  
MAIN COMPONENTS OF GAS PRODUCTS BY  
MICROWAVE PYROLYSIS OF SODIUM STEARATE

Power	CO <sub>2</sub> (%)	CO (%)	CH <sub>4</sub> (%)	C <sub>2+</sub> (%)	H <sub>2</sub> (%)
400 W	46.12	34.94	1.45	2.41	15.08
600 W	45.63	33.18	1.69	2.03	17.47
800 W	39.26	34.87	1.82	2.45	21.60

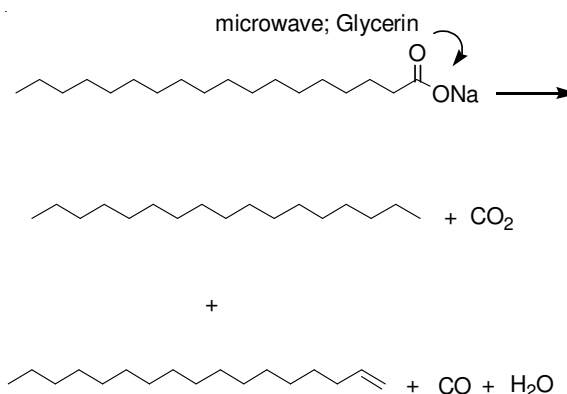


Fig. 4. Decarboxylation pathway of sodium stearate in microwave radiation

the specific mechanism has not been proved<sup>22</sup>. It was sure that naphthenic hydrocarbons, helpful for hydrocarbon fuel preservation, are more stable than *n*-alk-1-enes in pyrolysis. The content of *n*-alk-1-enes, *n*-alkanes and naphthenic hydrocarbon is increased with the increase of microwave power, while the dienes and oxygen compounds are gradually reduced. A lot of octadecanoic acid ethenyl ester found in microwave assisted pyrolysis products are not found in traditional pyrolysis previously mentioned<sup>23</sup>. This is due to the addition of glycerol which play an important role in reducing the activation energy as high-temperature locus in decarboxylation reaction, assumed hydrogen donor in the system. Glycerol and sodium stearate would also enhancing complex esterification. As the amount of glycerol is increased, octadecanoic acid and ethenyl ester are also regularly increased (Table-3).

**Decarboxylation of fatty acid salt for different metal salts, different saturation and different carbon chain length:** The microwave pyrolysis product distribution of sodium stearate, potassium stearate, sodium oleate and sodium laurate are shown in Fig. 5. The yield of sodium oleate liquid hydrocarbons was the highest, while the yield of heavy oil (wax) is zero. Under the conditions of microwave and because of the existence of sodium oleic double bond there may be an enhancement of the reaction activity in some areas of carbon chains. Double bonds can reduce the pyrolysis energy barrier of the proximate C-C single bonds and made β C-C fracture occupying the leading position and make it difficult to form long-chain wax. The probability of short-chain fatty acid salt got polymerized to form long-chain wax was also very small. As sodium stearate, the major product of potassium stearate; sodium oleate and sodium laurate pyrolysis was also *n*-alkanes, *n*-alk-1-enes and cyclic hydrocarbons, from C<sub>8</sub> to C<sub>20</sub>. Sodium stearate, potassium stearate and sodium laurate pyrolysis arranged regularly, but the product of sodium oleate pyrolysis was arranged complex. A large number of cycloolefin and cycloparaffins were produced in the product of sodium oleate

TABLE-3  
RELATIVE CONTENTS OF VARIOUS HYDROCARBONS IN LIQUID PRODUCTS FORMED FROM  
MICROWAVE PYROLYSIS OF SODIUM STEARATE UNDER DIFFERENT GLYCEROL CONTENT

Type	400 W	600 W			800 W
	10 % glycerol (%)	5 % glycerol (%)	10 % glycerol (%)	20 % glycerol (%)	10 % glycerol (%)
C <sub>3</sub> -C <sub>9</sub> hydrocarbons	3.64	3.37	4.11	3.31	3.68
C <sub>10</sub> -C <sub>20</sub> alkenes	38.5	41.92	40.50	41.98	39.08
Ring-containing alkenes	0.63	0.42	0.71	0.72	0.68
C <sub>10</sub> -C <sub>17</sub> alkanes	7.65	8.00	9.70	8.88	8.14
Ring-containing alkanes	7.95	8.44	9.16	8.78	8.84
Dienes	1.38	0.97	1.14	0.97	0.99
Octadecanoic acid, ethenyl ester	4.65	4.21	4.37	4.45	4.14
Other oxygen-containing	7.58	4.04	4.01	4.69	4.19
Others (unidentified)	28.02	28.63	26.30	26.22	30.26

TABLE-4  
MAIN COMPONENTS AND RELATIVE CONTENTS OF LIQUID PRODUCTS BY MICROWAVE  
PYROLYSIS FOR DIFFERENT SODIUM SALTS OF FATTY ACID

Type	Hydrocarbon	M <sup>a</sup>	Retention time (min)				Relative content (%)				
			Sodium stearate	Potassium stearate	Sodium oleate	Sodium laurate	Sodium stearate	Sodium stearate	Sodium oleate	Sodium laurate	
Alkenes	Octenes	112									
	Nonenes	126	-	-	4.95	-	-	-	0.44	-	
	Decenes	140	-	-	6.44	6.69	-	0.27	1.81	0.74	-
					6.79				0.36		
	Undecenes	154	-	8.45	8.37	8.39	-	0.15	2.06	1.49	14.28
					8.49				0.50		
	Dodecenes	168	9.75	9.74	9.88	9.85	3.93	4.03	0.79	0.15	0.46
					10.01				0.50		
	Tridecenes	182	11.23	11.24	11.20	11.12	4.27	5.23	2.96	11.30	1.27
					11.30				0.57		
	Tetradecenes	196	12.69	12.67	12.56	12.54	7.13	7.70	3.17	1.26	
	Pentadecenes	210	14.06	14.13	13.90	14.16	9.79	15.25	4.64	10.12	
	Hexadecenes	224	15.18	15.18	0	15.14	5.39	5.73	0	3.47	
	Heptadecenes	238	16.40	16.40	16.31	16.42	7.27	11.53	1.75	0.16	
Octadecenes	252	17.35	17.36	17.23	17.37	1.44	1.39	2.03	0.37		
Nonadecenes	266	18.40	18.57	18.27	18.26	0.48	3.58	1.29	19.26	2.14	
				19.26				0.76			
Eicosylenes	280	21.70	-	-	-	0.32	-	-	-	-	
Ring-containing alkenes	Methylcycloheptene	110	3.73	5.52	3.71	3.71	0.13	0.07	0.39	0.06	
	cycloheptene	96	5.54	4.55	-	4.54	0.08	-	-	0.22	
	Propyl cyclopentene	110	-	-	4.03	-	-	-	0.11	-	
	Propenyl cyclopentene	108	-	-	5.08	-	-	-	0.33	-	
	Butyl cyclopentenes	124	-	-	5.30	-	-	-	0.57	-	-
					5.70				0.64		
	Propyl cyclohexene	124	-	-	5.90	-	-	-	0.48	-	
	Cyclodecene	138	7.01	-	6.87	-	0.10	-	0.47	-	-
					7.48				0.73		
	Butyl cyclohexene	138	-	-	7.61	-	-	-	1.58	-	-
					8.70				1.73		
	Pentyl cyclohexene	152	-	-	8.90	8.71	-	-	0.75	-	0.37
					10.23				0.75		
	Cycloundecene	152	-	-	10.37	10.17	-	-	1.74	-	0.20
10.47					0.41						
Hexyl cyclohexene	166	-	-	12.05	-	-	-	0.67	-	0.39	
				12.07				0.67			
Octyl cyclopentene	180	-	-	12.23	12.26	-	-	0.89	-	0.31	
				13.42				3.12			
Cyclododecene	166	-	-	13.38	-	-	-	3.12	-	0.43	
				14.94				3.87			
Decyl cyclohexene	222	-	-	15.52	-	-	-	1.29	-	-	
Dienes	1,11-Dodecadiene	166	13.61	0	10.74	13.58	0.14	0	2.59	0.53	
	1,12-Tridecadiene	180	14.34	14.36	11.65	14.28	0.22	0.12	0.72	0.53	
	1,13-Tetradecadiene	194	14.89	14.89	12.38	14.86	0.19	0.12	0.51	0.41	
	1,14-Pentadecadiene	208	15.50	-	-	-	0.10	-	-	-	
	1,15-Hexadecadiene	222	16.08	16.07	16.15	16.11	0.26	0.18	7.43	3.29	
	1,16-Heptadecadiene	236	16.67	-	16.41	16.73	0.23	-	1.30	0.64	

Alkanes	Octanes	114	3.36	3.36	3.35	3.35	1.10	0.84	0.82	0.93
	Nonanes	128	4.90	4.88	4.86	4.94	1.80	1.54	0.98	3.42
	Decanes	142	6.62	6.60	6.56	6.64	2.01	1.56	0.61	0.62
	Undecanes	156	8.30	8.29	-	8.55	1.82	2.06	-	0.48
	Dodecanes	170	9.87	9.85	-	9.99	1.93	1.77	-	0.34
	Tridecanes	184	11.38	11.38	11.28	11.44	2.59	2.72	1.22	0.44
				11.50	11.52	11.60		0.35	0.36	0.46
	Tetradecanes	198	12.88	12.86	12.91	12.96	0.19	0.26	0.40	0.30
	Pentadecane	212	14.22	14.28	-	0	0.43	0.86	0	-
Hexadecane	226	15.37	15.37	-	-	0.23	0.34	0	-	
Heptadecane	240	16.56	16.62	16.52	-	0.50	1.01	0.50	-	
Ring-containing alkanes	Ethyl cyclohexane	112	3.86	3.85	3.86	-	0.10	0.06	0.35	-
					4.51				0.49	
	Hexyl cyclopropane	126	4.76	4.73	4.73	4.75	2.00	1.64	1.26	2.36
					4.12				0.16	
	Ethylidene cyclohexane	110	4.12	4.11	4.24	-	0.12	0.08	0.11	-
			4.40		4.40		0.10		0.27	
	Propenyl cyclohexane	126	5.08	-	5.44	-	0.23	-	0.40	-
	1,2-Dimethyl cyclooctane	140	6.47	6.45	-	6.57	3.29	2.71	-	7.09
	Pentyl cyclohexane	154	8.16	8.15	8.14	-	3.32	3.69	3.08	-
Cyclododecane	154	-	-	9.72	9.72	-	-	3.15	1.84	
				14.34				1.17		
Nonyl cyclohexane	210	-	-	14.68	-	-	-	2.46	-	
Cyclohexadecane	224	-	-	15.11	16.86	-	-	2.78	0.17	

<sup>a</sup> Relative molecular mass

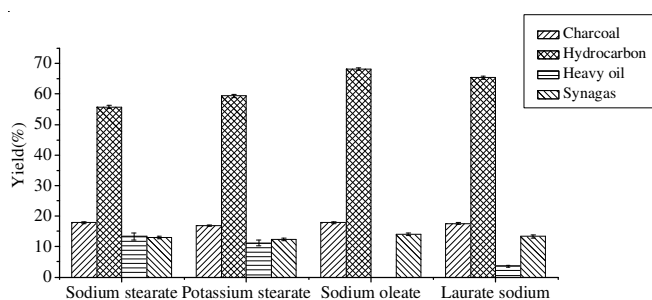


Fig. 5. Product yields (%) for different sodium salts of fatty acid (600 W and 10 min)

during microwave assisted pyrolysis, which may be due to microwave radiation accelerated cyclization reaction for compounds containing double bond<sup>24,25</sup> (Figs. 6-8, Table-4).

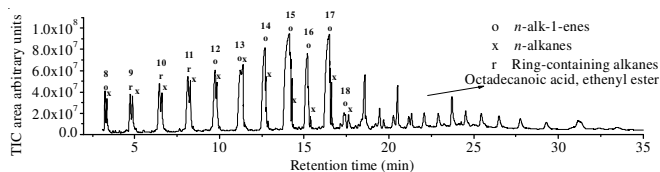


Fig. 6. Main products formed in the microwave pyrolysis experiments (600W and 10 min) on potassium stearate

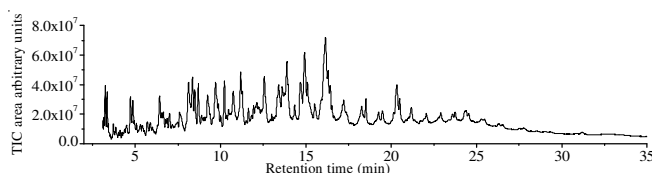


Fig. 7. Main products formed in the microwave pyrolysis experiments (600W and 10 min) on sodium oleate

In addition, the peak area of C<sub>15</sub>-C<sub>17</sub> *n*-alkanes and *n*-alk-1-enes are larger than other three materials. Because the carboxyl terminal of potassium stearate was kalium, for which

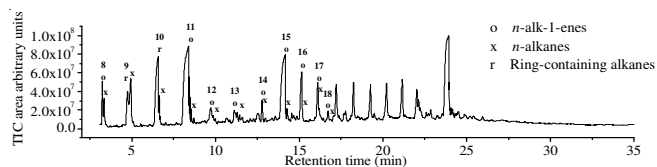


Fig. 8. Main products formed in the microwave pyrolysis experiments (600W and 10 min) on laurate sodium

the atomic radius and polarity are larger than that of sodium, the carboxy-terminal of this dipolar molecule is further polarized with microwave radiation. The Lorentz force of ions of dipolar molecules are moved in accordance with the way of electromagnetic waves leading to the formation of carbanion which is effectively promote the decarboxylation reaction. Moreover, the polarity of carboxy-terminal is stronger resulting in more easily decarboxylation. The decarboxylation mechanism of fatty acid salt is proved to be correct by another way in microwave radiation. Dienes content are the most important in pyrolysis products of sodium oleate. The double bonds are more hard to be cracked than the single bonds during pyrolysis decomposition. Thus, sodium oleate double bonds are kept in the liquid final product. At the same time, the existence of double bonds promoted the presence of cyclization reaction. C<sub>13</sub>-C<sub>19</sub> *n*-alkanes and *n*-alk-1-enes are found in pyrolysis products of laurate sodium (C<sub>12</sub>), due to polymerization. However, the reaction intensity is small (Table-5).

## Conclusion

The purpose of present study was to explore decarboxylation mechanism of fatty acid salt with microwave radiation. Sodium stearate, potassium stearate, sodium oleate and sodium laurate was chosen as a model compound, which proved the feasibility to produce high quality renewable hydrocarbon fuel with fatty acid salt by microwave assisted pyrolysis. The following conclusions were obtained: (a) It is feasible to produce high quality renewable hydrocarbon fuel using fatty

TABLE-5  
RELATIVE CONTENTS OF VARIOUS HYDROCARBONS IN LIQUID PRODUCTS FORMED FROM  
MICROWAVE PYROLYSIS FOR DIFFERENT SODIUM SALTS OF FATTY ACID

Type	Sodium stearate (%)	Potassium stearate (%)	Sodium oleate (%)	Sodium laurate (%)
C <sub>3</sub> -C <sub>9</sub> hydrocarbons	4.11	3.39	2.99	5.88
C <sub>10</sub> -C <sub>20</sub> alkenes	40.50	55.38	24.35	36.54
Ring-containing alkenes	0.71	0.35	20.56	1.98
C <sub>10</sub> -C <sub>17</sub> alkanes	9.70	10.93	3.09	2.64
Ring-containing alkanes	9.16	8.18	15.68	11.46
Dienes	1.14	0.42	12.55	5.40
Octadecanoic acid, ethenyl ester	4.37	5.01	0	0
Other oxygen-containing products	4.01	3.98	9.64	10.03
Others (unidentified)	26.30	12.36	11.14	26.07

acid salt by microwave assisted pyrolysis. (b) The mechanism of microwave promoting the fatty acid decarboxylation by acting on the carboxyl terminal is proved. The carboxy-terminal of this dipolar molecule is further polarized with microwave radiation. The Lorentz force of ions of dipolar molecules are moved in accordance with the way of electromagnetic waves, contribute to the formation of carbanion, which is effectively promote the decarboxylation reaction. (c) In the microwave field, as the carboxy-terminal polarity of potassium stearate is the strongest, thus the decarboxylation is most effective. The double bonds are more hard to be cracked than the single bonds during pyrolysis decomposition. Therefore, sodium oleate double bonds are kept in the liquid final product. At the same time, the existence of double bonds promoted the presence of cyclization reaction. (d) Glycerol surface formed high-temperature locus in the reaction system under the microwave field, which activated the reaction process as well as a role for hydrogen donor. But too much glycerol would lead to the formation of octadecanoic acid ethenyl ester. Saponification waste oil produced fatty acid salt also have glycerol as the by-product and some glycerol could be left in the system as natural catalyst providing a feasible method to produce high calorific value-hydrocarbon fuels by waste oil. (e) Carbon dioxide, carbon monoxide, methane, ethane, ethylene and acetylene are detected in the gas product which proved the inference of microwave assisted pyrolysis mechanism. (f) C<sub>8</sub>-C<sub>20</sub> *n*-alkanes and *n*-alk-1-enes are arranged regularly in liquid products comply with the hydrocarbon pyrolysis regular pattern; Homologous from C<sub>12</sub> to C<sub>17</sub> are detected in diene series; The cyclization of C<sub>9</sub>-C<sub>11</sub> *n*-alk-1-enes is promoted by microwave radiation provided opportunity to further enhance the stability of the liquid hydrocarbon fuel, yet the reaction mechanism needs to be discussed further.

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