

# Mechanism investigation on the formation of olefins and paraffin from the thermochemical catalytic conversion of triglycerides catalyzed by alkali metal catalysts

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**Abstract:** Triglycerides is a promising biomass feedstock that can be used for production of organic hydrocarbons including long-chain olefins and paraffin. The challenge on this production process lies on the lack and unclear of the conversion mechanism. In this work, the conversion mechanism from triglycerides to olefins and paraffin using alkali metal catalysts will be investigated adopting both computational calculation using Density Functional Theory (DFT) and experimental studies. The bond dissociation energies (BDEs) of the main bonds will be calculated, especially for  $\alpha$  carbon-carbon bond, which leads to effective removal of carboxyl groups for production of terminal olefins and normal paraffin. Dynamic behavior of triglycerides catalyzed by alkali metal catalysts was also investigated by TG analyses, it was found that Li ion has lowest activation energy below 200 KJ/mol comparing with other alkali ions. Catalytic conversion mechanism were proposed in this work based on the results from TG-IR, GC, GC-MS and XRD analyses, O atoms are removed as the form of CO, CO<sub>2</sub> and some H<sub>2</sub>O, leading to product M<sup>+</sup>O and M<sup>+</sup> which generated the M<sub>2</sub>CO<sub>3</sub> (M=Li, Na, K, Rb, Cs). A more detailed mechanism was proposed in this paper, which has significance guiding for the cleavage of triglycerides, for producing long-carbon-chain terminal olefins and normal paraffin.

**Keywords:** thermochemical conversion mechanism, activation energy, bond dissociation energies, alkali metal catalysts, stearates, triglycerides.

## 1. Introduction

Resource shortage and environment pollution have raised global concerns due to the exploitation of fossil fuel [1, 2]. Renewable energy such as wind, solar, hydro, hydroelectric and bio-energy, have generated greatly research interest[3] to meet the fuel demand[4, 5]. Among this, bio-energy is an alternative form has enormous potential for energy use, which is made available from materials derived from biological sources[6]. Triglyceride is an important biomass feedstock that has been extensively investigated in recent years. Triglyceride is widely existed in vegetable oil, animal fat and microalgae plant. Thus, adequate source of raw materials and abundant carbon sources give triglycerides great value with the potential to be converted into various organic hydrocarbons through biological or chemical transformation technologies [7, 8], especially for production green fuels, such as aviation bio-fuel[9-12] and second-generation biodiesel[2, 13-15].

Triglycerides consist of one glycerol and connect with three long hydrocarbons chains, which present the similar molecular structure with petroleum crude oil [9, 16, 17]. Deoxygenation is the key step for upgrading triglycerides to hydrocarbons products comparable with petroleum derived equivalents, which can suitable for industrialization. For example, triglycerides can be converted

into liquid hydrocarbons fuels by deoxygenation, which can significantly improve the chemical-physical properties (freezing point, heating value, acid number, viscosity and so on) of drop-in fuels[18]. In many cases, hydrogenation [19-25] and thermochemical conversion [8, 26-29] were two alternative deoxygenation approaches.

From the previous studies, hydrogenation was an efficient pathway to accomplish triglycerides deoxygenation by removed the O atoms as the form of CO, CO<sub>2</sub> and H<sub>2</sub>O, under the action of external hydrogen sources. In hydrogenation process, carbonyl carbon in triglycerides was first bind to the metal centers usually achieved by using noble metals [20-22] and sulfides catalysts [23-25]. The second step was cleavage of α C-C bond in the acyl group, under the influence of H<sub>2</sub>, leading to produce saturated hydrocarbons. In comparison, by introducing alkali metal ions to form fatty acid salts, BDEs of α C-C bond in the acyl group were reduced, which provides an alternative deoxygenation pathway by cost effectively thermo-decomposition method (Figure 1).

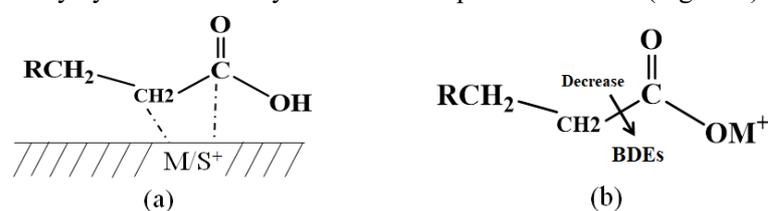


Figure. 1. The bond broken form of hydrogenation and thermochemical conversion process.

Our previous works investigated the catalytic performance by using alkali metal salt (K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>)[10, 16, 30, 31], approximately 70 wt % of triglyceride can be converted into the organic liquid production with a low acid number, implying alkali metal catalysts have greatly effect on the deoxygenation. Using Na<sub>2</sub>CO<sub>3</sub> to catalyze triglycerides have also been studied for many years, but the deoxygenation mechanism is still unclear. It was indicated that triglyceride was deoxidized through decarboxylation(DCO) and decarbonylation(DCO<sub>2</sub>) pathways to form hydrocarbon products mainly composed of alkanes and olefins[32, 33]. However, the mechanism of bonds breaking and converting to various hydrocarbon compounds with catalyst are unclear and need to be addressed.

Furthermore, terminal olefins was produced in the catalytic conversion process, as an important platform compound has enormous potential for material and energy use, such as plasticizers and lubricants[34]. Until now, the cracking of petroleum normal paraffin[35, 36] and the biological fermentation of stearic acid can produce terminal olefins[37-39]. But, the cracking of paraffin mainly obtained the short chain olefins, then produce long-chain terminal olefins need through polymerization reaction, was more complex experimental processes. The method of biological fermentation is a relatively popular method for producing long-chain terminal olefins. However, the cultivation of fermenting yeast is an obstacle to the improvement of production efficiency. Surprisingly, as our studies showed, more than 20 wt% terminal olefins (C8-C16) were exist in the mixed pyrolytic products, thus, investigating the thermochemical conversion mechanism of triglycerides also have greatly value for terminal olefins production.

The present work is aiming at proposing the thermochemical conversion mechanism for converting triglycerides into terminal olefins and normal paraffin. The BDEs changes will be investigated by selecting stearates as model compounds, due to that their structures are similar with the products which triglycerides were pyrolyzed by alkali metal catalysts. The effects of alkali metal ions on the dynamic behavior of triglycerides will be analyzed by the thermogravimetric (TG) tested

data. The mechanism will be eventually proposed by investigating the products through GC-MS, TG-IR, GC and XRD testing methods.

## 2. Experimental

### 2.1 Raw material

The soybean oil was obtained from industrial source, a yellow oily liquid, which density, heat value, viscosity and acid value were approximately, 0.91 ( $\text{kg}\cdot\text{m}^{-3}$ ), 38.8 ( $\text{MJ}\cdot\text{kg}^{-1}$ ), 64.5 (293 K,  $\text{mm}^2/\text{s}$ ) and 0.55 ( $\text{mg KOH}\cdot\text{g}^{-1}$ ), respectively. Model compounds were obtained from pharmaceutical reagent company: lithium stearate with a purity above 98% was produced by Adamas Reagent Co.,Ltd. China; sodium stearate and potassium stearate were with AR purity obtained from Sinopharm Chemical Reagent Co.,Ltd. China and Aladdin industrial corporation, China; rubidium stearate and cesium stearate with purity were above 98% both form Shanghai Dibo Biotechnology Co., Ltd. China.

### 2.2 Computational details

DFT calculations were performed by using the Gaussian 09 program[40]. In order to obtain the bond dissociation energies (BDEs) of the bond 1-6 (Figure 1), All geometries for the BDEs studied are fully optimized without using structural constrains or symmetry, geometry optimizations and frequencies were performed with same functional/basis set as B3LYP/6-311G\* level[41], aim to obtained the thermal correction to enthalpy ( $U_{\text{corr}}$ ). Single point energies ( $E_{\text{ele}}$ ) were computed as the M06-2X/6-311G\* level by using the optimized structures[42, 43].  $U(T) = E_{\text{ele}} + U_{\text{corr}}(T)$ . The reaction like as:  $A \rightarrow B + C$ ,  $\text{BDE} = U(T)_B + U(T)_C - U(T)_A$ . The calculated temperature is based on the thermogravimetric curve of the model compound, which are the average of the temperatures corresponding to the tangent of the five curves ( $\text{Li}^+ = 744 \text{ K}$ ,  $\text{Na}^+/\text{Rb}^+ = 766 \text{ K}$ ,  $\text{K}^+/\text{Cs}^+ = 763 \text{ K}$ ).

### 2.3 Kinetic analysis

As previous research has been reported that the thermochemical conversion mechanism of the triglycerides by the alkali metal catalysts such as  $\text{K}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$  were the triglycerides are decomposed to the fatty acids and then reaction with the alkali metal catalysts to form fatty acid alkali metal salts. Then, under the condition of external heating source, fatty acid salt deoxygenation and broken bond to production hydrocarbons. In order to investigate the influences of the different alkali metal ions on the cracking kinetic, corresponding model compounds (stearates) were tested by TG.

By using the distributed activation energy model (DAEM) method[44-46] to analyze the dynamic characteristic of pyrolysis the fatty acid salts. As the previous studies showed, Miura integral method[44] is a more accurate analysis method when analysis the dynamic characteristic thought TG test data in DAEM method. Miura integral method aim to calculate the activation energy and pre-exponential factor, and the calculating formula showed as follows:

$$\ln(\beta/T^2) = \ln(AR/E) + 0.75 - E/RT$$

T,  $\beta$ , A, E, are representative temperature, heating rate, pre-exponential factor and activation energy, respectively. The relationship between the conversion rate and temperature at disparate heating rates can measured according to the formula. Curves were made base on the TG experimental data, we can obtain the slope and intercept which representative the activation energy and pre-exponential factor. All the data was showed in the Table S1-S10.

## 2.4 TG-IR, GC analyses of model compounds for mechanism research

In order to study the catalytic conversion mechanism of the triglyceride by using the alkali metal salts (such as:  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Rb}_2\text{CO}_3$  and  $\text{Cs}_2\text{O}_3$ ) as catalysts. 5 model compounds (lithium stearate, sodium stearate, potassium stearate, rubidium stearate and cesium stearate) were analyzed by TG-IR, approximately 15 mg sample was used for the test, under the nitrogen atmosphere test temperature was raised from ambient to 1073 K with heating rate of 10 K/min, the components of each sample were tested by IR spectra. To study the deoxygenation pathways, thermal cracking experiments for each model compounds were carried out, for investigated the components of the pyrolysis gas. In a self-designed device (showed in the Figure S1-b), under the nitrogen atmosphere, 10 g stearates was thermal cracking at the temperature range of 573-773 K with the heating rate about 5 K/min, using the air bag collected the all pyrolytic gas, then the components of the gas were tested by gas chromatography.

## 2.5 Catalytic conversion of triglycerides by using alkali metal catalysts

Catalytic cracking of triglycerides (soybean oil) was also identified by using alkali metal salts ( $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ ) as catalysts. The catalytic cracking reaction were performed in a self-designed reactor (Figure S2-a), approximately 1200 g raw material and 10 wt% catalysts were pumped into the reactor, pyrolysis reaction were occurred at temperature range of 623-773 K under the atmospheric pressure. Reactor equipped with a rotor spun at a stirring speed of 350 rpm, the reactants were electrically heated (200 V) at a rate about 5 K/min, and the temperature of rectification column was set at 573 K. Approximately 623 K, water was the mainly product due to the neutralization reactions occur, as temperature raised the soybean oil was pyrolyzed and vaporized, and then vapor left the reactor pass through rectification column. Collected the whole liquid fuel products (the collected pyrolysis oil was performed by static liquid separation method, it can be clearly seen that there is water at the bottom, which is about 2-5 wt%) then the samples were identified by GC-MS analysis.

## 2.6 XRD analysis for the form of alkali metal ions in the solid residue

Thermochemical conversion of triglycerides to hydrocarbons were reaction with metal salts catalysts form fatty acid salts, then deoxygenation as the form of CO and  $\text{CO}_2$  to obtained hydrocarbons. But, the existence form of the metal element is still unclear after cracking reaction. Therefore, model compounds were combustion in the muffle furnace device at 772 K for 4 hour, and X-ray diffraction (XRD) was used to investigate the crystalline phases of the solid residue.

## 2.7 Analytical methods

Thermogravimetric (TG) analyses were performed on a Netzsch 409 PC synchronous analyzer, masses loss and DTG of different samples with temperature were measured during their decomposition. Approximately 3 mg of each stearates were tested under the nitrogen atmosphere at temperature ranging from room temperature to 1073K, and the heat rate were 5, 10, 20 or 30 K/min, respectively. TG-IR test setup equipped with a thermogravimetric analyzer (TG NETZSCH STA-449 F5) and a Fourier transform infrared spectrometry (Nicolet iS5). The test temperature was increased from ambient to 1073 K at the rate of 10 k/min with nitrogen as the carrier gas. TG-IR analysis was aim to investigate the changes of functional groups in molecular structure of different

stearates, the components of various stearates were obtained at 0.4 cm<sup>-1</sup> resolution from 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. Gas chromatography-mass spectrometry (GC-MS) was performed on an Agilent 6890N/5973N instrument, equipped with a 30m × 250µm × 0.25µm HP-5 capillary column, aim to determine the composition of the pyrolytic oil. Initial tested temperature was set to 323K holding for 2 min and then programmed to increase temperature to 553K at a rate of 5 K /min, and held for 20 min. 70 eV was the EI voltage of the MS ion source, and the mass spectral scanning range was 50–550 Da. The CO and CO<sub>2</sub> contents of pyrolytic gas composition were measured by the thermal conductivity detector of Tsushima GC-2104 gas chromatograph instrument (GC-TCD). The gases were analyzed by standard gas control method and peak area single point external standard method. Argon as the carrier gas, the oven temperature is set to 50 °C, and the TCD detector temperatures were at 373K. in order to study the crystalline phase of the solid residue, X-ray diffraction (XRD) analysis were performed on a D8 Focus diffractometer using CU-Kα radiation and operated at 40 KV, in the range of 2θ = 10-80 ° with a rate of 10 °.

### 3. Results and discussion

#### 3.1 Bond dissociation energy (BDE) analysis

Catalytic conversion of triglycerides to liquid hydrocarbons by metal salts catalysts have been studied many years. But, how did the metal ions effect on the bonds cleavage was not explained clearly. We used the computational method to illustrate the reason. The BDEs of bonds 1-6 as shown in Figure 2 were calculated to illustrate catalytic deoxygenation conversion. The results were listed in the Table 1. As Table 1 showed, when no catalyst cracking triglycerides, bond4 has the lowest BDE, leading to consume more carbon during deoxygenation. However, when introducing alkali metal in to the fatty acid, bond 3 becomes the lowest BDEs value compared with other bonds. Moreover, this can decrease the BDEs value up to 10 Kal/mol, leading to improve the likelihoods of cleavage the bond 3. Thus, introducing the metal ions into the long fatty acid chain can improve the carbon utilization economy of carbon atoms and deoxygenation efficiency due to the cleavage of bond 3.

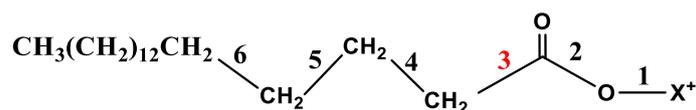


Figure.2. Bond 1-6 of the stearates content alkali metal ions.

Table.1. Bond dissociation energy of the stearates contain different alkali metal ion.

| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub> COOX | BDE <sub>1</sub> | BDE <sub>2</sub> | BDE <sub>3</sub> | BDE <sub>4</sub> | BDE <sub>5</sub> | BDE <sub>6</sub> |
|---|------------------|------------------|------------------|------------------|------------------|------------------|
| X=H   | 120.0            | 117.0            | 100.0            | 91.2             | 95.2             | 130.2            |
| X=Li  | 126.5            | 141.6            | 90.0             | 89.2             | 89.2             | 125.1            |
| X=Na  | 109.8            | 144.9            | 84.7             | 89.7             | 89.7             | 89.9             |
| X=K   | 109.7            | 144.0            | 83.9             | 88.0             | 88.0             | 88.3             |
| X=Rb  | 108.1            | 147.4            | 87.4             | 89.5             | 89.5             | 89.9             |
| X=Cs  | 113.6            | 144.0            | 89.0             | 92.9             | 92.9             | 92.9             |

Energies are in Kal/mol, calculation temperature: Li<sup>+</sup>=744 K, Na<sup>+</sup>/Rb<sup>+</sup>=766 K, K<sup>+</sup>/Cs<sup>+</sup>=763 K.

#### 3.2 Kinetic analysis

Computation calculations have been proved that introducing metal ions have influence on the

BDEs of deoxygenation reaction. Moreover, samples have different BDEs on bond broken due to the metal ions influence. In addition, the dynamic behavior also investigated by TG analyses, the results were showed in the Figure 3 a. As we can see, the activation energies of different stearates with the respective metal alkali ions decreased as the order:  $K^+ > Na^+ > Rb^+ > Cs^+ > Li^+$ , ranging from 190 KJ/mol to 240 KJ/mol. And potassium stearate have the maximal activation energy number about 238 KJ/mol, lithium stearate have the lowest activation energy approximately 193 KJ/mol. Implying that metal ions have effect on the dynamic behavior. To some extent, dynamic behavior also has connected with ions radius, the ions radius decreased as the order:  $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$  (Figure 3 b), we find the magnitude of the activation energy increases first and then decreases as the ionic radius increases. That is, ion radius and BDE are contradictory.

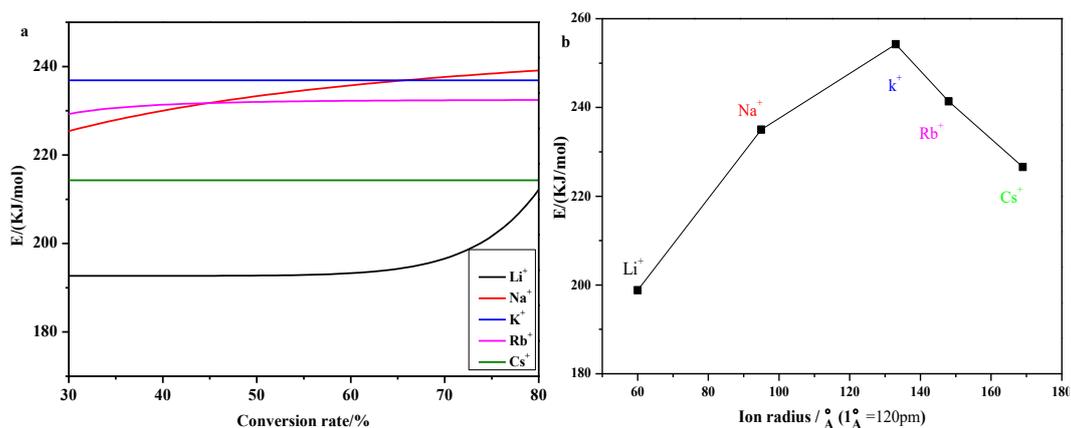


Figure.3. Activation energy variation curves of stearates containing different alkali metal ions (a). Curve of the relationship of activation energy and ions radius (b).

### 3.3 Thermochemical conversion mechanism investigated by TG-IR, GC, GC-MS, and XRD analyses

#### 3.3.1 TG-IR and GC analyses result

TG-IR tests were used to analyze the pyrolysis components during the catalytic conversion of triglycerides process (the process as same as the decomposition of stearates). And the detail information are showed in the Figure 4, a/b are TG/DTG curves of various stearates with the heating rate 10 K/min. As we can see, stearates were started decomposed at temperature about 693 K and end at the temperature approximately 783 K. Form the curves, the first weight loss were from loss of the moisture, and the second loss were form the bond broken, leading to obtained organic hydrocarbons. And a low activation energy reaction corresponds to the low pyrolysis temperature, for example, lithium stearate with corresponds lowest activation energy which decomposed at 683 K -763 K. On the other hand, conversion rate also have relationship with decomposed temperature, lower decomposed temperature have the higher conversion rate, especially for lithium stearate reach for about 84 %. On the other hand, form Figure 4b, DTG have the same variation trend with the TG curves, lower activation energy have the higher DTG (conversion rate/temperature) in lower temperature range. In a ward, at the temperature range of 683–763 K, lithium stearate have higher conversion rate exceed 80 %. For this, introducing lithium ion to catalytic triglycerides should be favored compared with others alkali metal ions.

In addition to exploring dynamic behavior, another purpose of this paper is to study the

mechanism of deoxygenation. TG-IR also can analyze the components of during the decomposition process. The results are presented in 3D and 2D forms in Figures 4 c-d and Figures S3. Figures 4 c-d are 3D (c) and 2D (d) representations of TG-IR analyses of the product evolved from lithium stearate. Form the 3D TG-IR diagram, decomposing reaction were started at about 50 min (~ 683K), and the stereoscopic peak strength representations main products are hydrocarbons (~3000 cm<sup>-1</sup>), CO (~2170 cm<sup>-1</sup>) and CO<sub>2</sub> (~671, 2350 cm<sup>-1</sup>). And the 2D diagram is IR absorption curves at 10, 30, 50 and 70 min, and we also know different characteristic peaks represent different groups, such as, =CH<sub>2</sub>- (~3085 cm<sup>-1</sup>), CH<sub>2</sub>- (2930 and 2850 cm<sup>-1</sup>), RCH<sub>2</sub>=CH<sub>2</sub>- (910 and 990 cm<sup>-1</sup>)[47, 48]. As for the other model compounds, as showed as in the Figure S2-S5, the characteristic peaks as same as the lithium stearate in general. Thus, form the TG-IR diagrams, we can propose that the decomposed of the stearates were first deoxygenation mainly as the form of CO and CO<sub>2</sub>, leading to obtain the long carbon chain radical.

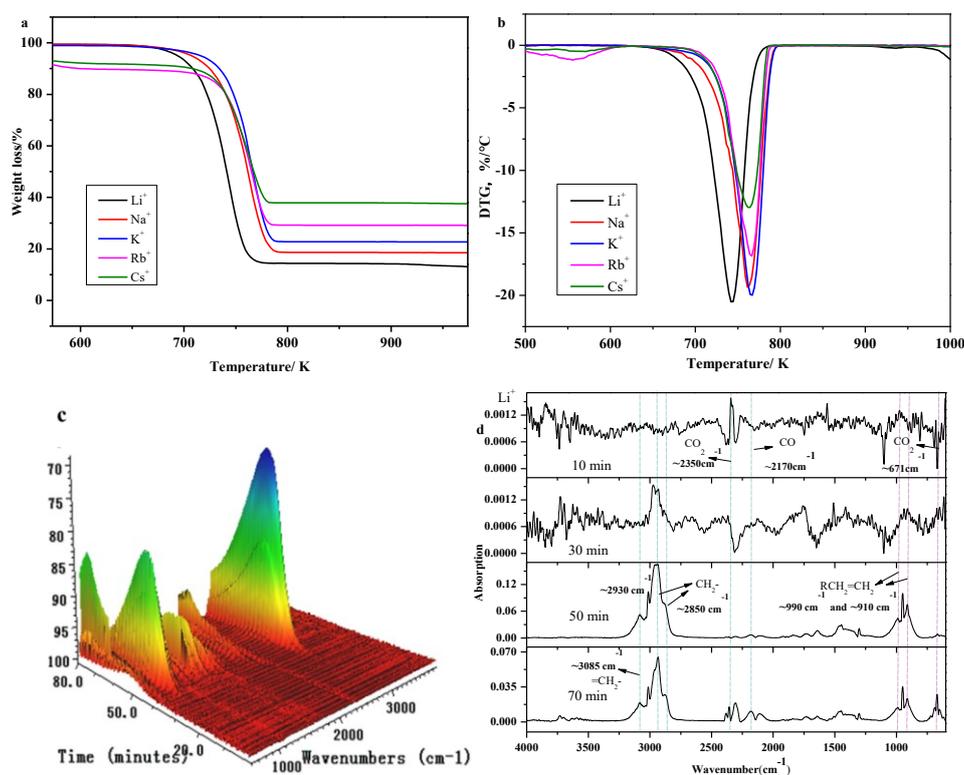


Figure.4. TG (a) and DTG (b) curves of various stearates with the heating rate 10 K/min. 3D (c) and 2D (d) representations of TG-IR analyses of the product evolved from lithium stearate.

Deoxygenations are mainly through DCN and DCX pathways, and we used GC-TCD analyze the gaseous products, collected form pyrolysis reaction of stearates. The contents ratio of CO/CO<sub>2</sub> are listed in Table 2, in general, CO contents ratio is higher than CO<sub>2</sub>, CO was usually detected as the major product in this type of stearate. Thus, the cleavages of carbon-oxygen bonds were predominant through DCN pathway.

Table.2. CO and CO<sub>2</sub> contents ratio of pyrolysis of stearates basis on GC-TCD analyses

| Stearates          | CO:CO <sub>2</sub> |
|--------------------|--------------------|
| Lithium stearate   | 2.27:1             |
| Sodium stearate    | 2.42:1             |
| Potassium stearate | 3.86:1             |

|                   |        |
|-------------------|--------|
| Rubidium Stearate | 2.20:1 |
| Cesium Stearate   | 4.23:1 |

### 3.3.2 GC-MS analysis result

Our aim were to investigate the thermochemical conversion mechanism, which including deoxygenation, and then undergo various reactions such as bond scission, disproportionation, hydrogen abstraction, isomerization and aromatization. As above mentioned, catalytic conversion triglycerides were first deoxygenated as the form of CO (main deoxygenation pathway), CO<sub>2</sub> and some H<sub>2</sub>O, leading to form the long carbon chain. For further to propose the bond broken and formed processes, the organic liquid were tested by GC-MS, which were obtained from catalytic cracking experiment of triglyceride by using Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> as the catalysts. As Figure 5 showed, pyrolysis products are with different carbon chain distribution at range of C8-17, and peaks also have disparate intensity representing their contents. We also investigated the GC-MS results, the content of the different products is roughly determined by the area ratio of the peaks. We find that the product mainly includes alkanes (paraffin and naphthenic), olefins, and aromatic hydrocarbons. Alkanes and olefins accounting for about 70% of the major portion, aromatic hydrocarbons are about 5-10%, and other products such as alkynes, aldehydes, ketones, acids, esters and other oxygenates.

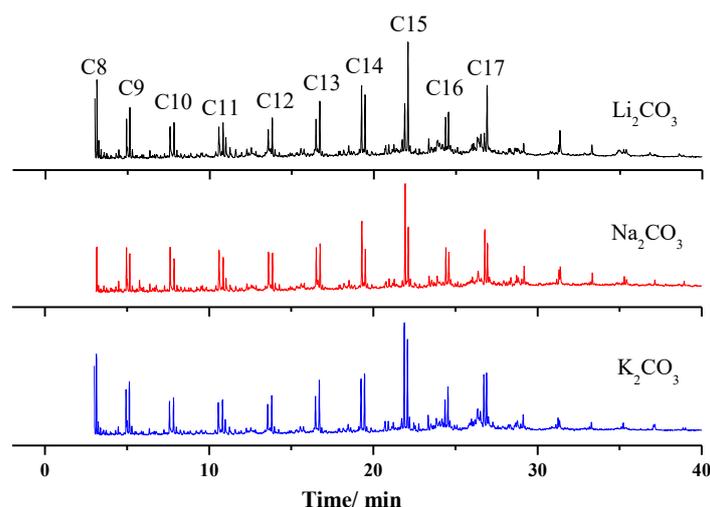


Figure.5. GC-MS chromatograms of pyrolysis oil by using Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> as the catalysts.

### 3.3.3 XRD analysis result

Catalytic conversions of triglycerides O atoms are removed as the CO, CO<sub>2</sub> and some H<sub>2</sub>O to form organic hydrocarbons. But, the form of alkali metal ions remains unclear, in order to investigate the catalytic mechanism, XRD was used to identify the crystalline phases of the pyrolysis solid. Figure 6 are the XRD spectra of the solid residue collected from the model compounds pyrolysis experiments, as the #1-5 were the solid residues collected from the lithium stearate, sodium stearate, potassium stearate, rubidium stearate and cesium stearate, respectively. As the #1 showed, different peaks appeared at 21.3°, 23.4°, 29.5°, 30.6°, 31.8°, 34.1°, 36.1°, 36.9°, 39.5°, 40.0°, 48.7° and 59.7°, respectively, which are respective the characteristic peaks of the Li<sub>2</sub>CO<sub>3</sub>[58]. As for the #2, peaks appeared at 26.0°, 27.6°, 30.1°, 33.1°, 34.2°, 34.5°, 35.2°, 38.0°, 39.9°, 41.2°, 44.5°, 46.6°, 48.3°, 48.4°, 53.6° and 62.7° were the characteristic peaks of Na<sub>2</sub>CO<sub>3</sub>[59]. Moreover, as we analyzed that

#3, #4 and #5 were respective  $K_2CO_3$ ,  $Rb_2CO_3$ ,  $Cs_2CO_3$ , respectively. And the XRD were also performed on  $M_2CO_3$  ( $M=Li, Na, K, Rb, Cs$ ), which XRD diagrams are showed in the Figure S4, comparing with those XRD diagrams, we find the metal ions are finally exist as the form of  $M_2CO_3$ .

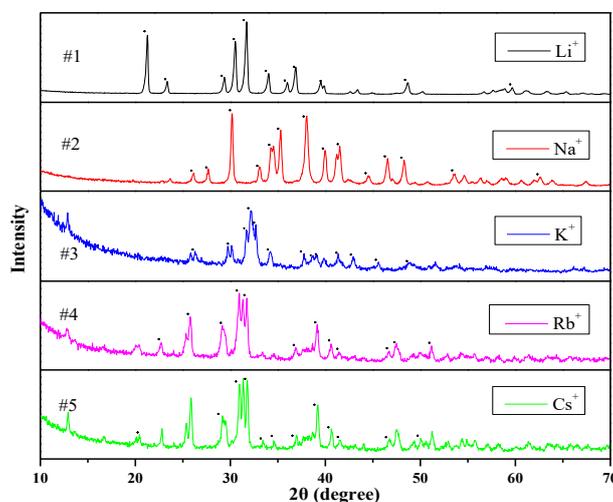


Figure.6. XRD spectra of solid residue of different stearates

### 3.4 Propose catalytic conversion mechanism

Catalytic conversion of triglycerides by introducing alkali metal ions was first to form fatty acid salts as the intermediate, as the calculation result that introducing alkali metal ions is help for decrease the BDEs, leading to the removal of O atoms. And the O atoms are removed as the form of CO,  $CO_2$  and  $H_2O$ . In addition, fatty acid salts decarboxylation to generate the long fatty acid carbon chain free radicals. Then, under the temperature of 623-773K, organic hydrocarbons were produced through different reaction (bond scission, disproportionation, hydrogen abstraction, isomerization and aromatization).

Therefore, the catalytic conversion mechanism was proposed in Figure 7, the reason for the inference is as follows:

(1)The way of removing oxygen atoms and the form of alkali metal ions: as the computational calculation showed, cleavage of bond 3 (Figure 2) were favored, and GC tested that O atoms are removed as form of CO,  $CO_2$  also with some  $H_2O$ . So, we speculate that mainly broken the bond 3. In addition, the XRD analyses of the solid residue showed the alkali metal ions are as the form of  $M_2CO_3$ . Thus, deoxygenation process were through DCN and DCX pathway to form  $M^+O$  and  $M^+$ , then reaction with the  $CO_2$  (form pyrolysis gas or air) to form the  $M_2CO_3$ . On the other hand, the content ratio of CO was higher than  $CO_2$ , thus, some part of the MO group most likely reaction with the hydrogen radicals to form  $H_2O$ .

(2) Key intermediates in the cleavage reaction- terminal olefins and hydrogen radicals: as the TG-IR analyses indicated, there are obvious terminal olefin characteristic peaks in the decomposition products of the stearates. And about 15-20 % terminal olefins were detected, which exist in the pyrolysis oil of the triglycerides (soybean oil). Therefore, long fatty acid carbon chain free radicals with the most maximum likelihood to dehydrogenate to form terminal olefins, which also produce hydrogen radical. This can explains the presence of the paraffin according to GC-MS analyses, due to the terminal olefin reaction with the shed hydrogen radical. In addition, as the calculation result showed (Figure S2 and Table S12), free radicals near the end of the long carbon chain are more likely to be fall off, leading to produced terminal olefin under the high temperature

condition.

Above all, catalytic conversion mechanism of triglycerides by introducing alkali metal ions were first form fatty acid salts. Then, under the temperature of 663-773 K, fatty acid salts were deoxygenation mainly through DCX and DCN pathways to form long fatty acid carbon chain free radicals, and producing  $M^+$  and  $M^+O$ , respectively. The alkali metal ions are finally reaction with  $CO_2$  to form the  $M_2CO_3$ . Then, long fatty acid carbon chain free radicals dehydrogenation to obtain terminal olefins and hydrogen radical. Under high temperature conditions, organic hydrocarbons were obtained through different reaction (such as bond scission, disproportionation, hydrogen abstraction, isomerization and aromatization).

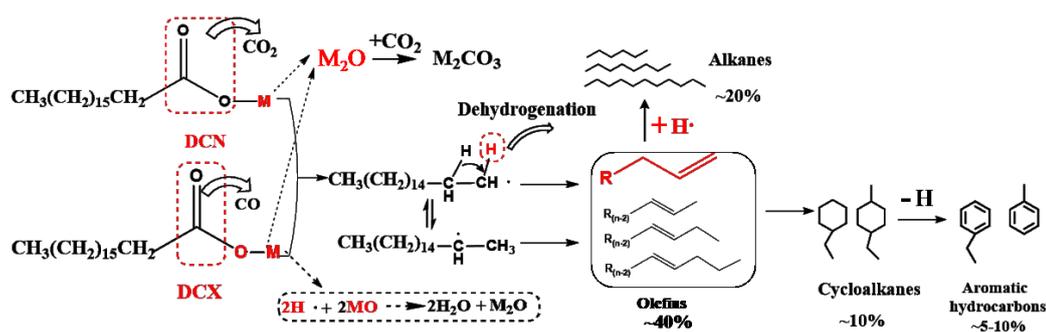


Figure.7. proposed catalytic conversion deoxygenation mechanism of triglycerides by introducing alkali metal ions.

#### 4. Conclusions

In this paper, DFT computation technology were used for bond dissociation energy calculation, results implying use alkali metal catalysts cracking triglycerides can decreased bond dissociation energy, especially for  $\alpha$  carbon-carbon bond, leading to effective deoxygenation for organic hydrocarbons production. In addition, according to bond dissociation energy data, the alkali metal ions have different influence on the dynamic behavior. Thus, the dynamic behavior of catalytic conversion of triglycerides by introducing alkali metal ions were investigated, using stearates as model compounds tested by TG analyses, and the activation energy of pyrolysis reaction also calculated, find that introducing the Li ion has the lowest activation energy. Indeed, we found low activation energy means low reaction temperature and high conversion rate.

Furthermore, thermochemical conversion mechanism of triglycerides catalyzed by alkali metal catalysts was investigated, according to TG-IR, GC, GC-MS and XRD analyses. Mechanism was proposed as follows: triglycerides decomposed to fatty acids and then neutralized with alkali metal ions to form fatty acid salts, under the 663-773 K condition, O atoms are mainly removed as the form of  $CO$ ,  $CO_2$  (less than  $CO$  content) and some  $H_2O$ . Like this, long fatty acid carbon chain free radicals and  $M^+O$  /  $M^+$  were produced, alkali metal ions finally exist as the form of  $M_2CO_3$  as the XRD analyses showed. And hydrogen leaving the terminal of the long fatty acid carbon chain free radicals to formed terminal olefins and hydrogen radicals. Due to the instability of olefin under the pyrolysis conditions, random reaction occurs (such as bond scission, disproportionation, hydrogen abstraction, isomerization and aromatization) to product various organic hydrocarbons.

Detailed thermochemical conversion mechanisms were proposed, clarifying well the catalytic conversion triglycerides process catalyzed by alkali metal catalysts. According to the mechanism and analyses of liquid products, terminal olefins can generated, which an important intermediate or

product, have great potential for molecular structure design for energy material and energy products. In addition, organic hydrocarbons generated from pyrolysis reaction has significant application prospects for hydrocarbons liquid biofuel (aviation biofuel and biodiesel). Thus, investigated mechanism has greatly effective for production utilization and guidance for catalytic cracking reactions of triglycerides.

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