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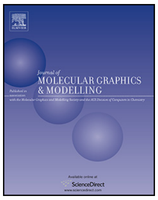

# Theoretical Study on Free Fatty Acid Elimination Mechanism for Waste Cooking Oils to Biodiesel over Acid Catalyst

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ABSTRACT

A theoretical investigation on the esterification mechanism of free fatty acid (FFA) in waste cooking oils (WCOs) has been carried out using DMol$^3$ module based on the density functional theory (DFT). Three potential pathways of FFA esterification reaction are designed to achieve the formation of fatty acid methyl ester (FAME), and calculated results show that the energy barrier can be efficiently reduced from 88.597 kcal/mol to 15.318 kcal/mol by acid catalyst. The molar enthalpy changes ($\Delta_r H_m{}^\circ$) of designed pathways are negative, indicating that FFA esterification reaction is an exothermic process. The obtained favorable energy pathway is: $H^+$ firstly activates FFA, then the intermediate combines with methanol to form a tetrahedral structure, and finally, producing FAME after removing a water molecule. The rate-determining step is the combination of the activated FFA with methanol, and the activation energy is about 11.513 kcal/mol at 298.15 K. Our results should provide basic and reliable theoretical data for further understanding the elimination mechanism of FFA over acid catalyst in the conversion of WCOs to biodiesel products.

## 1. Introduction

With the rapid development of international economy, the global energy supply has become more and more strained. However, the problems confronting us are worldwide energy shortages and rising energy prices due to the continuous consumption of non-renewable traditional fossil fuels. In the past decades, scientists have spared no effort to explore for new replacements of energy sources. Results found that the waste cooking oils (WCOs), including inedible vegetable oils or animal fats [1–5], could be used as feedstock for the synthesis of biodiesel because of its low price and abundant source, which had attracted worldwide attentions to employ biodiesel as the alternative of traditional fossil fuels [6–9].

At present, the homogeneous catalytic *trans*-esterification method is mainly used for the industrial synthesis of biodiesel products with acid or alkali catalysts. However, there exists a critical deficiency of the soap formation in catalytic process for the reason of its higher level of free fatty acid (FFA) using WCOs as feedstocks, which can consume the oils and catalysts, resulting in the difficulty for separation of products [10,11]. Therefore, it would become rather important to eliminate the FFA before biodiesel synthesis. For instance, Wang et al. employed ferric sulphate as heterogeneous acid catalyst to achieve the methanolysis of FFA in a new two-step catalysis process for the synthesis of biodiesel, exhibiting the higher conversion efficiency and several advantages, including no acidic wastewater, high efficiency, low equipment cost, easy recovery of catalysts, and so on [12]. Zafiropoulos et al. applied a novel diarylammonium catalyst to esterify the FFA in greases to fatty acid methyl ester (FAME) and successfully reached the FFA content of <1% [13]. Corro et al. reported that $ZnO/SiO_2$ heterogeneous photocatalyst exhibited an excellent efficient esterification of FFA [14], and $SiO_2 \cdot HF$ solid catalyst played a key role for the FFA esterification reaction in a two-step biodiesel producing process from *Jatropha curcas* crude oil [15]. Such experimental studies could provide us with experimental parameters like molar ratio, reaction time and temperature, but the correlative reaction mechanism, as an important aspect of catalytic reaction, has been ignored intentionally or unintentionally. Moreover, the potential theoretical mechanisms for FFA esterification have not been previously reported in the literature, motivating our intense initiative and interest. Based on quantum chemical methods at the molecular level, an insight into

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**Table 1**
Imaginary frequency of each transition state.

| Transition state | Imaginary frequency ($cm^{-1}$) |
|---|---|
| TS1-1 | −492.24 |
| TS2-1 | −424.03 |
| TS2-2 | −418.99 |
| TS3-1 | −412.92 |
| TS3-2 | −423.63 |

the FFA esterification reaction mechanism should provide basic theoretical information and significant guidance efficiently exploring efficient methods for FFA elimination using density functional theory (DFT).

In this work, oleic acid, as a typical kind of FFA in WCOs [16], has been selected as the representative reactant. Oleic acid was esterified with methanol by homogeneous acid catalyst in DMol$^3$ module to reveal the correlative mechanisms of FFA esterification via searching for the transition states and possible intermediates of the designed pathways, and analyzing the structure microscopic parameters, thermodynamic function change and kinetic function change. Our obtained results will provide a theoretical reference for FFA esterification reaction in the utilization of WCO for biodiesel synthesis.

## 2. Computational details

DFT calculations are conducted using the DMol$^3$ module in Materials Studio (MS) 6.0 developed by Accelrys Inc. Firstly, the geometry optimization for reactants and products are performed at the Generalized Gradient Approximation (GGA) level [17] to ensure the calculation efficiency. The double numerical basis set with polarization functions (DNP) is chosen as the basis set, whose accuracy is comparable to a Gaussian 6–31 (d) basis and exhibits excellent consistency with experiments. In the geometry optimization process, the convergence tolerance of energy is $1.0 \times 10^{-5}$ Ha, maximum force is 0.002 Ha/Å, and maximum displacement is 0.005 Å. Moreover, in order to ensure high quality results, the real space global orbital cutoff radius is set as high as 4.0 Å and the smearing of electronic occupations is 0.005 Ha. Then geometry-optimized reactants and products involved in each step are considered for defining atom-pairing, so that a 3D trajectory file representing the reaction pathway preview is generated for each step with the Reaction Preview tool of MS software. These 3D trajectory files are used as inputs to obtain the corresponding transition states (TS) by Complete LST/QST approach [18,19], with the B3LYP/DNP method [20,21] which has been demonstrated to give more accurate results for the energetics, structures and vibrational properties of molecules than GGA and Local Density Approximation (LDA) functions [22]. The linear-synchronous-transit (LST) is conducted to bracket the maximum between the reactants and products, followed by repeated conjugate gradient minimizations and the quadratic-synchronous-transit (QST) maximizations until a transition state was located. The root-mean- square (RMS) force is 0.01 Ha/Å and the maximum number of allowed QST maximization cycles is 10. In addition, frequency analysis has been used to validate the transition state with only one imaginary frequency (shown in Table 1), which implies that the transition state should be a saddle point on the potential energy surface, and TS confirmation is performed on every transition state to confirm that they lead to the presumed reactants and products by the intrinsic-reaction-coordinate (IRC) analysis. It validates a transition state with the nudged elastic band method[19] by introducing a fictitious spring force that connects the neighboring points to ensure continuity of the path, and then it projects the force, so that the system converges to the minimum energy path [23]. The convergence tolerance in TS confirmation is the same as geometry optimization. Meanwhile, the electronic energy (Eelec) and Mulliken atomic charges of all the structures are calculated, and the standard entropy ($S^\circ$), enthalpy ($H^\circ$) and Gibbs free energy ($G^\circ$) are obtained by frequency analysis.

## 3. Results and discussion

### 3.1. Designed pathways for the FFA eliminating reaction

The typical FFA eliminating reaction is an esterification reaction of FFA with methanol over acid catalyst to produce FAME. It is generally designed as the first step in a two-step process for biodiesel synthesis from WCO. In this paper, an esterification reaction between oleic acid and methanol is catalysed by $H^+$ in DMol$^3$ module, and three potential pathways of FFA esterification reaction mechanism are shown in Fig. 1.

Path 1 is a simply oleic acid one-step esterification reaction without catalyst. The esterification process catalyzed by $H^+$ is generally represented using a SN2 mechanism in organic chemistry textbook, as in the designed Path 2. Path 2 is a four-step process catalyzed by $H^+$. Step 1 is the protonation of the carboxylic moiety of FFA, and oleic acid is activated to form an intermediate 1 (IM2-1). In Step 2, the activated oleic acid combines with methanol to form a tetrahedral structure (IM2-2). Step 3 belongs to the water-removing process existing in the IM2-2 molecule. Step 4 is a $H^+$ desorption process, and finally producing oleic methyl ester. The esterification, as a nucleophilic process, could occur in the following SN1 mechanism, thus a SN1 pathway is designed as Path 3 in this paper. Path 3 includes four steps. Step 1 is a hydrogen-bond adsorption process between oleic acid and $H^+$ because of the higher electric density of O-atom in oleic acid, and the oleic acid is activated to form an intermediate (IM3-1). Step 2 is a water-removing process happening in the activated oleic acid. In Step 3, methanol combines with the $C^+$ that has been formed. Step 4 is a $H^+$ desorption process, and finally producing oleic methyl ester.

### 3.2. The structures of reactants, intermediates, transition states and products

Firstly, the structures of reactants, intermediates and products should be geometrically optimized, obtaining the transition states after the process of TS confirmation. Meanwhile, five chemical bonds, closely related to the reaction mechanism, are monitored, including C1–O1, C3–O3, H3–O1, H3–O2 and H3–O3 (marked in Fig. 2), to reveal the interaction among species involved in each pathway.

The calculated chemical bond lengths are presented in Fig. 3, and the relevant energies of stationary points for the three pathways are shown in Fig. 4. In Path 1, oleic acid interacts with methanol to produce oleic methyl ester via TS1 with only one imaginary frequency. Methanol migrates to C1 followed by C1–O1 cleavage, and the bond length alternates from 1.373 to 2.915 Å. The energy barrier of 88.579 kcal/mol is relatively higher, indicating that the formation of TS1 is very difficult. In Path 2, the bond lengths have no significant change between R2 and IM2-1, except the reduction of H3-O2, corresponding to the protonation of carboxylic moiety of oleic acid. Then the C3-O3 bond length has an increasing tendency, from 1.433 Å (IM2-1) to 1.460 Å (TS2-1) and finally to 1.463 Å (IM2-2), because of the repelling effect caused by large steric hindrance of the tetrahedral structure. The calculated energy barrier of 15.318 kcal/mol is relatively higher than next step, suggesting that it should need more energy to overcome steric hindrance than to break the C1-O2 bond. At the same time, C1-O1 bond length