Transesterification of Biodiesel by Molecular Modeling and Simulation

Wimonmas Masomboon, Thanita Sonthisawate, Pirawat Thongjun and Thongchai Rohitatisha Srinophakun*
Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok, Thailand

* Corresponding author. E-mail: fengtcs@hotmail.com
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Abstract
Transesterification of alkyl esters plays an important role in biodiesel production, and a critical substance in this mechanism is triacylglycerol. A molecular modeling technique is used in this study to determine the geometrical parmeters of triacylglycerol via semi-empirical AM1, PM3 and ab initio HF/6-31G with the GaussView 03W and GAUSSAIN 03W pieces of software. The results obtained from these three models showed that the geometrical parameters of the triacylglycerol molecules are in the same range. Hence, these molecular models can be used in the simulation of the transesterification mechanism. There are six possible mechanisms for the biodiesel transesterifications. Each type of mechanism contains six reaction steps. Using the B3LYP/6-31G//PM3 method, the transesterification mechanism was simulated to determine the best possible pathway.

Keywords: *Transesterification, Biodiesel, Molecular modeling, Triacylglycerol molecule*

1 Introduction

Biodiesel, as mono-alkyl esters of fatty acid derived from vegetable oils or animal fats, has demonstrated a number of beneficial characteristic, including lower exhaust emissions. Generally, biodiesel can be produced from renewable resources, thereby relieving reliance on petroleum fuel imports. Compared to petroleum-based diesel, biodiesel is biodegradable and essentially non-toxic, while having lower emissions of carbon monoxide and a higher flash point [1,2]. These make it a good alternative to petroleum based fuel and have led to its use in many countries, especially in environmentally sensitive areas [3]. Biodiesel has good heating power and provides exhaust gas with almost no sulfur or aromatic polycyclic compounds. However, there are many problems associated with using it directly in diesel engines (especially in a direct injection engine). These include coking and trumpet formation on the injectors. Fuel atomization does not occur properly, or is even prevented, as a result of plugged orifices, carbon deposits, oil ring sticking and thickening or gelling of the lubricating oil as a result of contamination by vegetable oils, while lubricating problems [4] are limited because of the high viscosity (nearly 10 times that of gas oil) [5]. The main process that has been investigated in attempts to overcome these drawbacks and improve the properties of the vegetable oils is called "Transesterification" or "Alcoholysis" [6].

Specific catalytic system needs to be implemented to transesterification. Alkali, acid or enzymes. Alkali catalyzed transesterification is much faster than acid catalyzed one [7]. The alcohols are primary and secondary monohydric aliphatic alcohol having 1-8 carbon atoms [8] that can be used in the transesterification. It can quickly react with triglyceride after formulated the oxide form with sodium hydroxide (NaOH). After transesterification of triglyceride, the products are a mixture of esters, glycerol, alcohol, catalyst and tri-, di- and monoglyceride [9]. The monoglyceride causes turbidity in the mixture of

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esters. The by-product (glycerol) needs to be recovered because of its additional value for industrial chemical.

Molecular modeling would therefore appear to be concerned with ways to mimic the behavior of molecules and molecular systems. The model that most chemist first encounter are molecular models such as the "stick" models devised by Dreiding or the "space filling" models of Corey, Pauling and Koltun (commonly referred to as CPK models) [10].

Cummins and Gready [11] used semi-empirical AM1 and PM3 methods to describe molecular interactions. Their method was applied to calculate the free energy of the enzymatic reduction of dihydrofolate (DHF) with nicotinamide adenine dinucleotide phosphate (NADPH) via *Escherichia coli* dihydrofolate reductase. The free energy change of this reaction agreed with the experimental results. *Ab initio* methods have used density functional theory (DFT), which was suitable for simulating reactions [12,13].

In this study, molecular model and dynamics will be applied to help researchers for better understanding of biodiesel production with the new approaches and without spending unnecessary materials and expense in exercising the experiment.

2 Methodology

All molecular geometries in this study are formulated by GaussView [14]. Gaussian 03W is used to predict the properties of molecules and reactions. Even though, geometrical parameters are determined by gas phase assumption, that stable molecular structure is acceptable by means of the minimum molecular energy. The exact structures or possible structures with the lowest molecular energy will be used in the stage of molecular simulation to complete the transesterification mechanism in molecular level. At first, the stable geometrical molecular structures of triacylglycerol as shown in Figure 1 will be formulated and studied. Other substances such as alcohol (methanol), catalyst (sodium methoxide ion, potassium methoxide ion etc.) can be modeled directly due to their well-known structures available.

The transesterification can be divided into three steps according to acylglycerol (mono-, di-, and triacylglycerol) reactions. These steps refer to an experimental result and will be confirmed by simulation. In this article, in each step, the reactions will be introduced and optimized by PM3, AM1 and HF/6-31G. PM3 (Parameterized Model number 3) and AM1 (Austin Model 1) are semi-empirical methods for the quantum calculation of molecular electronic structure. They are based on the Neglect of Differential Diatomic Overlap integral approximation. HF/6-31G is a method of Gaussian 03 by Hartree-Fock. 6-31G is basis sets defined as part of the Complete Basis Set methods [14].

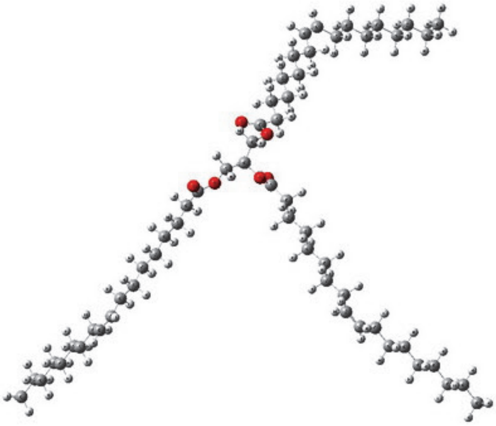


Figure 1: Molecular structures of triacylglycerol.

In the first step, the acylglycerol and methoxide ion as the catalyst will formulate an intermediate I. Then, this intermediate I and methanol produce an intermediate II. The intermediate II is reformed to fatty acid methyl ester (FAME) and glycerol. Figure 2 concludes those steps for triacylglycerol, diacylglycerol and monoacyl-glycerol.

There are two simultaneous reactions at the beginning of the transesterification process: acylglycerol with a methoxide ion and with methanol. The distance between active sites in the transesterification reaction can be determined. The first active site is found between the carbon atom in the carbonyl group of acylglycerol (C=O) and the oxygen atom of a methoxide ion. The second active site is a site between an oxygen atom next to the carbon atom in the carbonyl group of acylglycerol (C=O) and a hydrogen atom of methanol. The distance between acylglycerol and the methoxide ion is in a range of 1.430 to 1.600 Å, and the distance between the product of the first reaction (intermediate I, or product of step 1) and methanol is in a range of 0.9 to 1.2 Å. Finally, all reactions are simulated based on semi-empirical PM3 to find the minimum reaction distance.

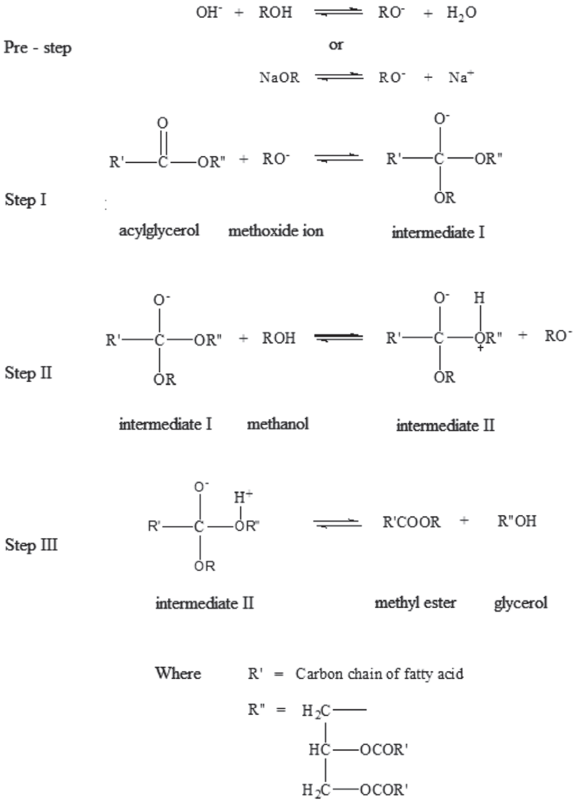


Figure 2: Mechanism of base catalyzed transesterification.

3 Results and Discussion

The geometrical parameters of the triacylglycerol molecule are shown by the relationship between molecular energy and optimization step numbers. A Gaussian simulation can propose the possible and stable transesterification reactions in biodiesel production.

3.1 *Geometrical parameters of triacylglycerol*

The optimal bond lengths of the triacylglycerol molecule, calculated by semi-empirical AM1 and PM3 and *ab initio* HF/6-31G, are listed in Table 1.

The single bond lengths of triacylglycerol from *ab initio* HF/6-31G are longer than from semi-empirical AM1 and PM3, while the double bond lengths of triacylglycerol from semi-empirical AM1 are longer than from semi-empirical PM3 and *ab initio* HF/6-31G. The optimization steps in the three methods are shown in Figure 3.

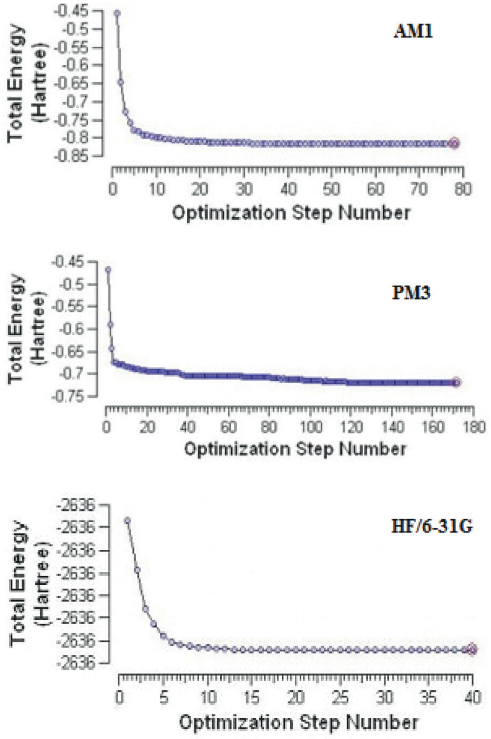
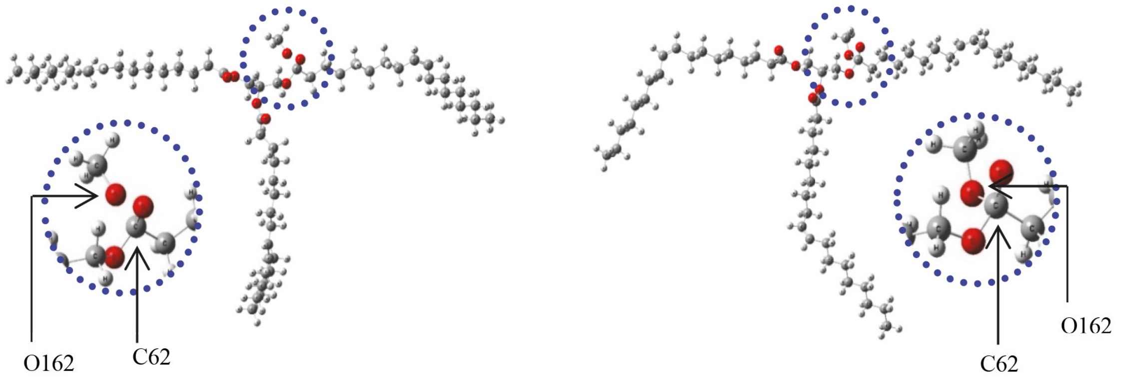


Figure 3: Total energy of triacylglycerol optimization in semiempirical AM1, PM3 and *ab initio* HF/6-31G models.

Table 1: Equilibrium geometrical parameters of the triacylglycerol molecule in the ground state

Parameter	Semi-empirical		*Ab initio*
	AM1	PM3	HF/6-31G
C2 - O8	1.427	1.416	1.438
C5 - O61	1.435	1.419	1.438
C166 - O1	1.437	1.433	1.440
C9 - O8	1.374	1.372	1.396
C62 - O61	1.370	1.369	1.396
C114 - O1	1.369	1.365	1.397
C9 = O10	1.232	1.215	1.215
C62 = O63	1.232	1.214	1.215
C114 = O115	1.231	1.215	1.214
C32 = C34	1.338	1.334	1.313
C85 = C87	1.338	1.334	1.313
C137 = C139	1.338	1.334	1.313

The number of optimization steps is different according to the model employed: AM1, PM3 and HF/6-31G have 80, 180 and 40 steps, respectively (Figure 3). Triacylglycerol optimization is studied by the *ab initio* method HF/6-31G. This method requires a



(a) Triacylglycerol + methoxide ion (b) Intermediate I

Figure 4: Reaction structure of triacylglycerol and methoxide ion in transesterification of triacylglycerol: (a) input and (b) output.

lengthy computational time. The initial structure is then used for calculating the optimal molecular structure by PM3 method. From these optimal structures, the molecular energy is expressed in terms of relative energy, which is based on the B3LYP/6-31G//PM3 method. The relative energy, calculated using B3LYP/6-31G//PM3 and B3LYP/6-31G//HF/6-31G models, is -1.39 and -34.16 kcal/mol, respectively. From consideration in molecular energy, the AM1, PM3 and HF/6-31G methods as same as optimal structure and molecular energy. These three methods can then be used in molecular optimization.

Semi-empirical AM1 and PM3 and *ab initio* HF/6-31G can identify the geometrical parameters of triacylglycerol. From a molecular optimization viewpoint, the PM3 method is most suitable for studying the molecular reactions of the transesterification mechanism because of its shorter computational time and high accuracy.

3.2 *Transesterification mechanism (in Type 1)*

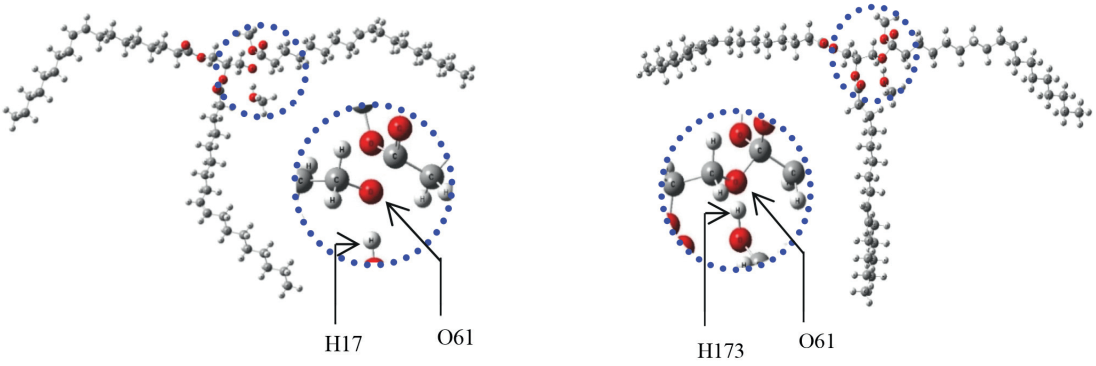
The mechanism of the transesterification reaction is calculated by the semi-empirical PM3 method, while the estimation of molecular energy is performed by the *ab initio* B3LYP/6-31G method (B3LYP/6-31G//PM3 method). From this simulation, the mechanism of the transesterification reaction can be predicted by its relative energy. The reaction can be categorized into six types, with each type containing six steps.

From the simulation, it can be concluded from the 36 reactions that the reactions are classified into six types. Type I is an irreversible reaction with a complete product. Type II is an irreversible reaction but the output molecule structures are reactants instead of product. Type III is an irreversible reaction in which the output molecule structure is similar to the product of type II but without an active site bond. Type IV is a reversible reaction with only reactants as the outcome molecules. Type V is a reversible reaction; therefore, the final product is the reactants. Type VI is a reversible reaction but the output molecule structure is similar to the product of type V but without an active site bond.

This paper focuses on the transesterification reaction steps in a type I reaction. For other reaction types, the models are the same as for type I but with differences in the position of the carbon atom in triacylglycerol when interacting with a methoxide ion. The reaction steps in type I are described by six simulations.

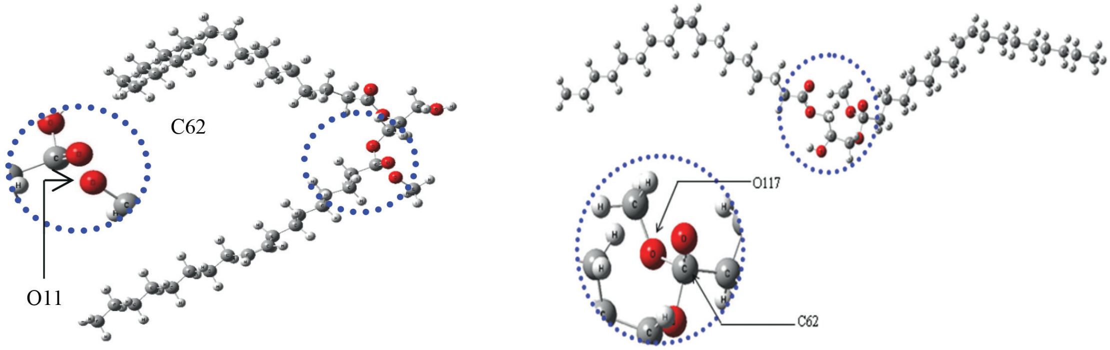
The first simulation is the reaction of a carbon atom of triacylglycerol and the oxygen atom of a methoxide ion. The product structure is designated as intermediate I (triacylglycerol–methoxide ion). The reaction between C62 in the carbonyl group of triacylglycerol (C=O) and O162 of a methoxide ion is shown by the molecular structure in Figure 4.

The second simulation is the reaction of the product from the first simulation (intermediate I) and methanol. This reaction, transesterification of triacylglycerol (step 2 + step 3 in Figure 2), is between oxygen (O61) of triacylglycerol and hydrogen (H173) of methanol. The product structure is FAME and diacylglycerol. The input and output molecular structures are shown in Figure 5.



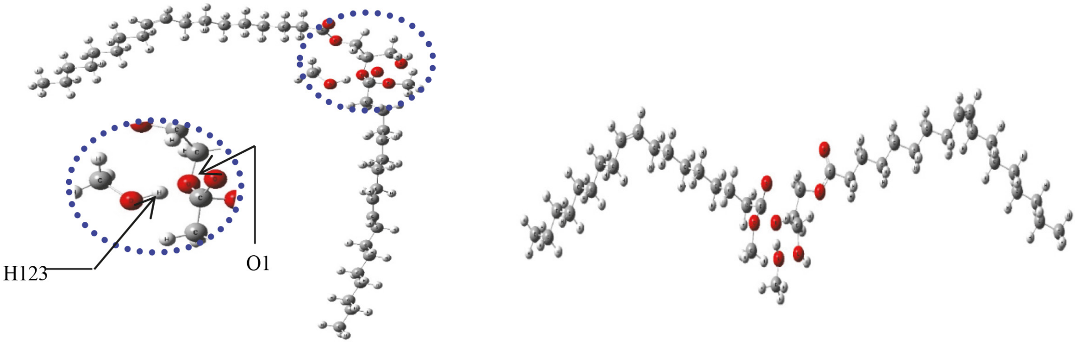
(a) Intermediate I + methanol (b) FAME + diacylalycerol

Figure 5: Reaction structure of intermediate1 and methanol in transesterification of triacylglycerol: (a) input and (b) output.



(a) acylglycerol + methoxide ion (b) Intermediate II

Figure 6: Reaction structure of diacylglycerol and methoxide ion in transesterification of diacylglycerol: (a) input and (b) output.

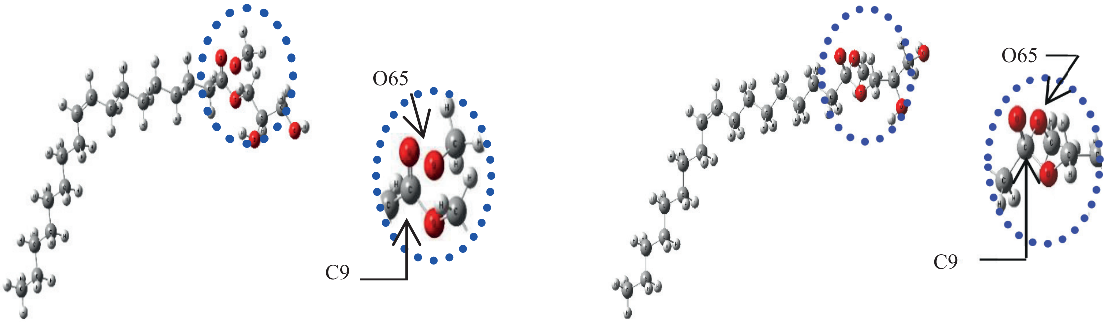


(a) Intermediate II + methanol (b) FAME + monoacylglycerol

Figure 7: Reaction structure of intermediateI and methanol in transesterification of diacylglycerol: (a) input and (b) output.

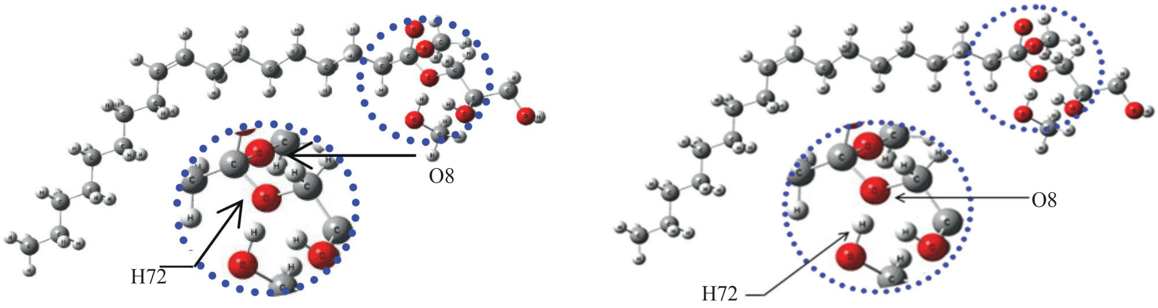
The third simulation (Figure 6) shows the reaction between C62 in the carbonyl group of diacylglycerol (C=O) and O117 of a methoxide ion, forming intermediate II (diacylglycerol–methoxide ion).

The fourth simulation uses intermediate II and methanol in transesterification of diacylglycerol. The reaction occurs between O1 of diacylglycerol and H123 of methanol. The products are FAME and monoacylglycerol. This simulation structure is shown in Figure 7.



(a) Monoacylglycerol + methoxide ion (b) Intermediated III

Figure 8: Reaction structure of monoacylglycerol and methoxide ion in ransesterification of monoacylglycerol: (a) input and (b) output.



(a) Intermediate III + methanol (b) FAME + glycerol

Figure 9: Reaction structure of monoacylglycerol and methoxide ion in transesterification of monoacylglycerol: (a) input and (b) output.

The fifth simulation involves the reaction between carbon in the carbonyl group of monoacylglycerol (C=O) and oxygen of a methoxide ion. The product structure is an intermediate III (monoacylglycerol-methoxide ion) in transesterification of monoacylglycerol. The reaction between C9 in the carbonyl group of monoacylglycerol (C=O) and O65 of a methoxide ion produces the biodiesel molecular structure in Figure 8.

The reaction of intermediate III and methanol is performed in the sixth simulation. The final products are FAME and glycerol. This simulation is shown in Figure 9.

3.3 *Transesterification mechanism*

The minimum distance for the reaction between the carbon atom in the carbonyl group of acylglycerol (C=O) and the oxygen atom of a methoxide ion is 1.517 Å. The minimum distance of the reaction between the product of the first reaction (intermediate I, or product of step 1) and methanol is 1.100 Å.

The transesterification mechanism can be classified into six reaction types. Six simulations are individually calculated for every reaction type. A total of 36 simulations can be optimized. All of these possible reactions and molecules can be illustrated in a simple diagram (Figure 10).

In Figure 10, red, blue and green circles represent molecules of triacylglycerol when the reaction occurs in lines 1, 2 and 3 respectively. Even though there are 36 mechanisms to simulate, the possibility of transesterification can be calculated from the relative energy between the total molecular energy of the reactant and the product by B3LYP/6-31G//PM3. The relative energy of the six reaction steps for the six reaction types is shown in Table 2. The relative energy values for the reaction steps in Figure 11 correspond to the steps in Figure 10 (indicated by R1-1, R1-2, etc.).

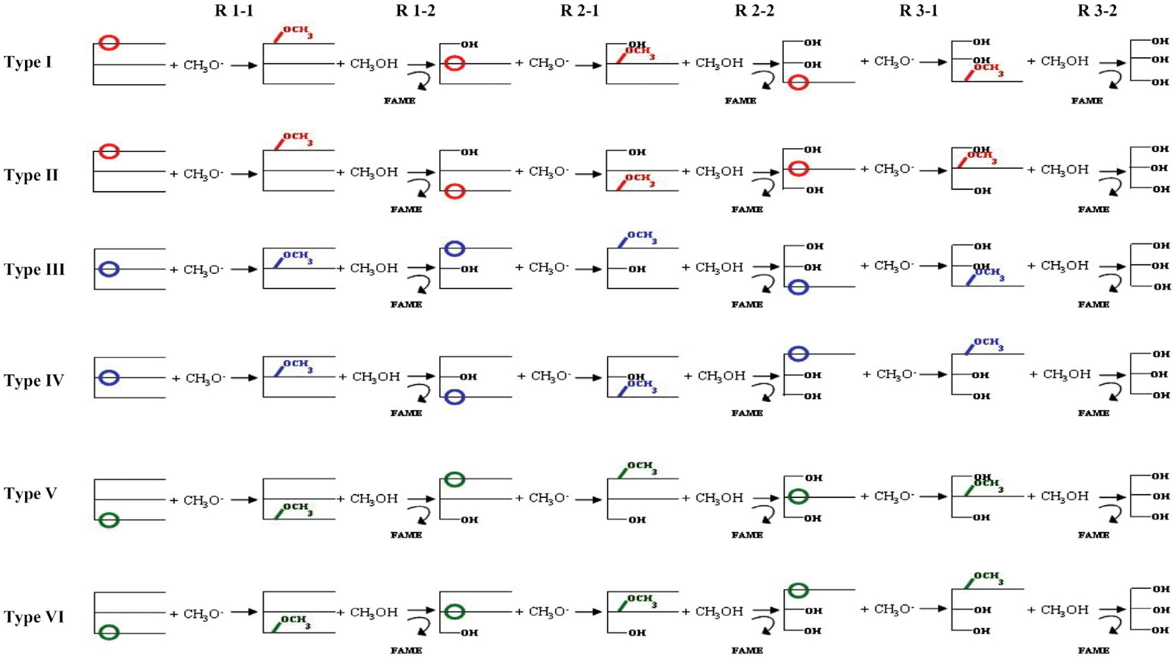


Figure 10: Simple diagram of transesterification mechanism. R 1-1, step 1; R 1-2, step 2; R 2-1, step 3; R 2-2, step 4; R 3-1, step 5; R 3-2, step 6. Red, blue and green circles are molecules of triacylglycerol when the reaction occurs in lines 1, 2 and 3, respectively.

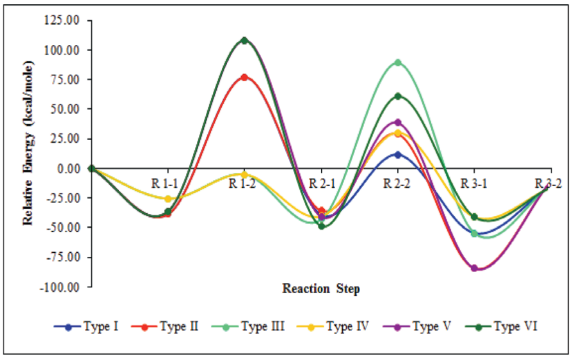


Figure 11: Relative energy comparison of the reaction steps for each type of transesterification reaction.

Table 2: Relative energy transesterification model

Reaction Step	Relative energy (kcal/mole)					
	Type I	Type II	Type III	Type IV	Type V	Type VI
1. R 1-1	-38.49	-38.49	-25.52	-25.52	-35.99	-35.99
2. R 1-2	76.98	76.98	-4.97	-4.97	108.19	108.19
3. R 2-1	-38.98	-35.88	-42.76	-40.36	-40.82	-48.66
4. R 2-2	11.77	28.97	89.05	30.31	38.54	60.86
5. R 3-1	-54.63	-84.42	-54.63	-41.04	-84.42	-41.04
6. R 3-2	-14.15	-10.57	-14.15	-15.98	-10.57	-15.98

In the first step, a methoxide ion can interact with the oxygen atom of triolein to generate methyl oleate and diolein; the methoxide ion interacts at the second chain of triolein (lowest activation energy in step 1 and step 2 [indicated by R 1-1 and R 1-2 in Figure 10 and Table 2]). Diolein then generates methyl oleate and monoolein. The activation energy of type I is lower than type II (in step 3 and step 4, R 2-1 and 2-2), so a type I reaction will occur. Lastly, methyl oleate and glycerol are generated from monoolein (in step 5 and step 6, R 3-1 and 3-2).

The possibility of a reaction is related to the activation energy. If the activation energy is considerably low, the reaction can easily generate the product. The reaction steps in type IV have the highest potential to occur since a type IV reaction has the lowest activation energy.

4 Conclusions

This report focuses on the molecular simulation of triacylglycerol, a critical substance in transesterification for biodiesel production, to find the best conformation with the lowest molecular energy and to propose the optimal transesterification pathway. The study of the transesterification mechanism starts with the determination of geometrical parameters of the triacylglycerol molecule. Three methods – AM1, PM3 and *ab initio* HF/6-31G – give good agreement. The proposed model of the triacylglycerol molecule can be used in the simulations of the transesterification mechanism, which are performed by Gaussian 03W and GaussView 03W.

The active site distances are found from the simulation. The minimum distance for the reaction between the carbon atom in the carbonyl group of acylglycerol (C=O) and the oxygen atom of the methoxide ion is 1.5165 Å. The minimum distance for the reaction between the product of the first reaction and methanol is 1.1000 Å.

In total, six types of transesterification mechanisms (or 36 reactions) are studied, based on an *ab initio* Hartree–Fock method with 3-21G and 6-31G basis sets. The reactions are divided into six types:

Type I is an irreversible reaction with a complete product.

Type II is an irreversible reaction but the output molecule structures are reactants instead of product.

Type III is an irreversible reaction in which the output molecule structure is similar to the product of type II but without an active site bond.

Type IV is a reversible reaction with only reactants as the outcome molecules.

Type V is a reversible reaction; therefore, the final product is the reactants.

Type VI is a reversible reaction but the output molecule structure is similar to the product of type V but without an active site bond.

The possibility of a reaction is related to the activation energy. Type IV is the most likely reaction to occur because it has the lowest activation energy.

Most transesterification reactions are reversible, so excess methanol is usually added to ensure that the reaction is complete. The energy of the reactant in each step of the transesterification mechanism is higher than the energy of the product. The energy in each type of reaction in the transesterification mechanism is similar to the others. The possible transesterification reactions are found in all types of transesterification mechanisms.

Acknowledgments

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