RESULTS AND DISCUSSIONS

This chapter proposes the geometrical parameters of triolein molecule and the relationship between molecular energy and optimization step numbers. The mechanisms of the transesterification are presented to find the possible transesterification mechanism of biodiesel production.

Geometrical Parameters

Refer to Fig. 6(a) and Fig. 6(b), the optimum bond lengths of triolein molecule calculated with the semiempirical AM1, PM3 and *ab initio* HF6-31G is concluded in Table 1 for the first geometric of triolein and Table 2 for the second one.

Table 3 Equilibrium geometrical parameters of the 1st triolein molecule from Fig. 6(a) in the ground state

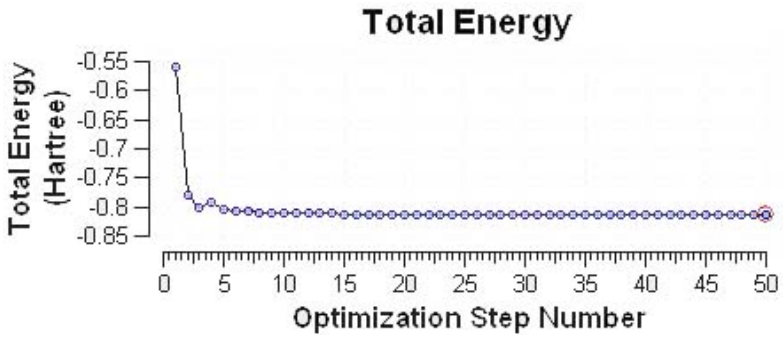
Parameter	Semiempirical		*Ab initio*
	AM1	**PM3**	**HF6-31G**
C2 - O8	1.436	1.427	1.438
C5 - O61	1.436	1.427	1.438
C166 - O1	1.429	1.424	1.441
C9 - O8	1.370	1.366	1.397
C62 - O61	1.370	1.366	1.397
C114 - O1	1.368	1.366	1.394
C9 = O10	1.232	1.214	1.215
C62 = O63	1.232	1.214	1.215
C114 = O115	1.232	1.215	1.215
C32 = C34	1.338	1.334	1.313
C85 = C87	1.338	1.334	1.313
C137 = C139	1.338	1.336	1.313

Table 4 Equilibrium geometrical parameters of the 2nd triolein molecule from Fig. 6(b) in the ground state

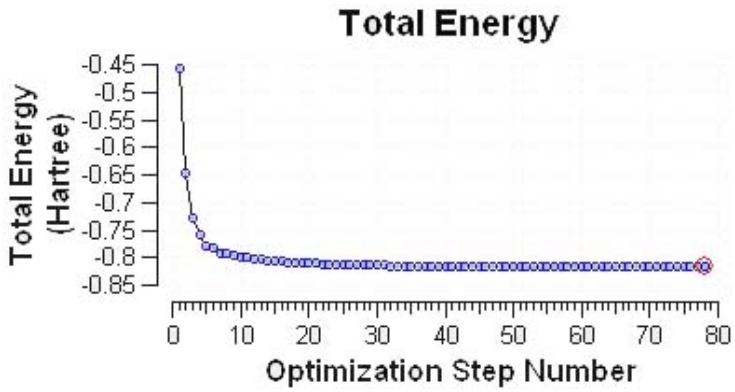
Parameter	Semiempirical		*Ab initio*
	AM1	**PM3**	**HF6-31G**
C28 - O27	1.427	1.416	1.438
C31 - O34	1.435	1.419	1.438
C88 - O61	1.437	1.433	1.440
C25 - O27	1.374	1.372	1.396
C35 - O34	1.370	1.369	1.396
C62 - O61	1.369	1.365	1.397
C25 = O26	1.232	1.215	1.215
C35 = O36	1.232	1.214	1.215
C62 = O63	1.231	1.215	1.214
C1 = C2	1.338	1.334	1.313
C58 = C60	1.338	1.334	1.313
C85 = C87	1.338	1.334	1.313

The single bond lengths of triolein from *ab initio* HF are longer than the semiempirical AM1 and PM3 but the double bond lengths of triolein from the semiempirical AM1 are longer than the semiempirical PM3 and *ab initio* HF.

In Fig. 14, it shows the relationship between molecular energy and optimization step numbers. The relation of this figure is for triolein molecule using AM1 and the optimization step number in the range of 50-80 steps depending on the conformation before optimization. From this figure, we can conclude that molecular energy in Hartree (627.51 kcal/mol) will decrease until stable because triolein will try to adjust molecular structure for the best stability. The relative energy of triolein optimization in semiempirical AM1of the 1st triolein and the 2nd triolein is 2.08 kcal/mol.



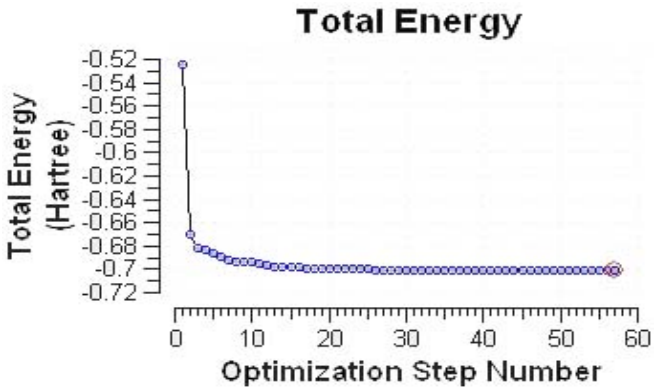
(a)



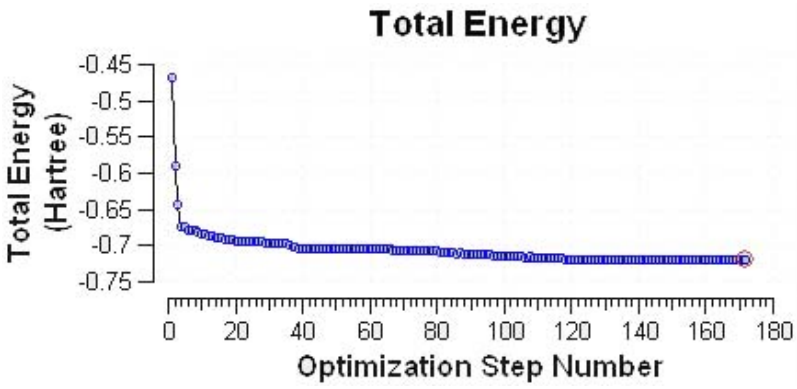
(b)

Figure 14 Total energy of triolein optimization in semiempirical AM1: (a) 1st triolein and (b) 2nd triolein.

In Fig. 15, it shows the relationship between molecular energy and optimization step numbers. The relation of this figure is for triolein molecule using PM3 and the optimization step number in the range of 55-180 steps depending on the conformation before optimization. From this figure, we can conclude that molecular energy decrease until stable because triolein will try to adjust molecular structure for the best stability. The relative energy of triolein optimization in semiempirical PM3 of the 1st triolein and the 2nd triolein is 11.90 kcal/mol.



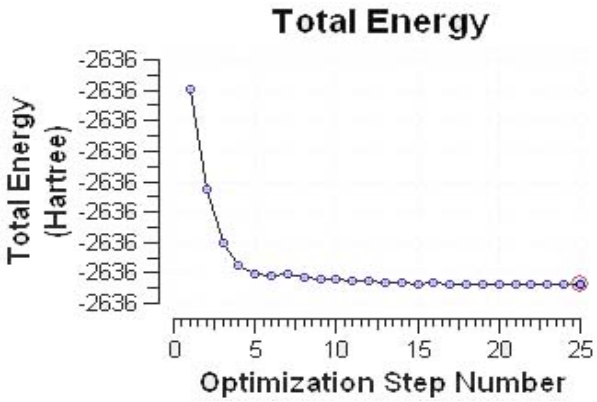
(a)



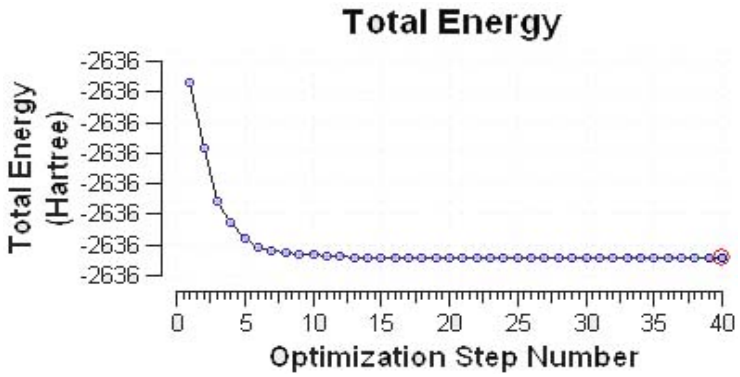
(b)

Figure 15 Total energy of triolein optimization in semiempirical PM3: (a) 1st triolein and (b) 2nd triolein.

In Fig. 16, it shows the relationship between molecular energy and optimization step numbers. The relation of this figure is for triolein molecule using HF6-31G and the optimization step number in the range of 25-40 steps depending on the conformation before optimization. From this figure, we can conclude that molecular energy will decrease until stable because triolein will try to adjust molecular structure for the best stability. The relative energy of triolein optimization in *ab initio* HF6-31G of the 1st triolein and the 2nd triolein is 2.35 kcal/mol.



(a)



(b)

Figure 16 Total energy of triolein optimization in *ab initio* HF6-31G: (a) 1st triolein and (b) 2nd triolein.

Generally, this semiempirical AM1, PM3 and *ab initio* HF6-31G can identify the geometrical parameters of triolein. And from the previous descriptions in Fig.14 – Fig. 16, the extrapolation of the *ab initio* HF6-31G results into the geometrical parameters of triolein molecule can be used *ab initio* HF6-31G to simulate the transesterification mechanism.

Transesterification mechanism

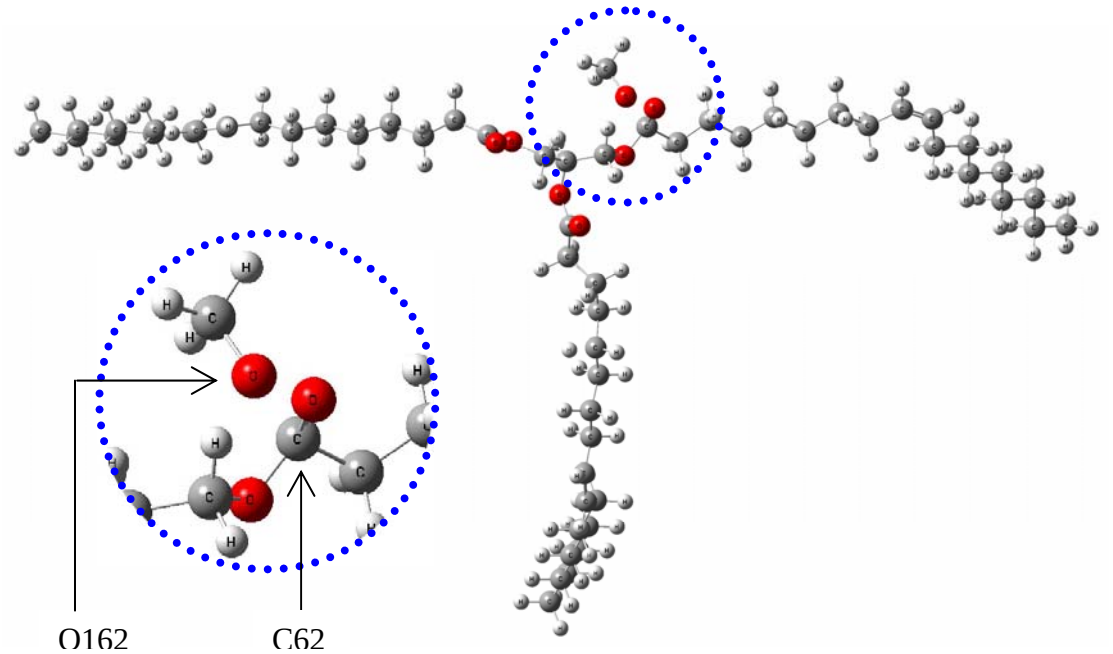
Transesterification mechanism in Fig. 3 can be proposed into six mechanisms as shown in Fig. 7 to 12. In six simulations were individually calculated for every mechanisms. Totally, thirty six simulations were optimized.

Two input files needed for the simulations of each glyceride (tri-, di-, monoolein) were divided into. These input files were constructed by GaussViewW and then optimized by GAUSSIAN 03W as the output files. The first input file is step 1 in transesterification mechanism. And the second input file is step 2 in transesterification mechanism.

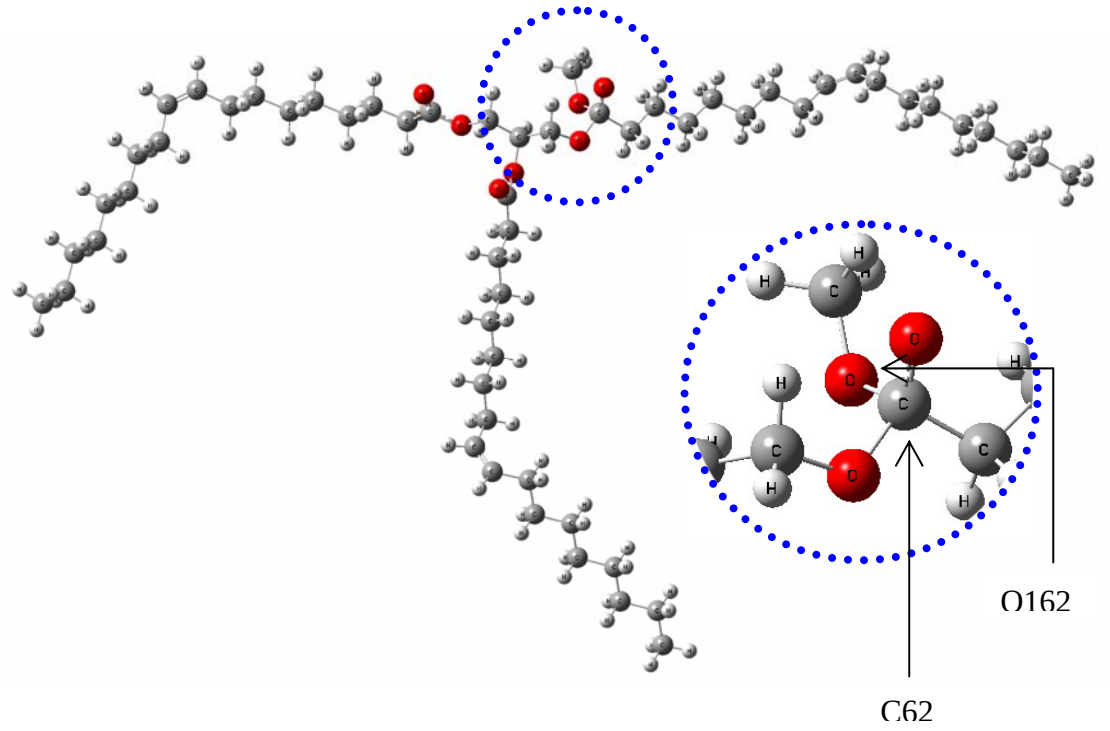
The two distances between an active site in transesterification mechanism were determined in this thesis. The first active sites is a site between carbon atom in carbonyl group of glyceride (C=O) and oxygen atom of methoxide. The second active site is a site between oxygen atom that is next to the carbon atom in carbonyl group of glyceride (C=O) and hydrogen atom of methanol. These two active sites were based on transesterification mechanism in Fig. 3. The distance between glyceride and methoxide varies in a range of 1.4300 to 1.6000 angstrom (Å). The distance between product of the first reaction (intermediate1 or product in step 1) and methanol varies from 0.9 to 1.2 Å. Next, the all of reactions in transesterification mechanism were simulated based on semiempirical PM3 to find the minimum reaction distance. Therefore, the minimum distance of the reaction between carbon atom in carbonyl group of glyceride (C=O) and oxygen atom of methoxide is 1.5165 Å. The minimum distance of the reaction between product of the first reaction (intermediate1 or product in step 1) and methanol is 1.1000 Å. For more accuracy the *ab initio* Hartree-Fock was simulated all of reactions again.

Transesterification mechanism Type 1

The first simulation from Fig. 7(a.1) is the reaction of triolein and methoxide. The amount of atoms in the input file was 172. The reaction between C62 in carbonyl group of triolein (C=O) and O162 of methoxide was calculated based on HF6-31G method. The result found that the product structure was intermediate1 as the product of step 1 in transesterification of triolein. The relative energy between input structures and output structures of the reaction is 97.78 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 17.



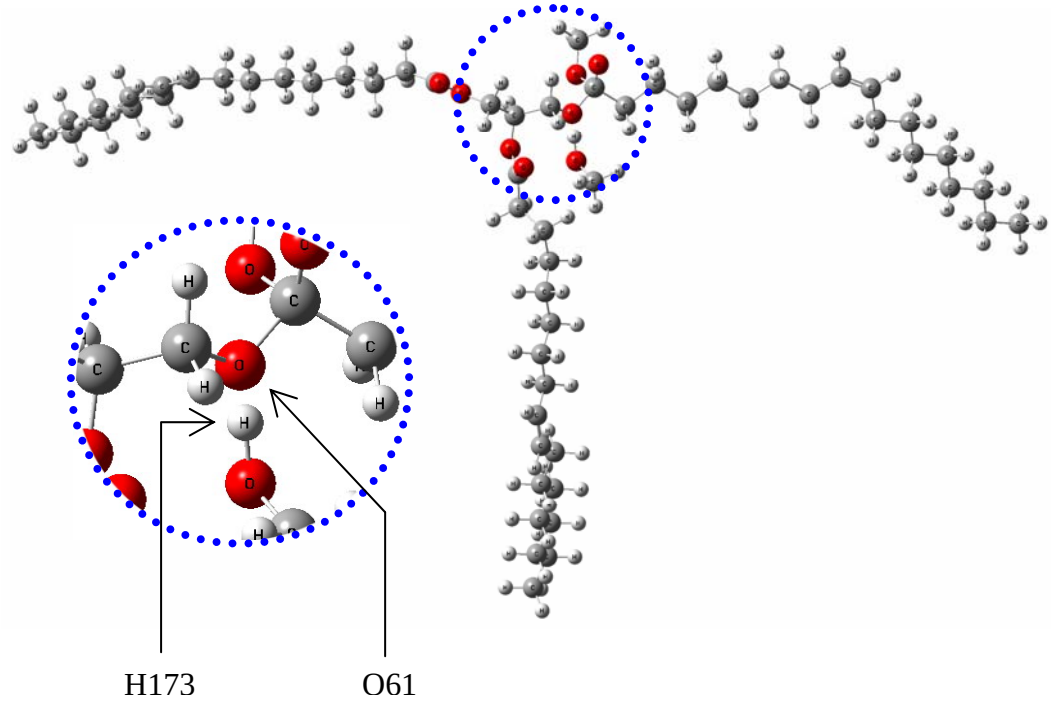
(a)



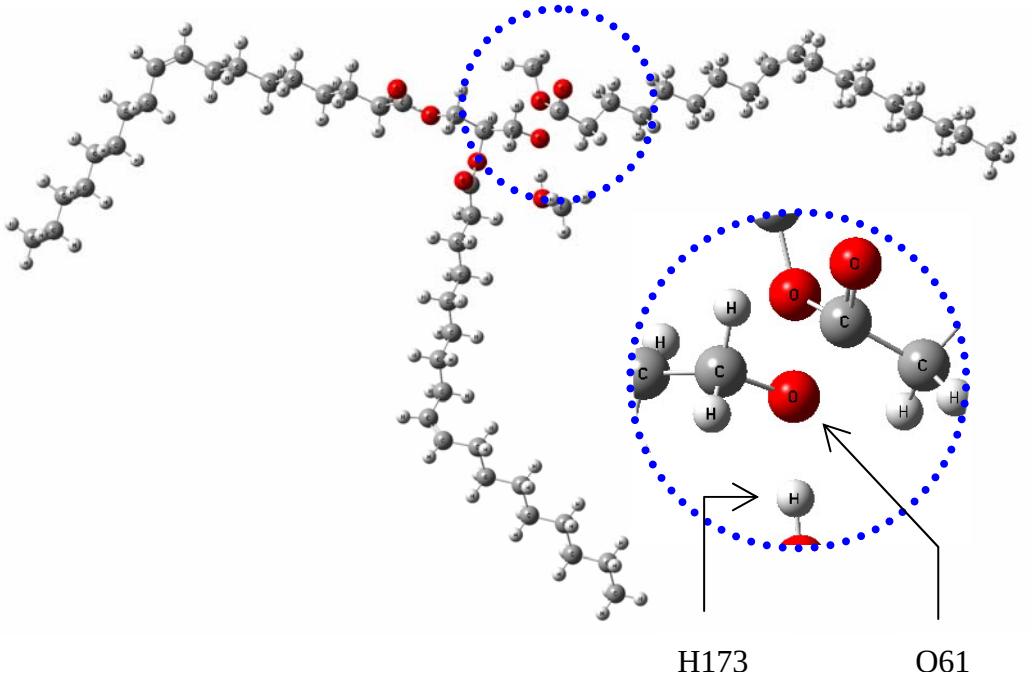
(b)

Figure17 The reaction structure of triolein and methoxide in transesterification of triolein: (a) input and (b) output.

The second simulation from Fig. 7(a.2) is the reaction of the product in the first simulation (intermediate1) and methanol in transesterification of triolein. The amount of atoms in the input file was 178. The reaction between O61 of triolein and H173 of methanol was calculated based on HF6-31G method. The result found that the product structure was ester and diolein as shown in Fig. 7(a.3) instead of intermediate2 as shown in Fig. 7(a.2). The final products, ester and diolein, appeared in the 22^{nd} – 24^{th} and 32^{nd} of the simulation cycles. Hence, this simulation is a reversible reaction. The relative energy between input structures and output structures of the reaction is 72.20 kcal/mol. The input and output structure were shown in Fig. 18.



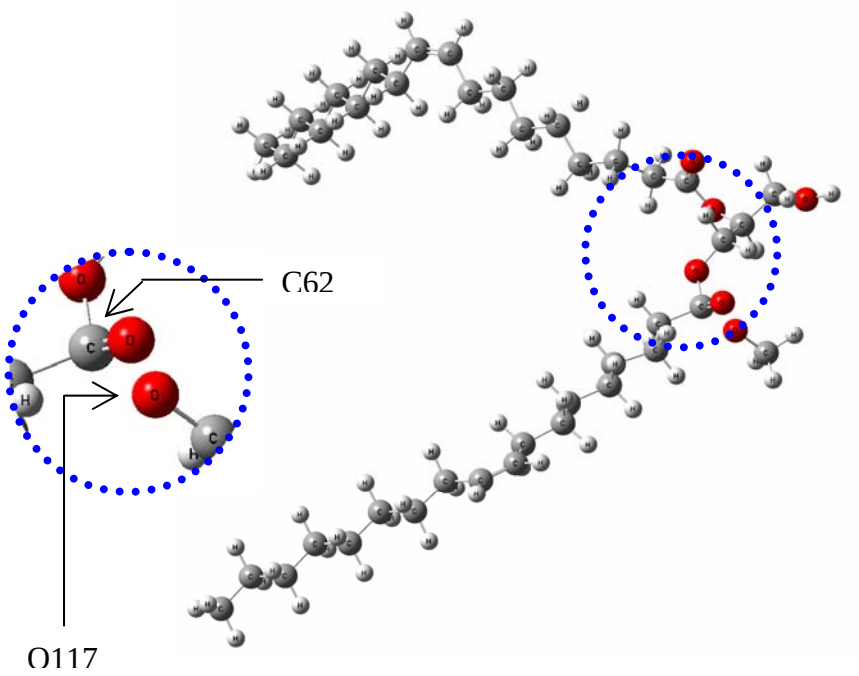
(a)



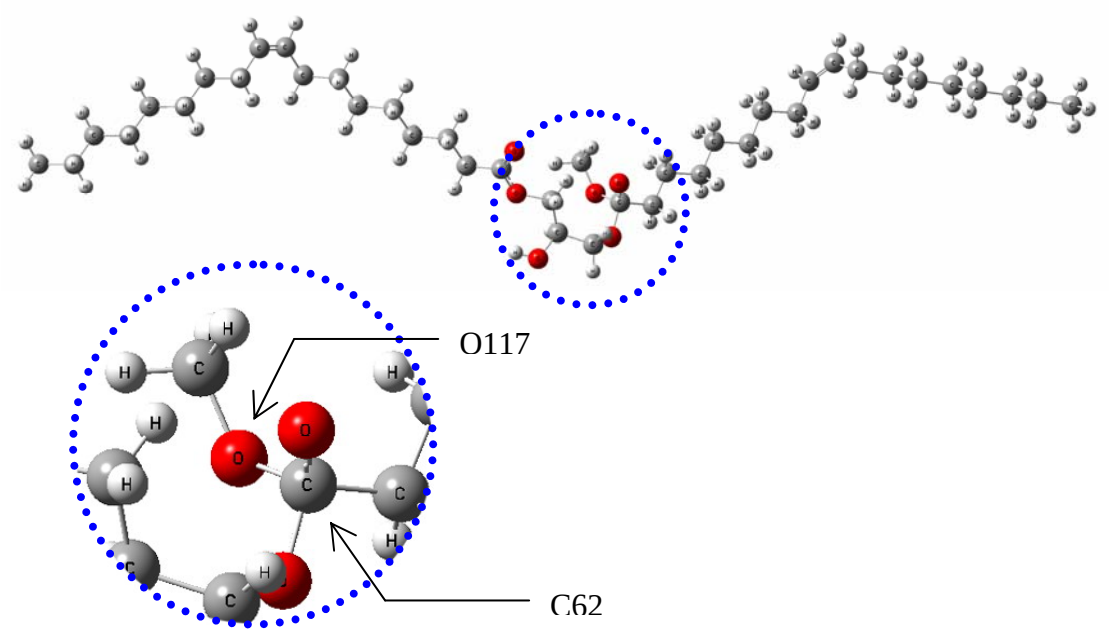
(b)

Figure18 The reaction structure of intermediate1 and methanol in transesterification of triolein: (a) input and (b) output.

The third simulation from Fig. 7(b.1) is the reaction of diolein and methoxide. The amount of atoms in the input file was 121. The reaction between C62 in carbonyl group of diolein (C=O) and O117 of methoxide was calculated based on HF6-31G method. The result found that the product structure was intermediate1 as the product of step 1 in transesterification of diolein. And intermediate1 appeared in the 40th and 44th of the simulation cycles. Hence, this simulation is a reversible reaction. The relative energy between input structures and output structures of the reaction is 246.54 kcal/mol. The input and output structure were shown in Fig. 19.



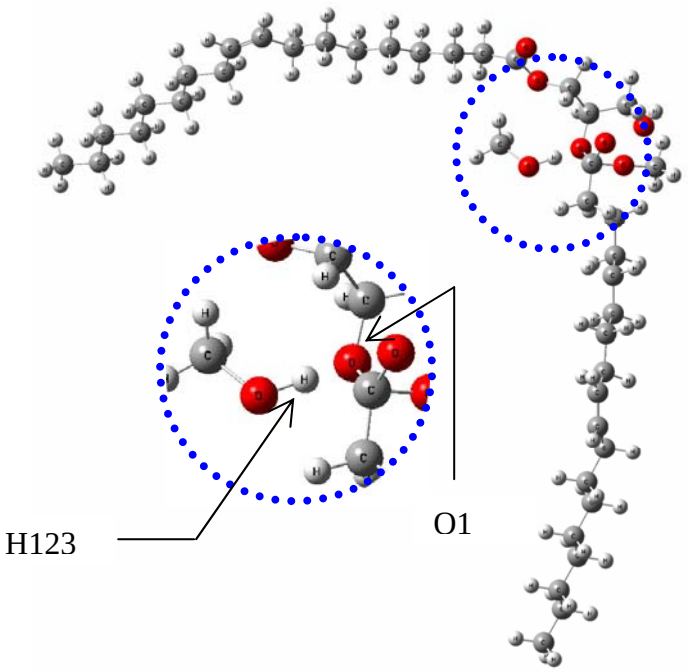
(a)



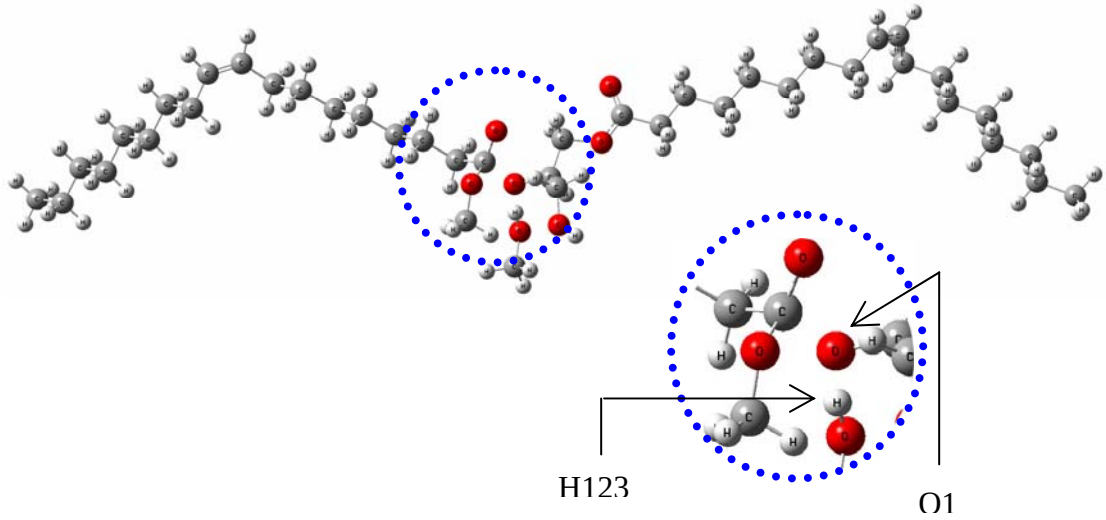
(b)

Figure19 The reaction structure of diolein and methoxide in transesterification of diolein: (a) input and (b) output.

The forth simulation from Fig. 7(b.2) is the reaction of the product in the third simulation (intermediate1) and methanol in transesterification of diolein. The amount of atoms in the input file was 127. The reaction between O1 of diolein and H123 of methanol was calculated based on HF6-31G method. The result found that the product structure was ester and monoolein as shown in Fig. 7(b.3) instead of intermediate2 as shown in Fig. 7(b.2). The final products are ester and monoolein. The relative energy between input structures and output structures of the reaction is 326.51 kcal/mol. The input and output structure were shown in Fig. 20.



(a)



(b)

Figure20 The reaction structure of intermediate1 and methanol in transesterification of diolein: (a) input and (b) output.

The fifth simulation from Fig. 7(c.1) is the reaction of monoolein and methoxide. The amount of atoms in the input file was 70. The reaction between C9 in carbonyl group of monoolein (C=O) and O65 of methoxide was calculated based on HF6-31G. The result found that the product structure wasn't as shown in Fig. 7(c.1) or intermediate1 in transesterification of monoolein. So, the method was changed to HF3-21G. And the result showed that the product was intermediate1. The relative energy between input structures and output structures of the reaction is 175.70 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 21.

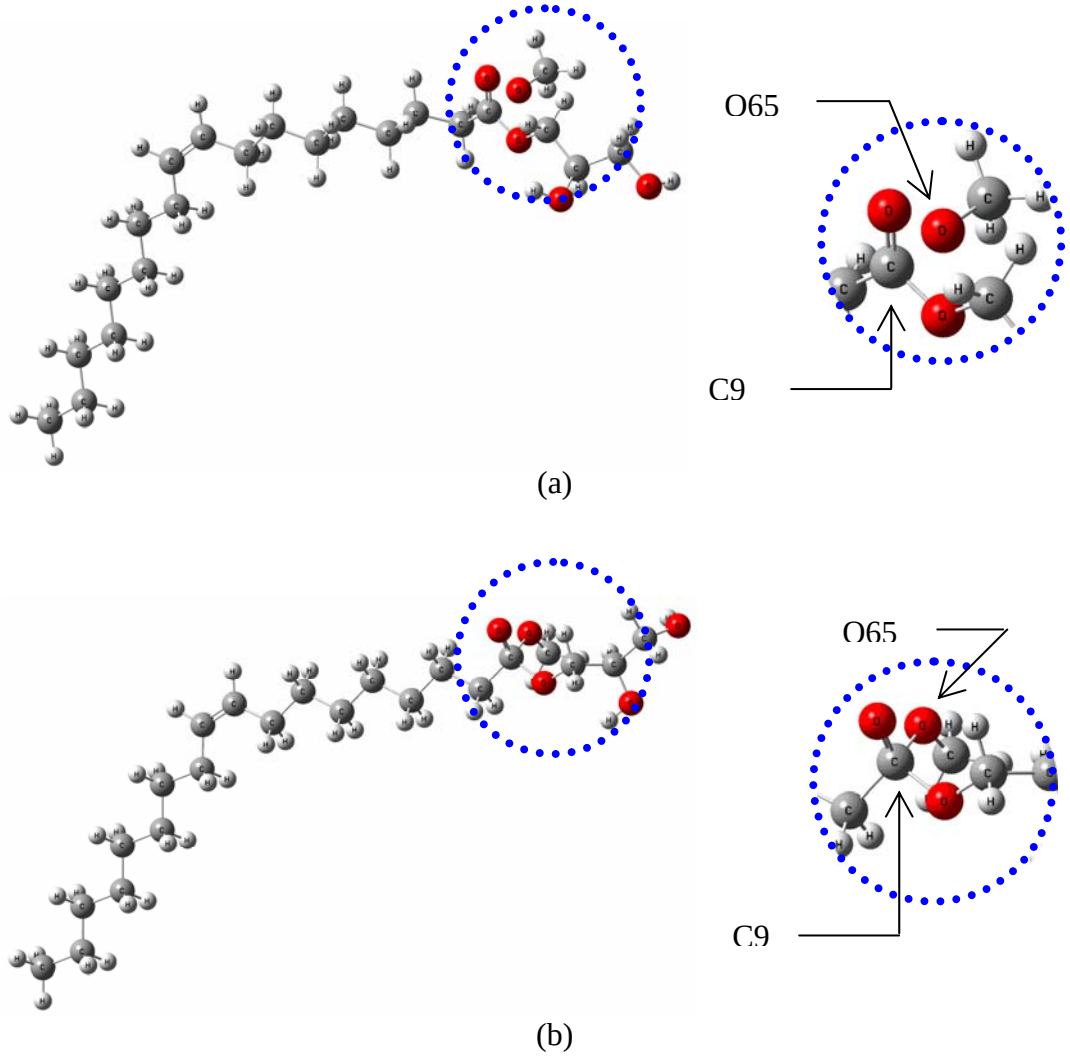
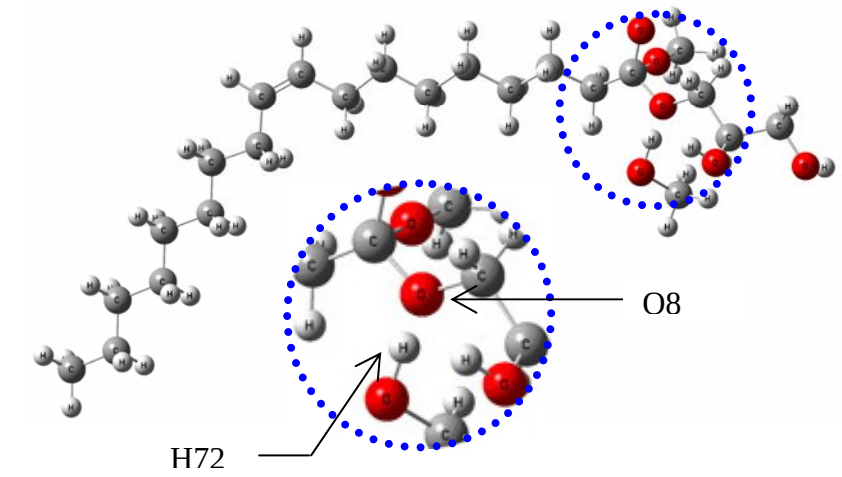
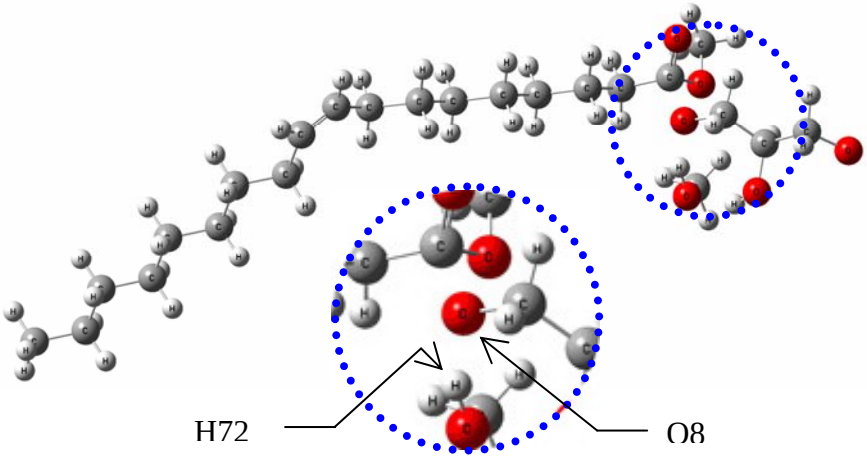


Figure21 The reaction structure of monoolein and methoxide in transesterification of monoolein: (a) input and (b) output.

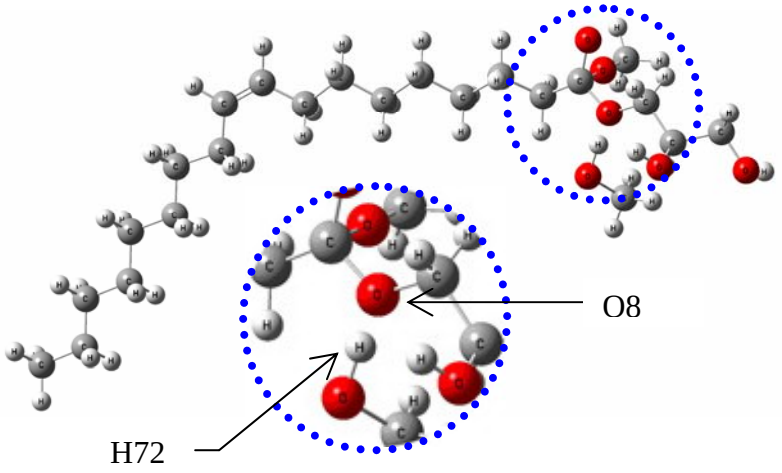
The sixth simulation from Fig. 7(c.2) is the reaction of the product in the first simulation (intermediate1) and methanol in transesterification of monoolein. The amount of atoms in the input file was 76. The reaction between O8 of triolein and H72 of methanol was calculated based on HF6-31G. The result found that the product structure wasn't intermediate2 as shown in Fig. 7(c.2) and weren't ester and glycerol as shown in Fig. 7(c.3). The final products were intermediate1 and methanol as the reactant in this simulation. But ester and glycerol appeared in the 19th, 20th, and 25th of the simulation cycles. Hence, this simulation is a reversible reaction. The relative energy between input structures and output structures of the reaction is 244.73 kcal/mol. The input, structure of 19th cycle and output structure were shown in Fig. 22.



(a)



(b)

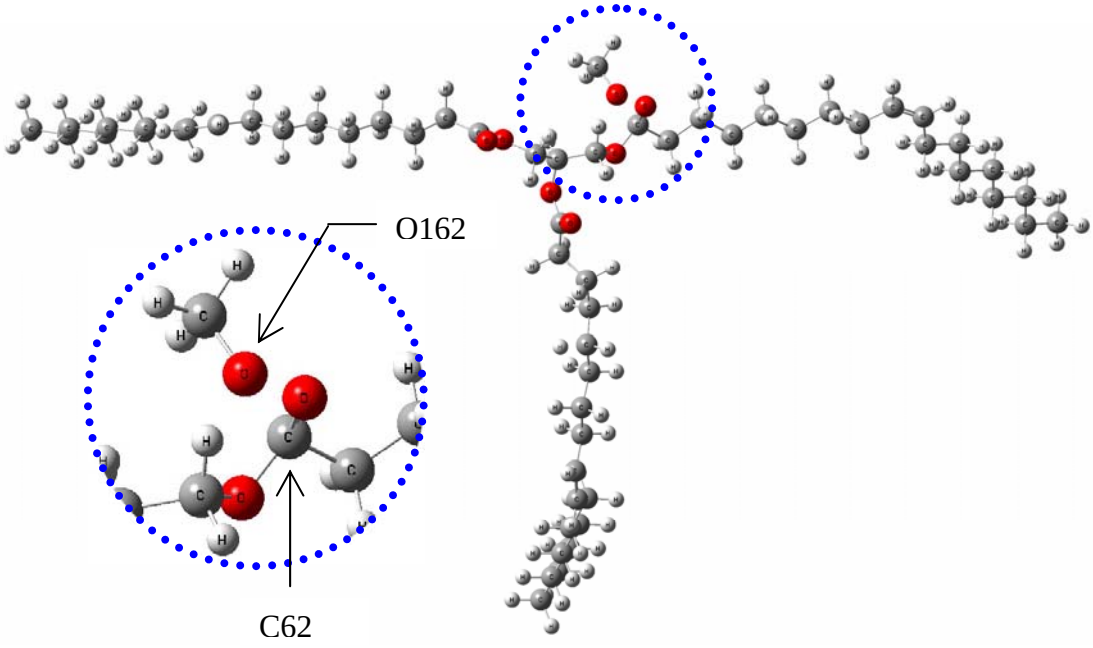


(c)

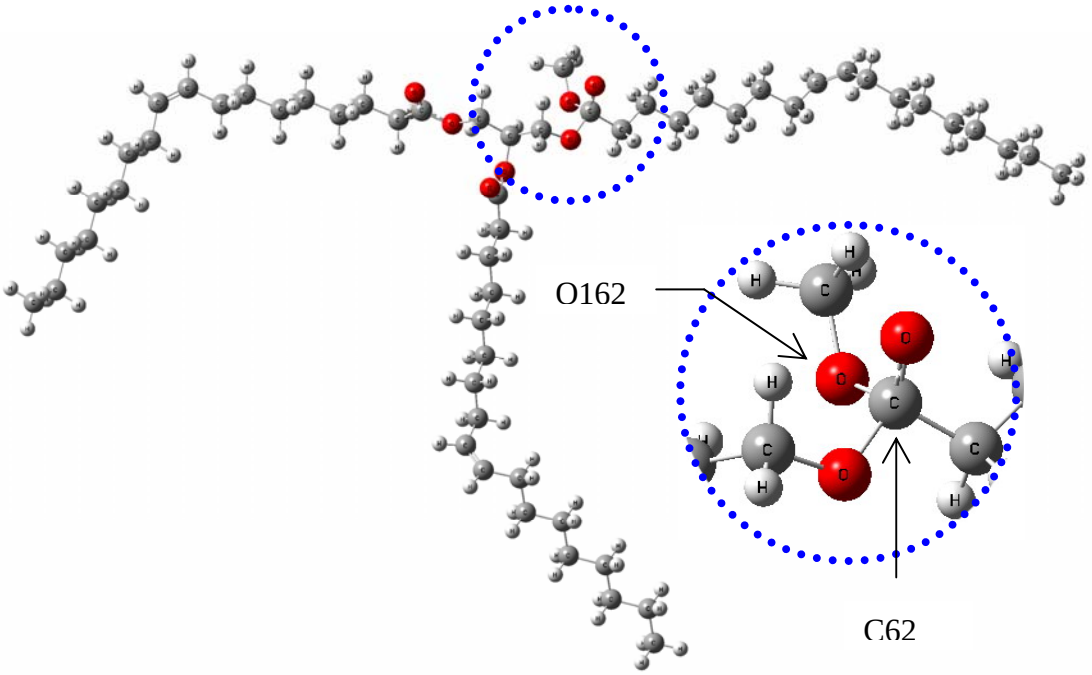
Figure22 The reaction structure of monoolein and methoxide in transesterification of monoolein: (a) input, (b) structure of 19th cycle and (c) output.

Transesterification mechanism Type 2

The first simulation from Fig.8 (a.1) is the reaction of triolein and methoxide. The amount of atoms in the input file was 172. The reaction between C62 in carbonyl group of triolein (C=O) and O162 of methoxide was calculated based on HF6-31G method. The result found that the product structure was intermediate1 as the product of step 1 in transesterification of triolein. The relative energy between input structures and output structures of the reaction is 97.78 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 23.



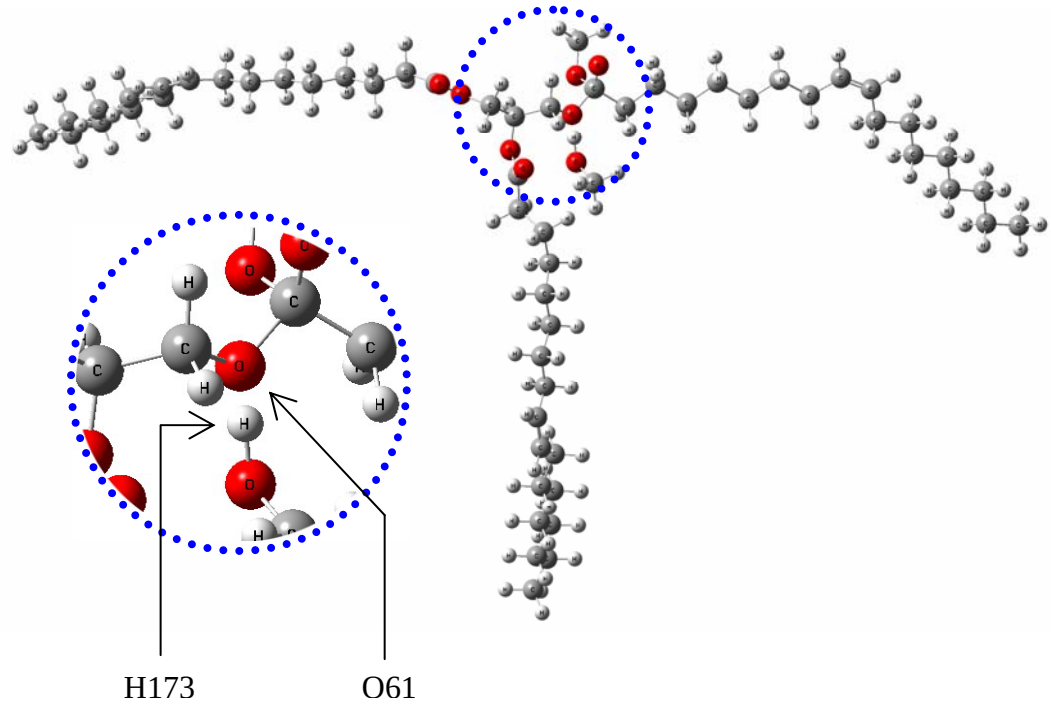
(a)



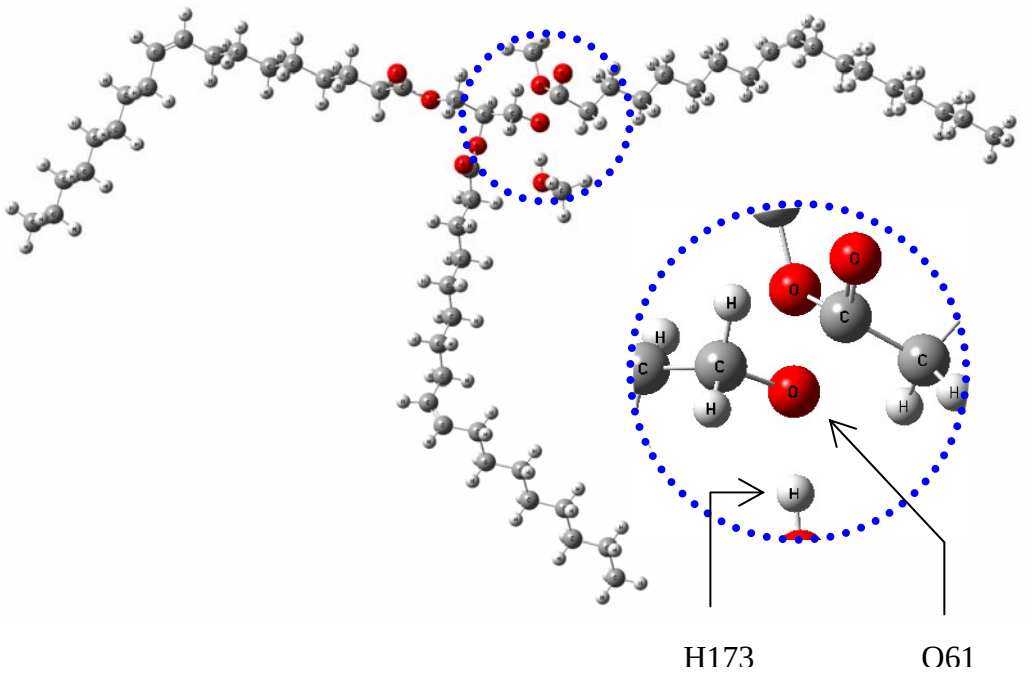
(b)

Figure23 The reaction structure of triolein and methoxide in transesterification of triolein: (a) input and (b) output.

The second simulation from Fig.8 (a.2) is the reaction of the product in the first simulation (intermediate1) and methanol in transesterification of triolein. The amount of atoms in the input file was 178. The reaction between O61 of triolein and H173 of methanol was calculated based on HF6-31G method. The result found that the product structure was ester and diolein as shown in Fig. 8 (a.3) instead of intermediate2 as shown in Fig. 8 (a.2). The final products, ester and diolein, appeared in the 22nd – 24th and 32nd of the simulation cycles. Hence, this simulation is a reversible reaction. The relative energy between input structures and output structures of the reaction is 72.20 kcal/mol. The input and output structure were shown in Fig. 24.



(a)



(b)

Figure24 The reaction structure of intermediate1 and methanol in transesterification of triolein: (a) input and (b) output.

The third simulation from Fig. 8 (b.1) is the reaction of diolein and methoxide. The amount of atoms in the input file was 121. The reaction between C9 in carbonyl group of diolein (C=O) and O117 of methoxide was calculated based on HF6-31G method. The result found that the product structure wasn't as shown in Fig. 8 (b.1) or intermediate1 in transesterification of diolein. So, the method was changed to HF3-21G but the product wasn't the intermediate1. Then the method was changed again to the semiempirical PM3. The last result showed the product as the product structure of step 1 or intermediate1 in transesterification of diolein. The relative energy between input structures and output structures of the reaction is 98.68 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 25.

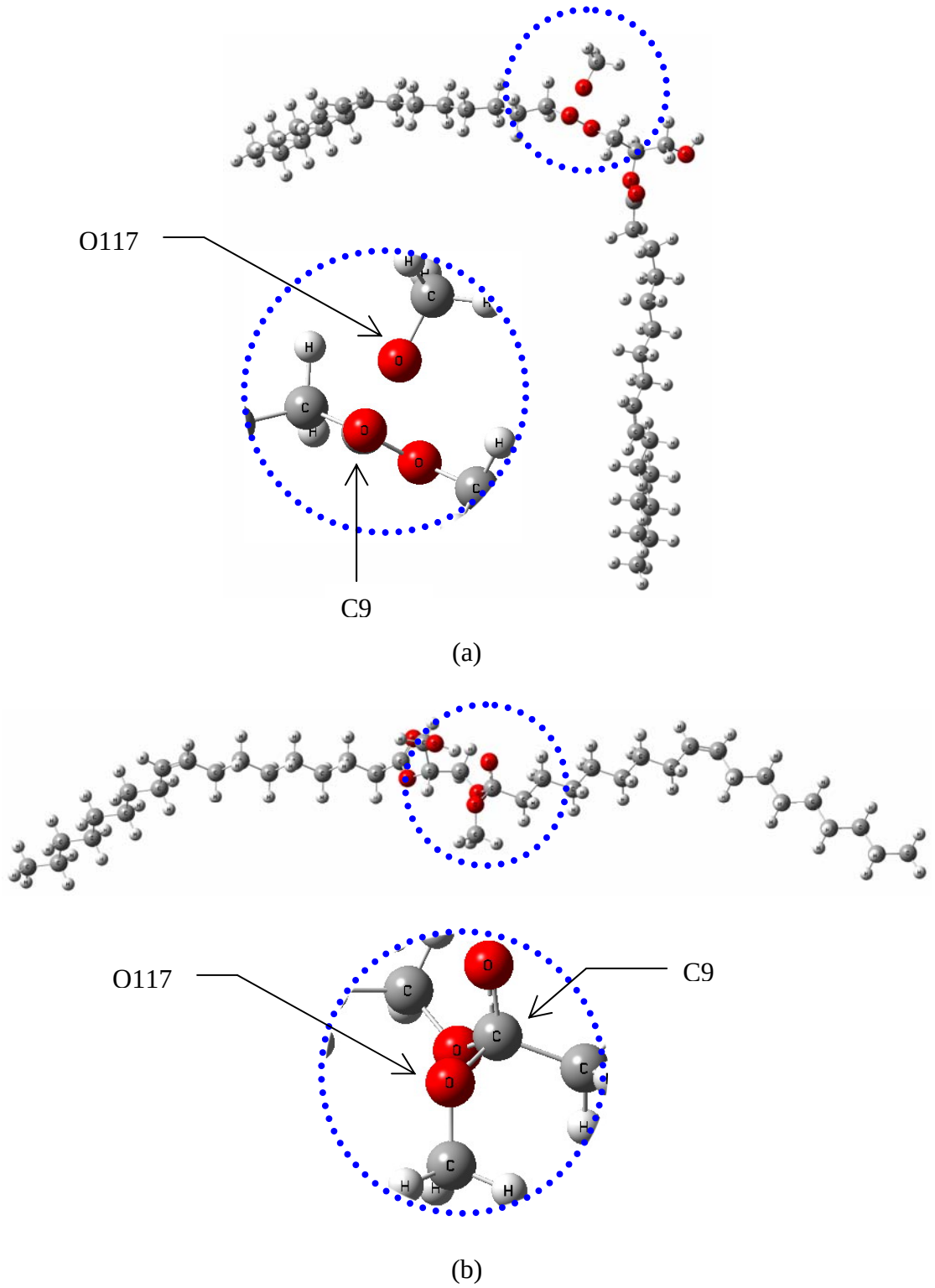
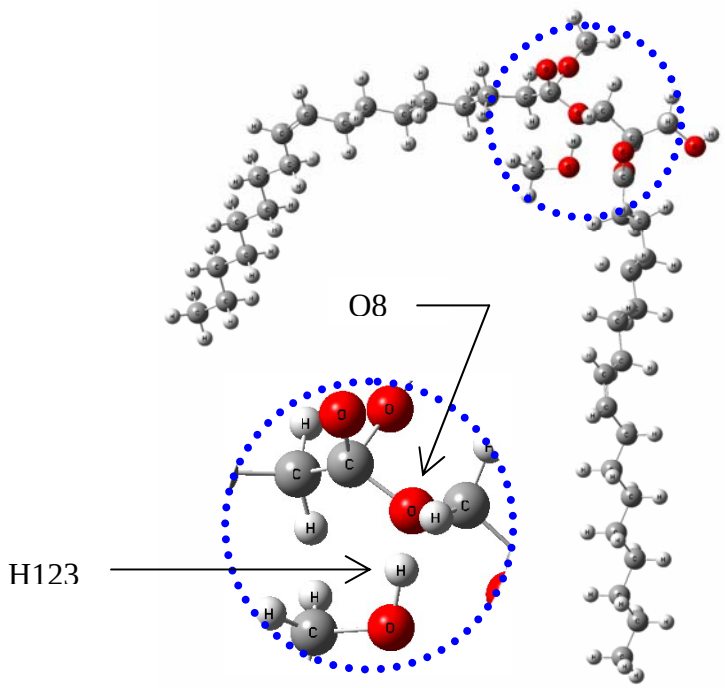
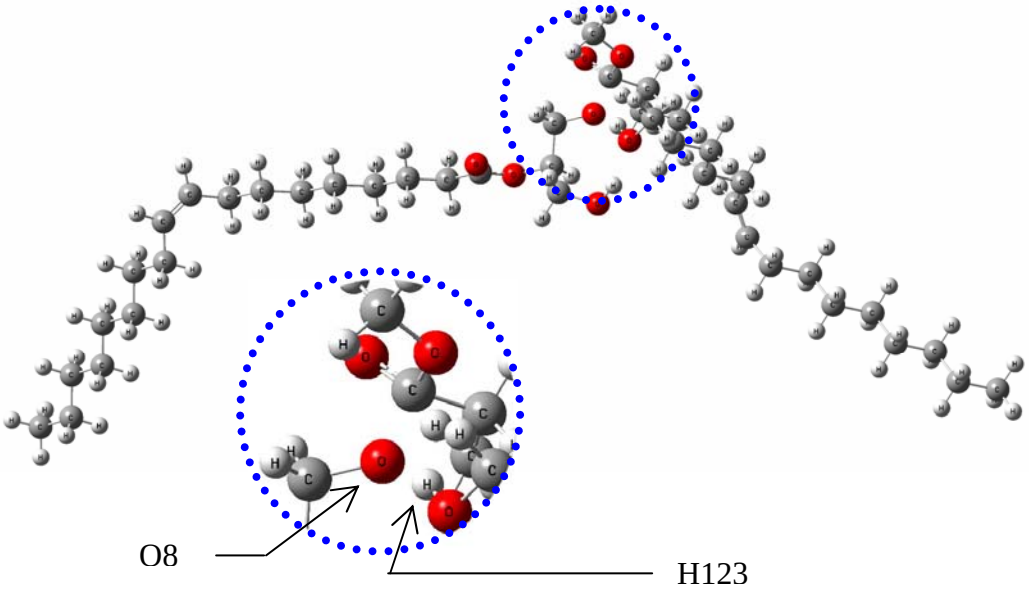


Figure25 The reaction structure of diolein and methoxide in transesterification of diolein: (a) input and (b) output.

The forth simulation from Fig. 8 (b.2) is the reaction of the product in the third simulation (intermediate1) and methanol in transesterification of diolein. The amount of atoms in the input file was 127. The reaction between O8 of diolein and H123 of methanol was calculated based on HF6-31G method. The result found that the product structure was or ester and monoolein the product as shown in Fig. 8 (b.3) instead of intermediate2as shown in Fig. 8 (b.2). The final products are ester and monoolein. The relative energy between input structures and output structures of the reaction is 288.65 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 26.



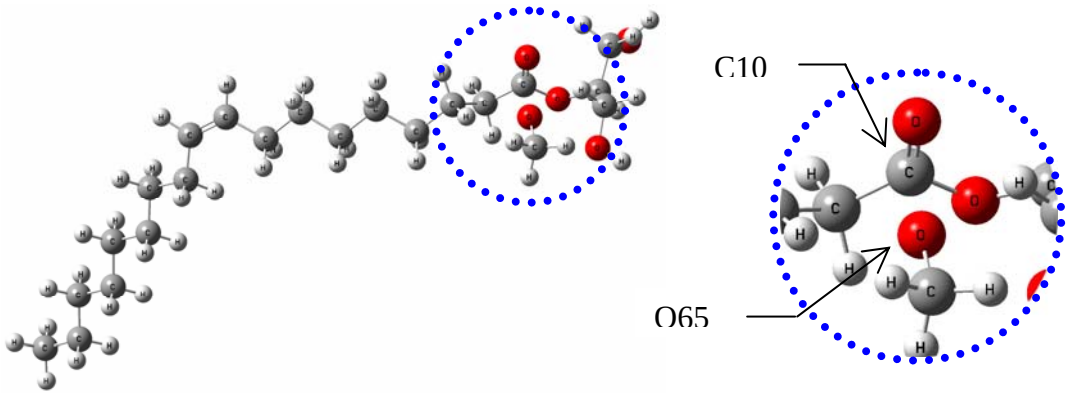
(a)



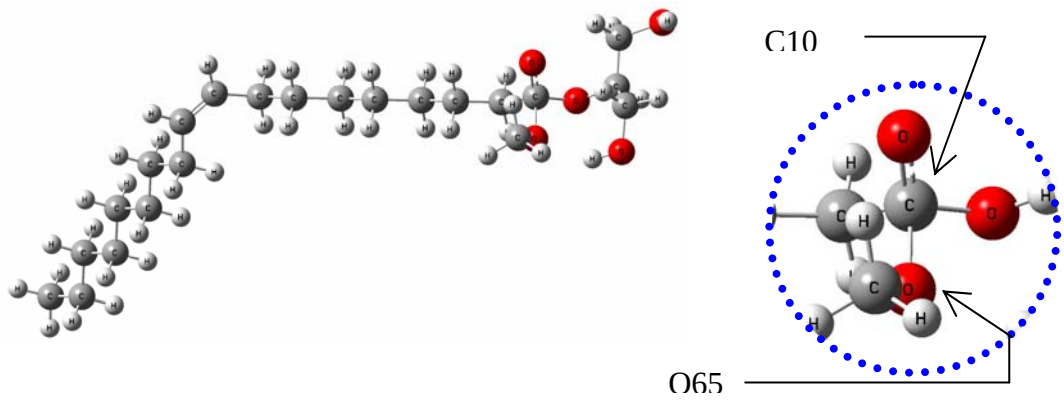
(b)

Figure26 The reaction structure of intermediate1 and methanol in transesterification of diolein: (a) input and (b) output.

The fifth simulation from Fig. 8 (c.1) is the reaction of monoolein and methoxide. The amount of atoms in the input file was 70. The reaction between C10 in carbonyl group of monoolein (C=O) and O65 of methoxide was calculated based on HF6-31G. The result found that the product structure was intermediate1 as the product of step 1 in transesterification of triolein. The relative energy between input structures and output structures of the reaction is 163.15 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 27.



(a)

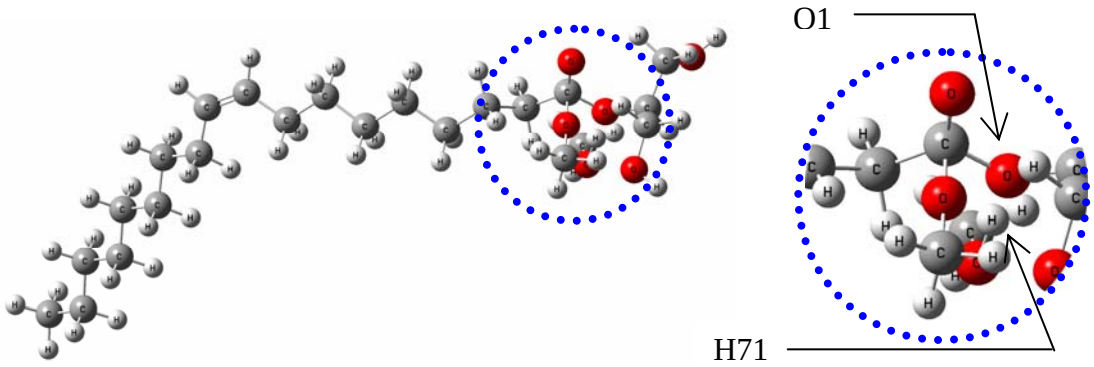


(b)

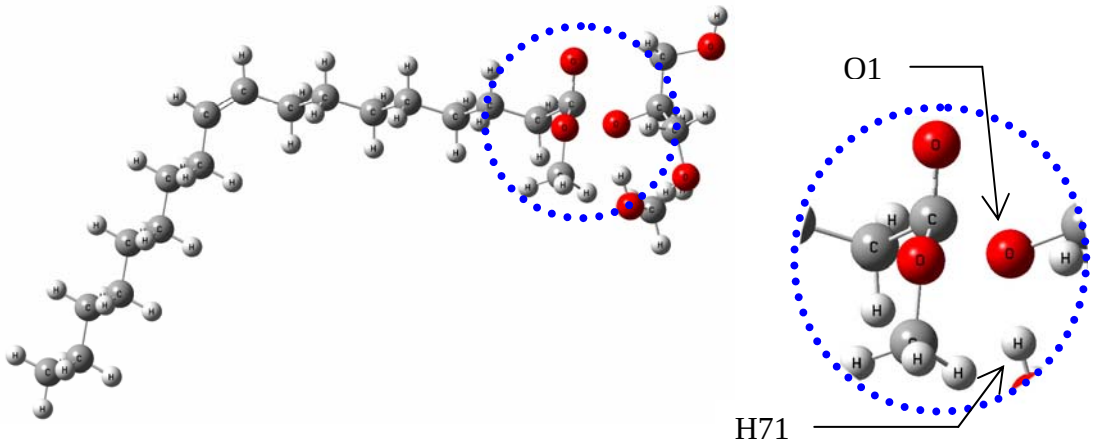
Figure27 The reaction structure of monoolein and methoxide in transesterification of monoolein: (a) input, and (b) output.

The sixth simulation from Fig. 8 (c.2) is the reaction of the product in the first simulation (intermediate1) and methanol in transesterification of monoolein. The amount of atoms in the input file was 76. The reaction between O1 of triolein and H71 of methanol was calculated based on HF6-31G. The result found that the product structure was ester and monoolein as shown in Fig. 8 (b.3) instead of intermediate2 as shown in Fig. 8 (b.2). The final products, ester and monoolein, appeared in the 7^{th} – 10^{th} of the simulation cycles. Hence, this simulation is a reversible reaction. The

relative energy between input structures and output structures of the reaction is 282.38 kcal/mol. The input and output structure were shown in Fig. 28.



(a)

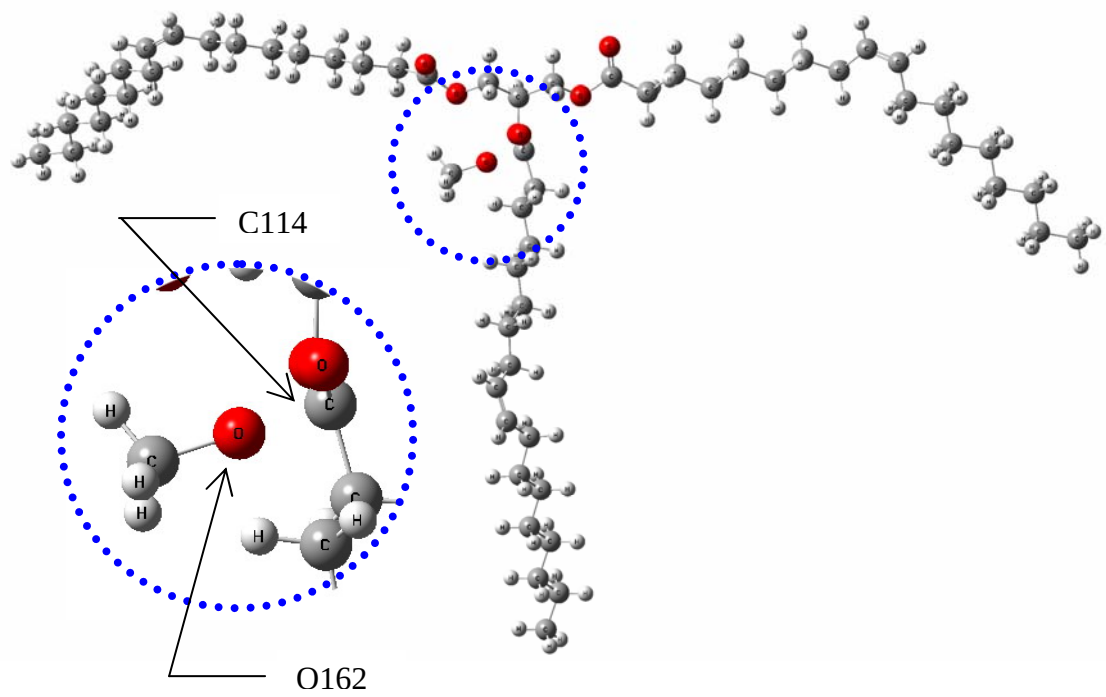


(b)

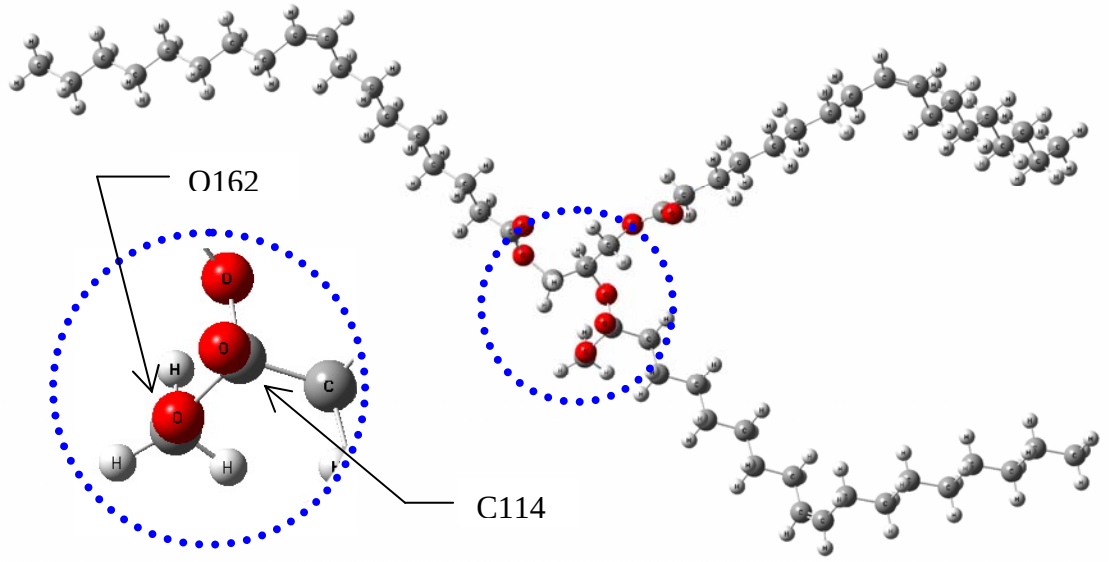
Figure28 The reaction structure of monoolein and methoxide in transesterification of monoolein: (a) input and (b) output.

Transesterification mechanism Type 3

The first simulation from Fig. 9 (a.1) is the reaction of triolein and methoxide. The amount of atoms in the input file was 172. The reaction between C114 in carbonyl group of triolein (C=O) and O162 of methoxide was calculated based on HF6-31G method. The result found that the product structure was intermediate1 as the product of step 1 in transesterification of triolein. The relative energy between input structures and output structures of the reaction is 97.78 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 29.



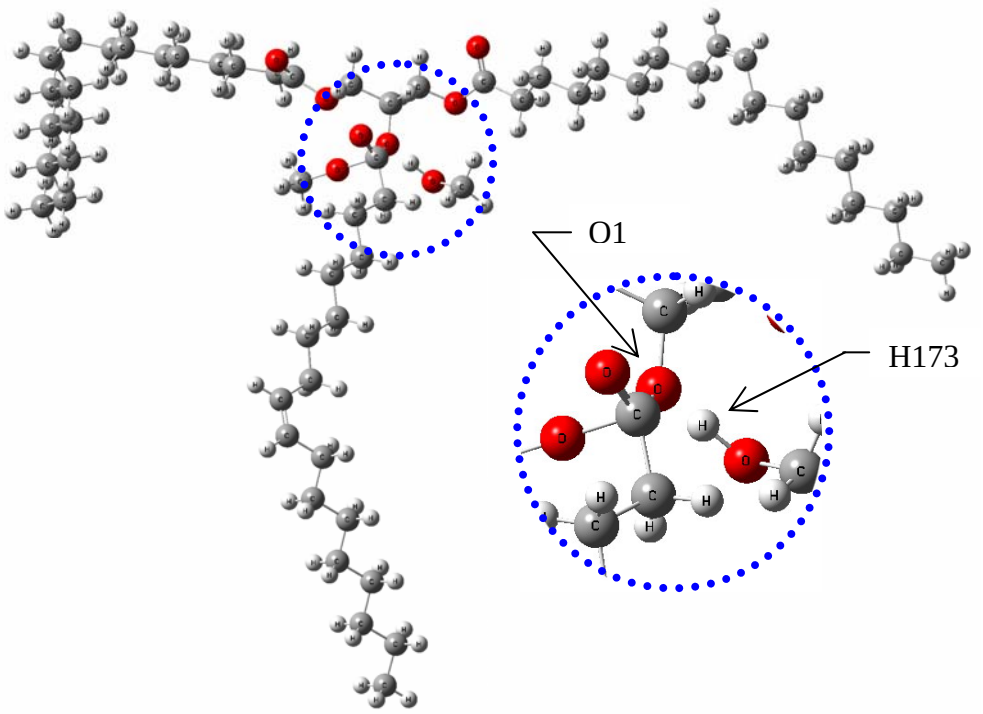
(a)



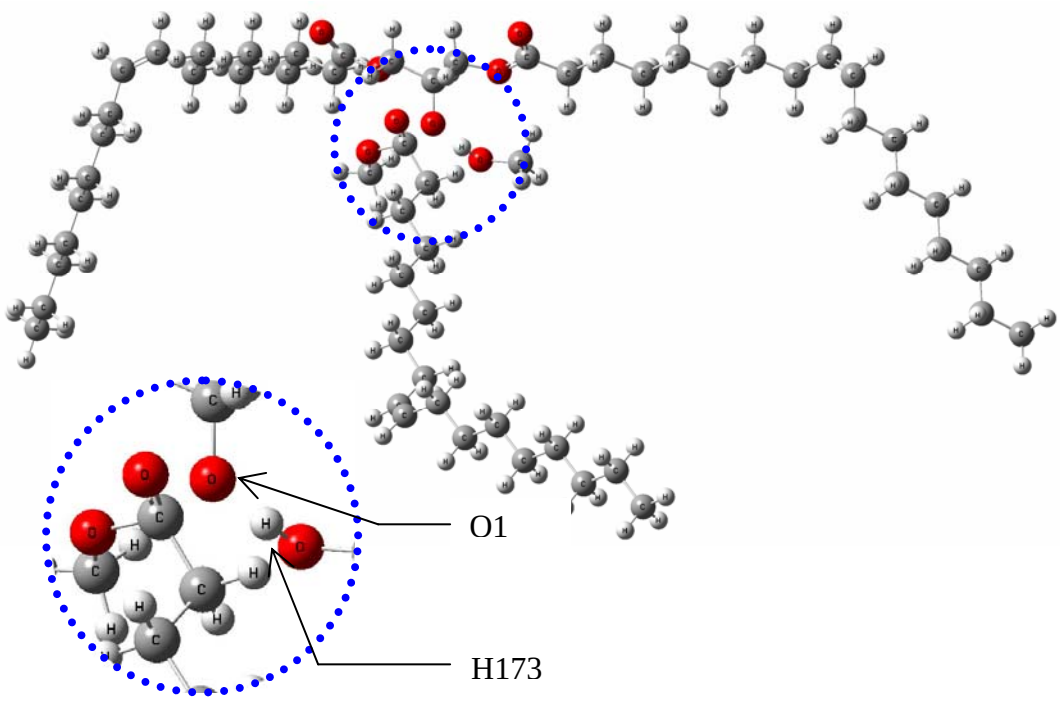
(b)

Figure29 The reaction structure of triolein and methoxide in transesterification of triolein: (a) input and (b) output.

The second simulation from Fig. 9 (a.2) is the reaction of the product in the first simulation (intermediate1) and methanol in transesterification of triolein. The amount of atoms in the input file was 178. The reaction between O1 of triolein and H173 of methanol was calculated based on HF6-31G method. The result found that the product structure was ester and diolein as shown in Fig. 9 (a.3) instead of intermediate2 as shown in Fig. 9 (a.2). The final products are ester and diolein. The relative energy between input structures and output structures of the reaction is 56728.79 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 30.



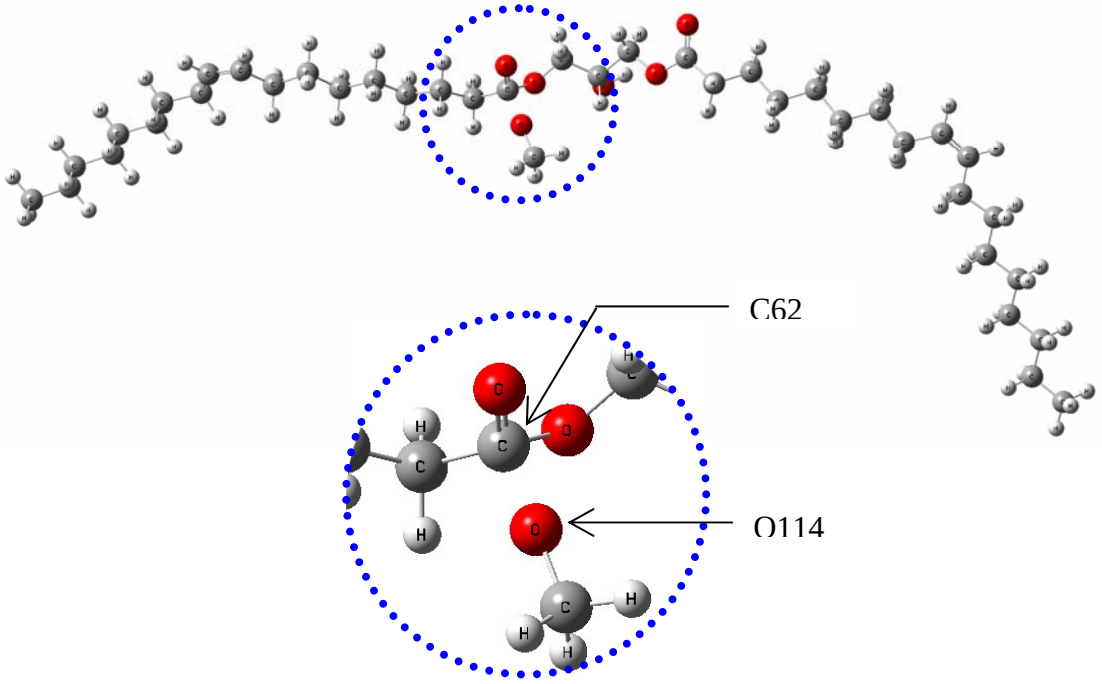
(a)



(b)

Figure30 The reaction structure of intermediate1 and methanol in transesterification of triolein: (a) input and (b) output.

The third simulation from Fig. 9 (b.1) is the reaction of diolein and methoxide. The amount of atoms in the input file was 121. The reaction between C62 in carbonyl group of diolein (C=O) and O114 of methoxide was calculated based on HF6-31G method. The result found that the product structure was intermediate1 as the product of step 1 in transesterification of diolein. And intermediate1 appeared in the 17th – 24th of the simulation cycles. Hence, this simulation is a reversible reaction. The relative energy between input structures and output structures of the reaction is 78.57 kcal/mol. The input and output structure were shown in Fig. 31.



(a)

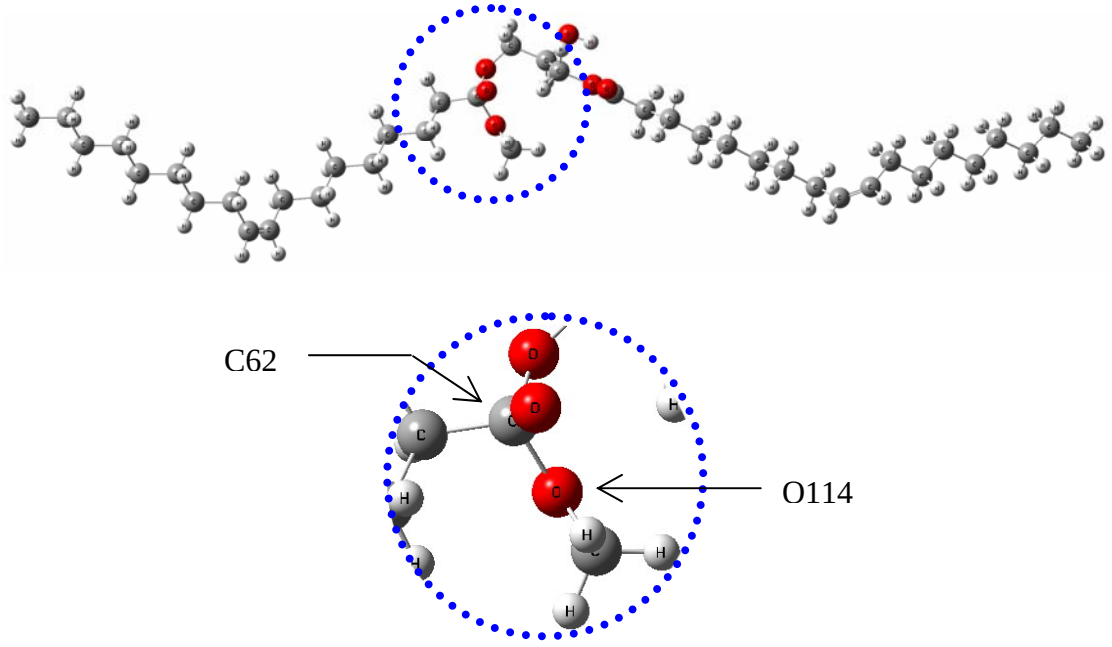
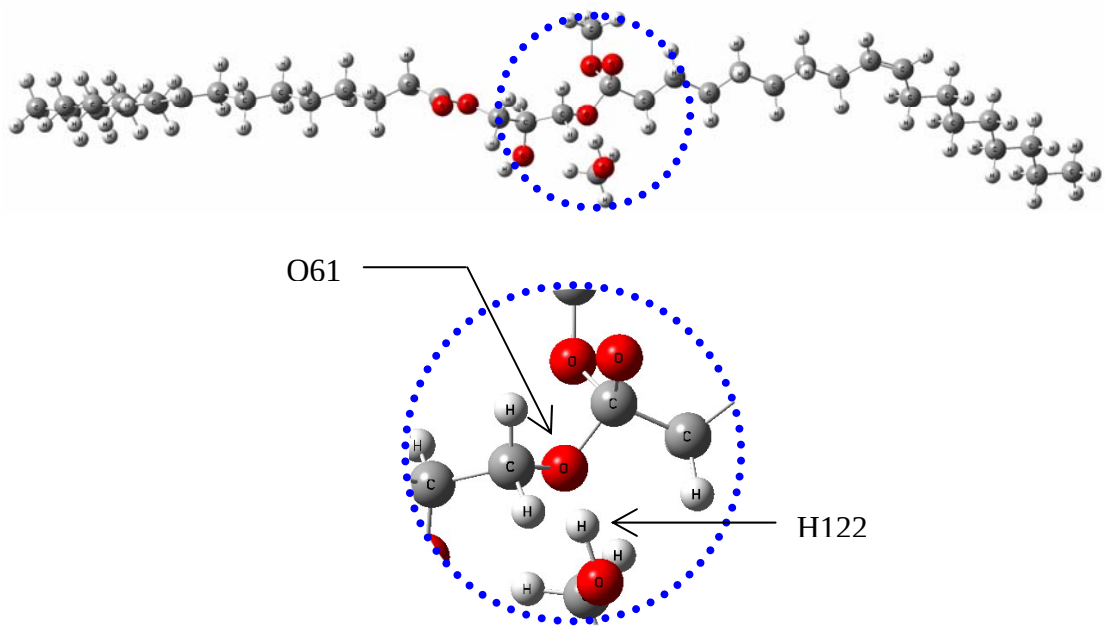
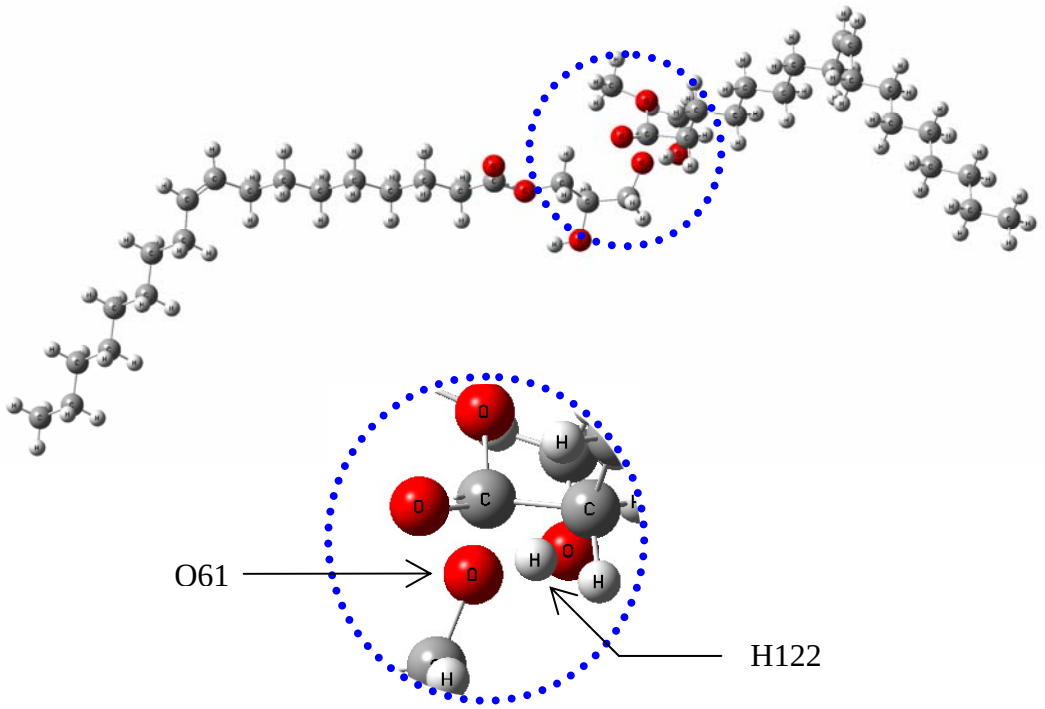


Figure31 The reaction structure of diolein and methoxide in transesterification of diolein: (a) input and (b) output.

The forth simulation from Fig. 9 (b.2) is the reaction of the product in the third simulation (intermediate1) and methanol in transesterification of diolein. The amount of atoms in the input file was 127. The reaction between O61 of diolein and H122 of methanol was calculated based on HF6-31G method. The result found that the product structure was ester and monoolein as shown in Fig. 9 (b.3) instead of intermediate2 as shown in Fig. 9 (b.2). The final products, ester and monoolein, appeared in the 11^{th} – 17^{th} and 20^{th} – 25^{th} of the simulation cycles. Hence, this simulation is a reversible reaction. The relative energy between input structures and output structures of the reaction is 125.50 kcal/mol. The input and output structure were shown in Fig. 32.



(a)



(b)

Figure32 The reaction structure of intermediate1 and methanol in transesterification of diolein: (a) input and (b) output.

The fifth simulation from Fig. 9 (c.1) is the reaction of monoolein and methoxide. The amount of atoms in the input file was 70. The reaction between C9 in carbonyl group of monoolein (C=O) and O65 of methoxide was calculated based on HF6-31G. The result found that the product structure wasn't as shown in Fig. 9 (c.1) or intermediate1 in transesterification of monoolein. So, the method was changed to HF3-21G. And the result showed that the product was intermediate1. The relative energy between input structures and output structures of the reaction is 175.70 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 33.

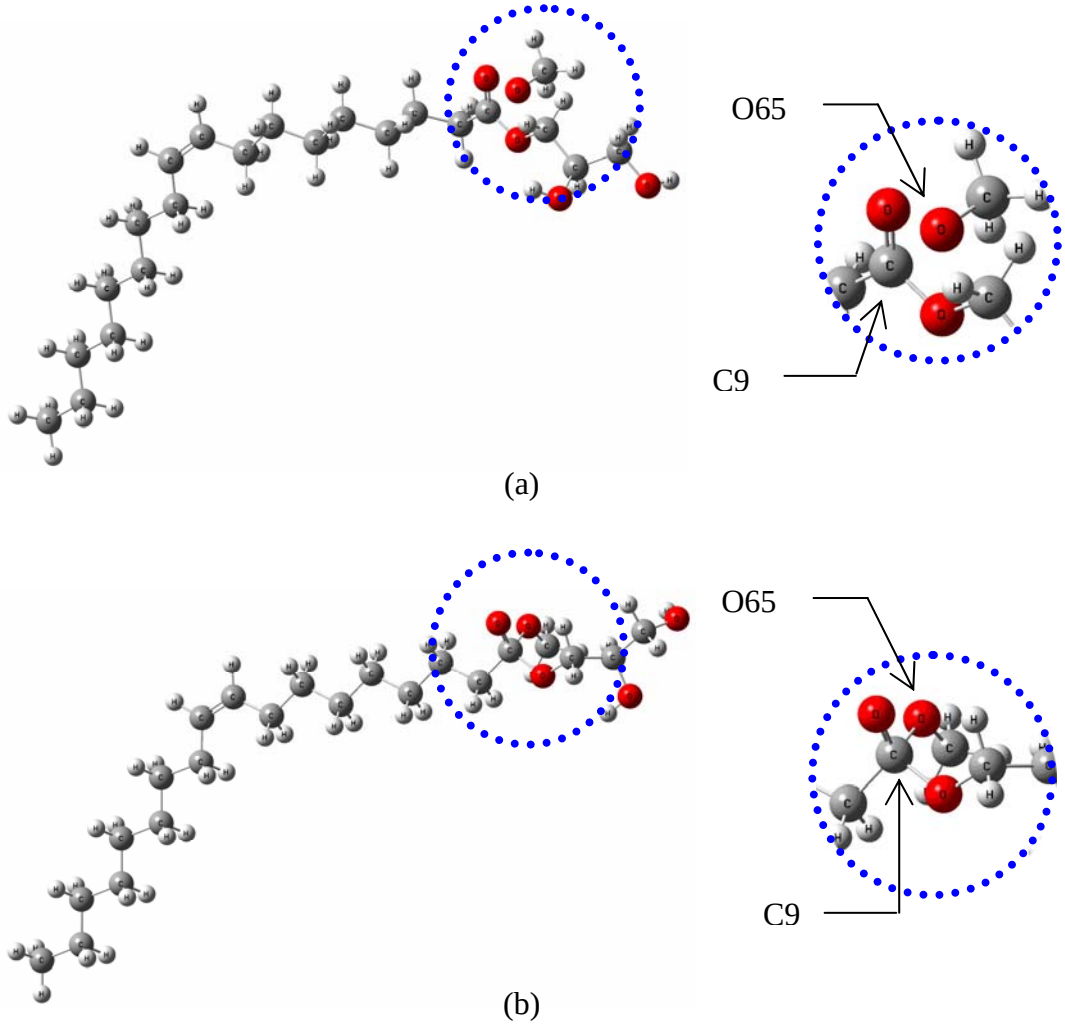
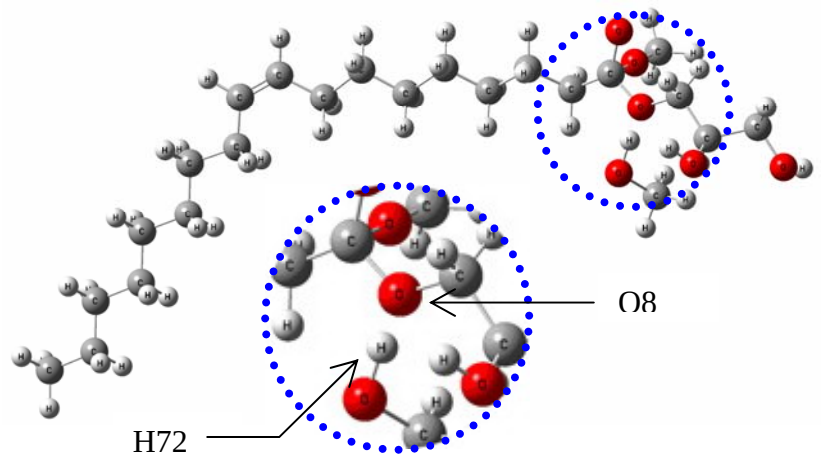
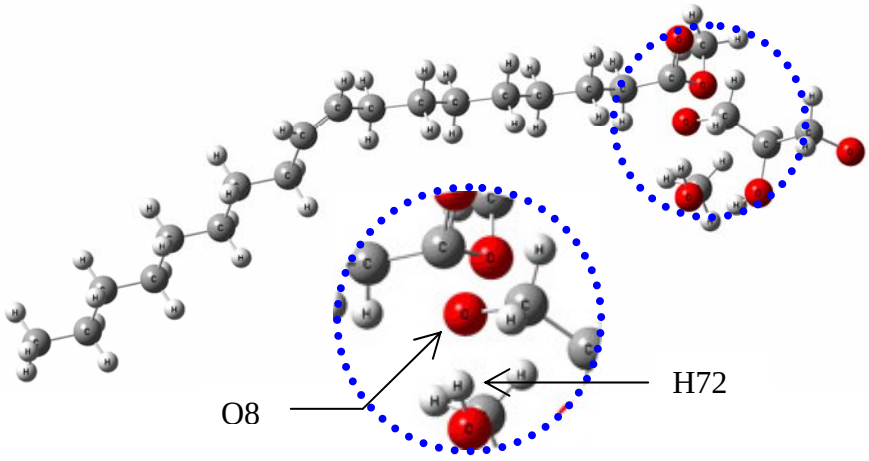


Figure33 The reaction structure of monoolein and methoxide in transesterification of monoolein: (a) input and (b) output.

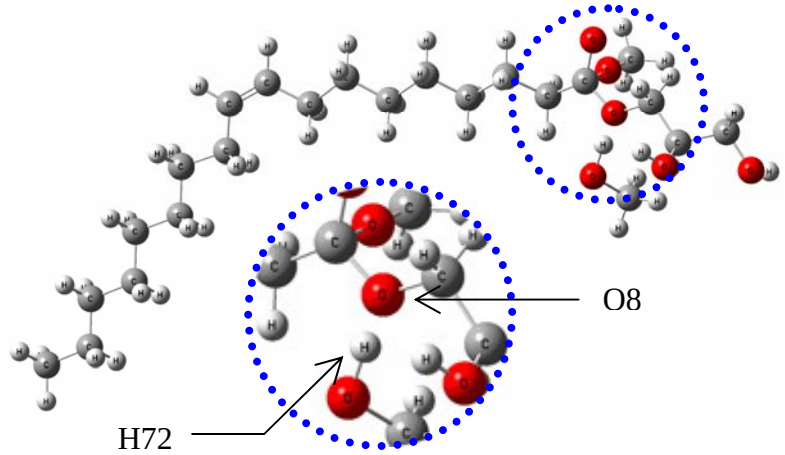
The sixth simulation from Fig. 9 (c.2) is the reaction of the product in the first simulation (intermediate1) and methanol in transesterification of monoolein. The amount of atoms in the input file was 76. The reaction between O8 of triolein and H72 of methanol was calculated based on HF6-31G. The result found that the product structure wasn't intermediate2 as shown in Fig. 9 (c.2) and weren't ester and glycerol as shown in Fig. 9 (c.3). The final products were intermediate1 and methanol as the reactant in this simulation. But ester and glycerol appeared in the 19th, 20th, and 25th of the simulation cycles. Hence, this simulation is a reversible reaction. The relative energy between input structures and output structures of the reaction is 238.45 kcal/mol. The input, structure of 19th cycle and output structure were shown in Fig. 34.



(a)



(b)

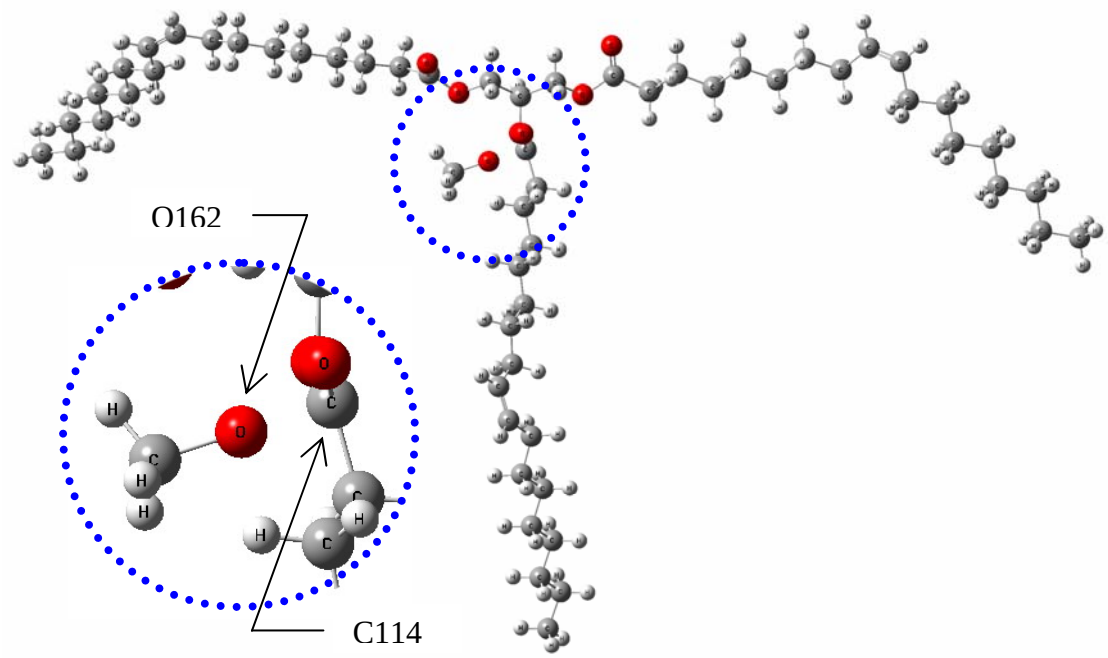


(c)

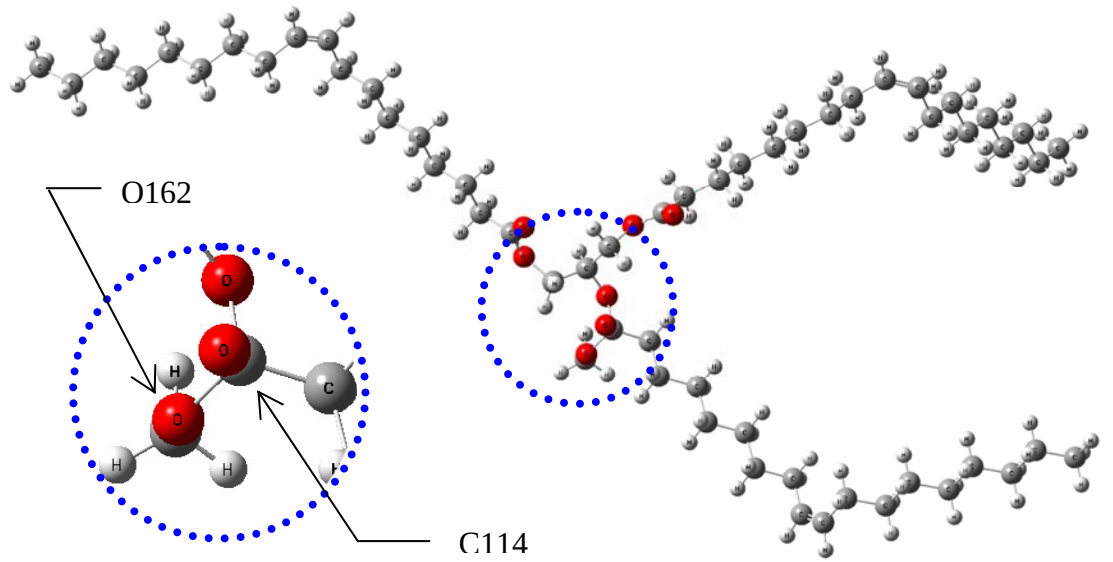
Figure34 The reaction structure of monoolein and methoxide in transesterification of monoolein: (a) input, (b) structure of 19th cycle and (c) output.

Transesterification mechanism Type 4

The first simulation from Fig. 10(a.1) is the reaction of triolein and methoxide. The amount of atoms in the input file was 172. The reaction between C114 in carbonyl group of triolein (C=O) and O162 of methoxide was calculated based on HF6-31G method. The result found that the product structure was intermediate1 as the product of step 1 in transesterification of triolein. The relative energy between input structures and output structures of the reaction is 97.78 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 35.



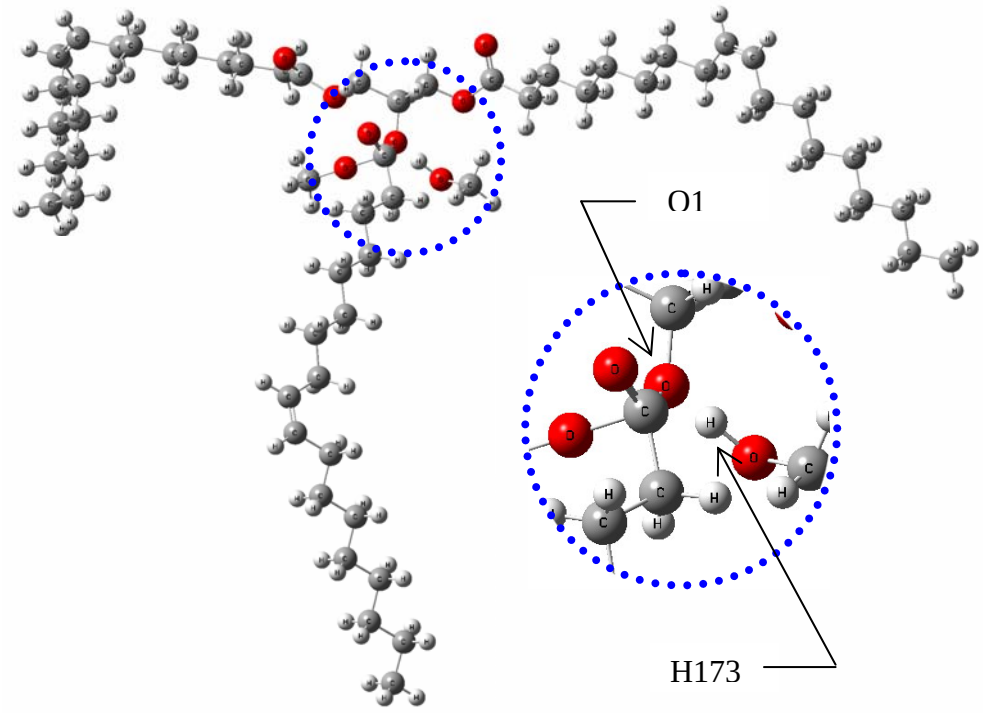
(a)



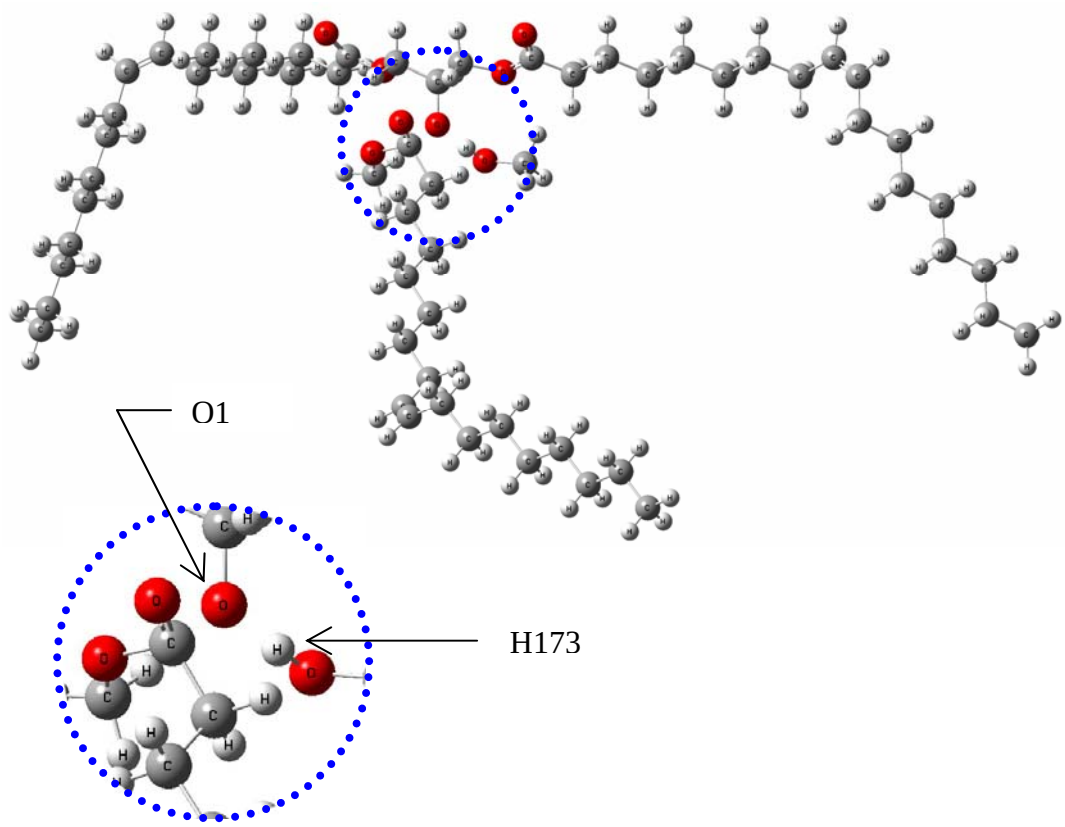
(b)

Figure35 The reaction structure of triolein and methoxide in transesterification of triolein: (a) input and (b) output.

The second simulation from Fig. 10 (a.2) is the reaction of the product in the first simulation (intermediate1) and methanol in transesterification of triolein. The amount of atoms in the input file was 178. The reaction between O1 of triolein and H173 of methanol was calculated based on HF6-31G method. The result found that the product structure was ester and diolein as shown in Fig. 10 (a.3) instead of intermediate2 as shown in Fig. 10 (a.2). The final products are ester and diolein. The relative energy between input structures and output structures of the reaction is 56728.79 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 36.



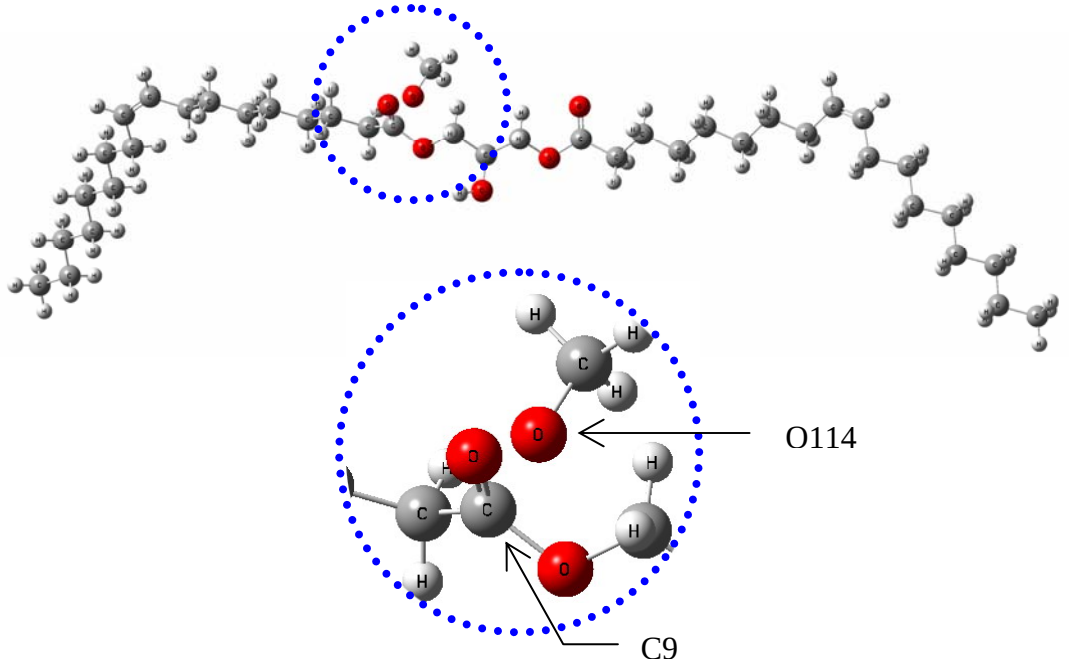
(a)



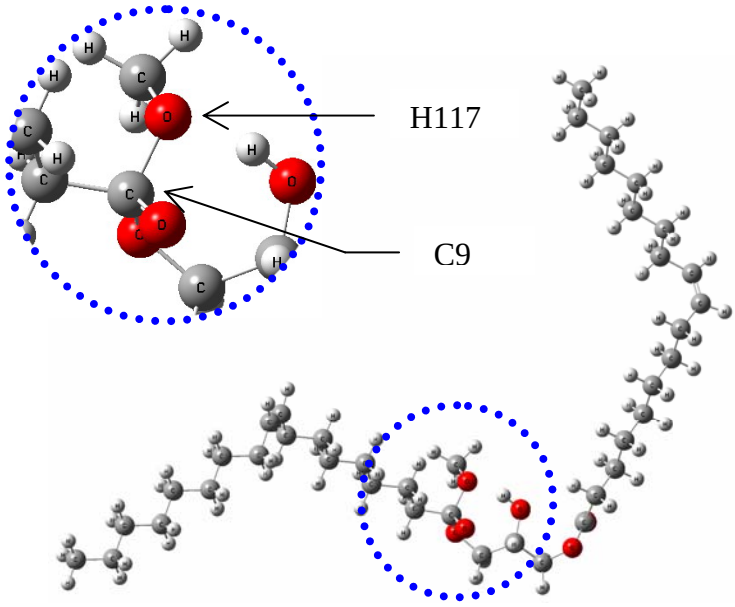
(b)

Figure36 The reaction structure of intermediate1 and methanol in transesterification of triolein: (a) input and (b) output.

The third simulation from Fig. 10 (b.1) is the reaction of diolein and methoxide. The amount of atoms in the input file was 121. The reaction between C9 in carbonyl group of diolein (C=O) and O114 of methoxide was calculated based on HF6-31G method. The result found that the product structure wasn't intermediate1 in transesterification of diolein. So, the method was changed to HF3-21G. And the result showed that the product was intermediate1 as the product structure of step 1 in transesterification of diolein. And intermediate1 appeared in the 20^{th} – 24^{th} of the simulation cycles. Hence, this simulation is a reversible reaction. The relative energy between input structures and output structures of the reaction is 163.15 kcal/mol. The input and output structure were shown in Fig. 37.



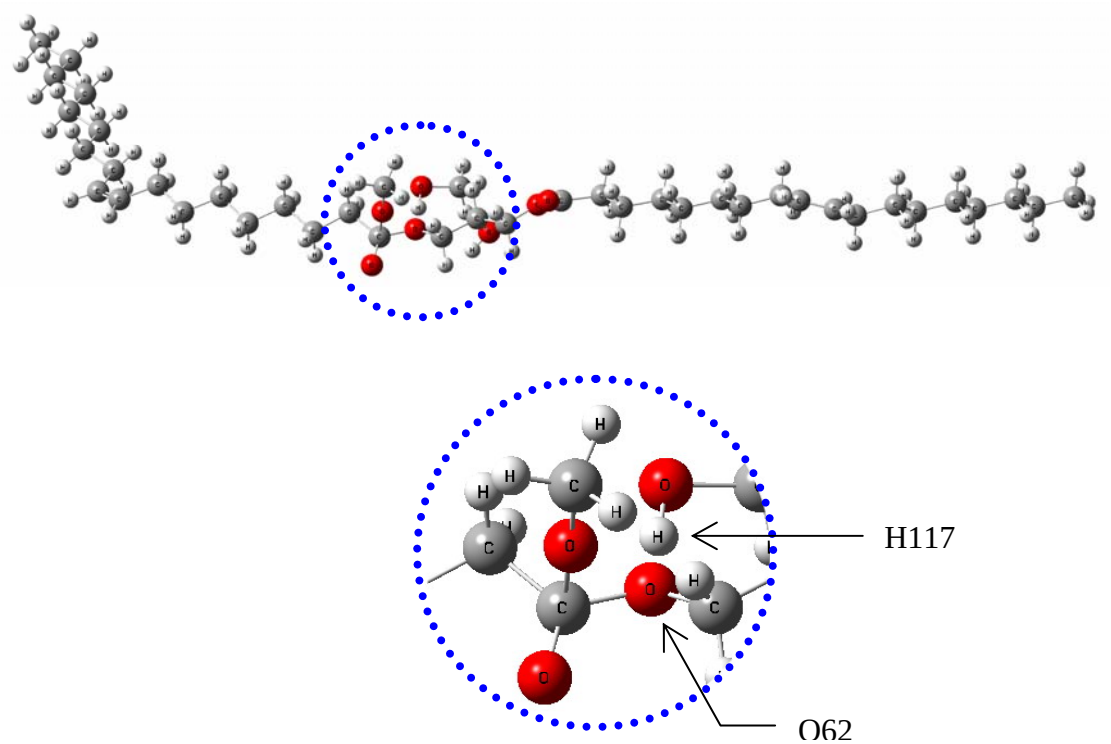
(a)



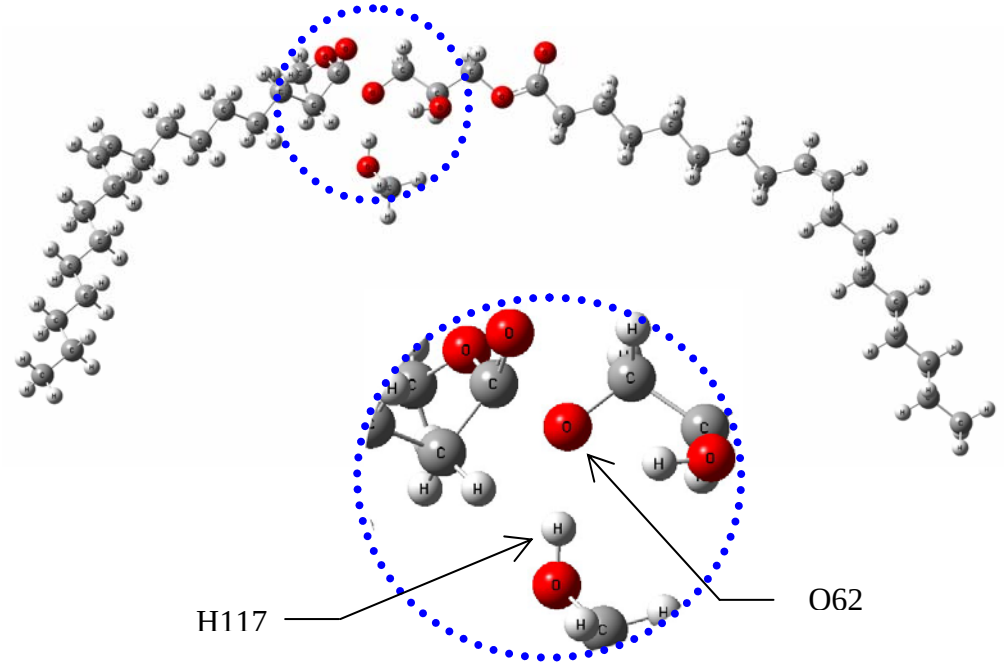
(b)

Figure37 The reaction structure of diolein and methoxide in transesterification of diolein: (a) input and (b) output.

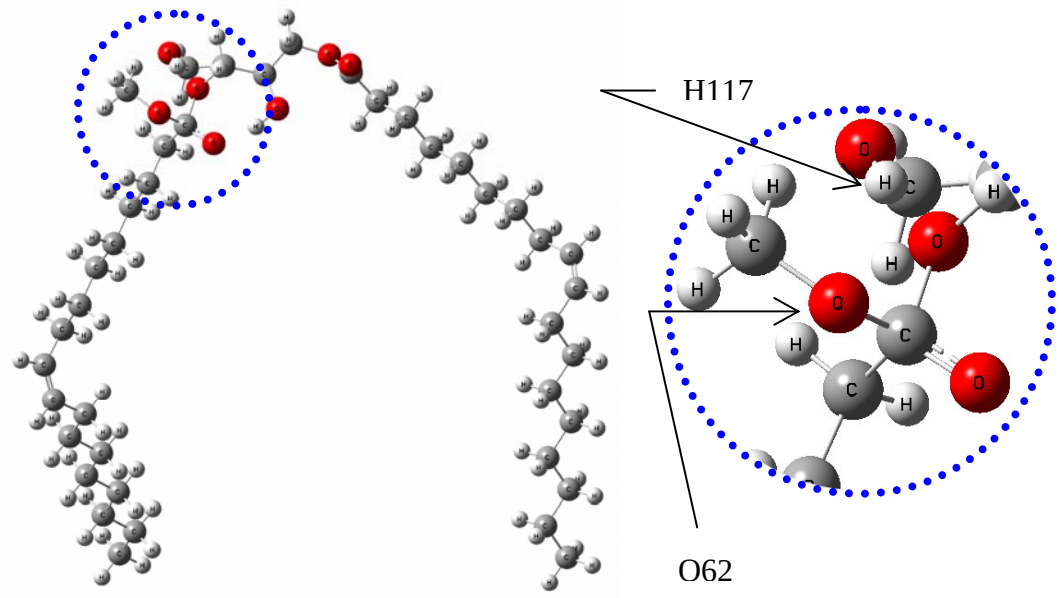
The forth simulation from Fig. 10 (b.2) is the reaction of the product in the third simulation (intermediate1) and methanol in transesterification of diolein. The amount of atoms in the input file was 127. The reaction between O62 of diolein and H117of methanol was calculated based on HF6-31G method. The result found that the product structure wasn't intermediate2 as shown in Fig. 10 (b.2) and weren't ester and monoolein as shown in Fig. 10 (b.3). The final products were intermediate1 and methanol as the reactant in this simulation. But ester and monoolein appeared in the 17^{th} - 27^{th}, 29^{th}, 30^{th} and 40^{th} of the simulation cycles. Hence, this simulation is a reversible reaction. The final products were ester and monoolein. The relative energy between input structures and output structures of the reaction is 238.45 kcal/mol. The input, structure of 17^{th} cycle and output structure were shown in Fig. 38.



(a)



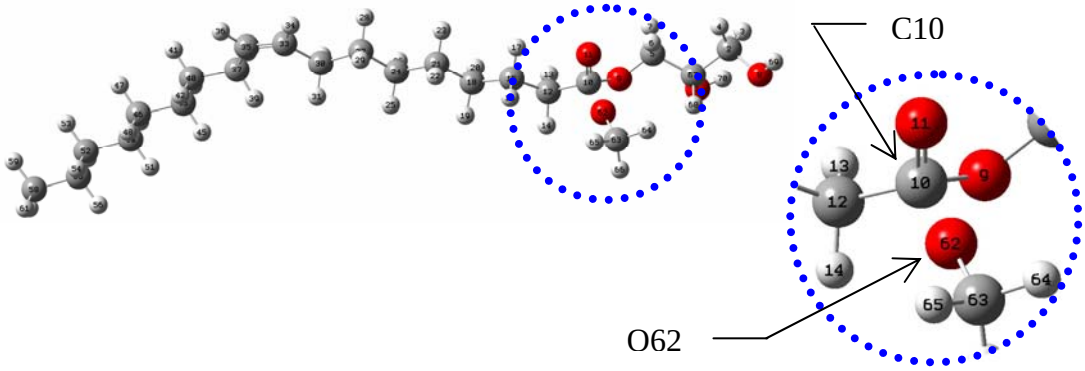
(b)



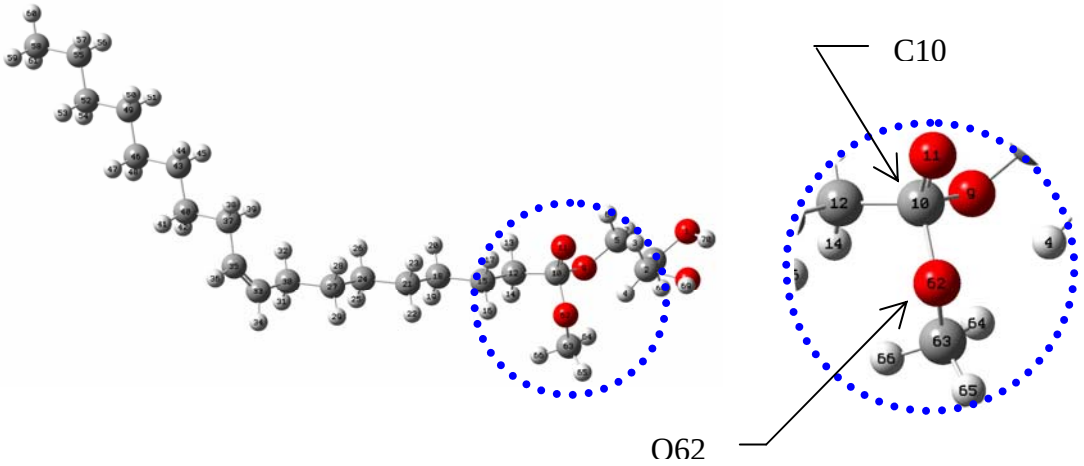
(c)

Figure38 The reaction structure of intermediate1 and methanol in transesterification of diolein: (a) input, (b) structure of 17th cycle and (c) output.

The fifth simulation from Fig. 10 (c.1) is the reaction of monoolein and methoxide. The amount of atoms in the input file was 70. The reaction between C10 in carbonyl group of monoolein (C=O) and O62 of methoxide was calculated based on HF6-31G. The result found that the product structure wasn't intermediate1 as shown in Fig. 10 (c.1) in transesterification of monoolein. So, the method was changed to HF3-21G. And the result showed that the product was intermediate1. The relative energy between input structures and output structures of the reaction is 125.50 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 39.



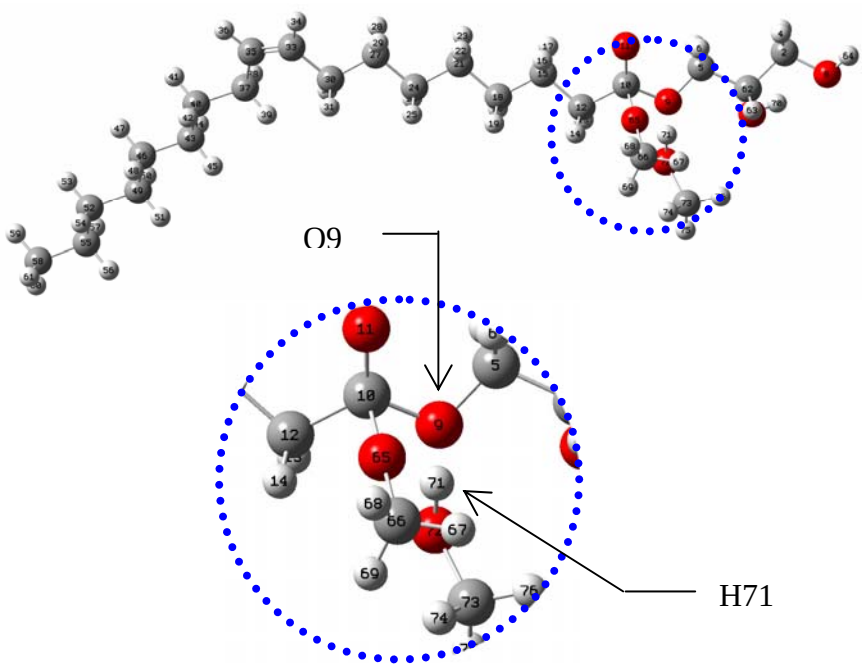
(a)



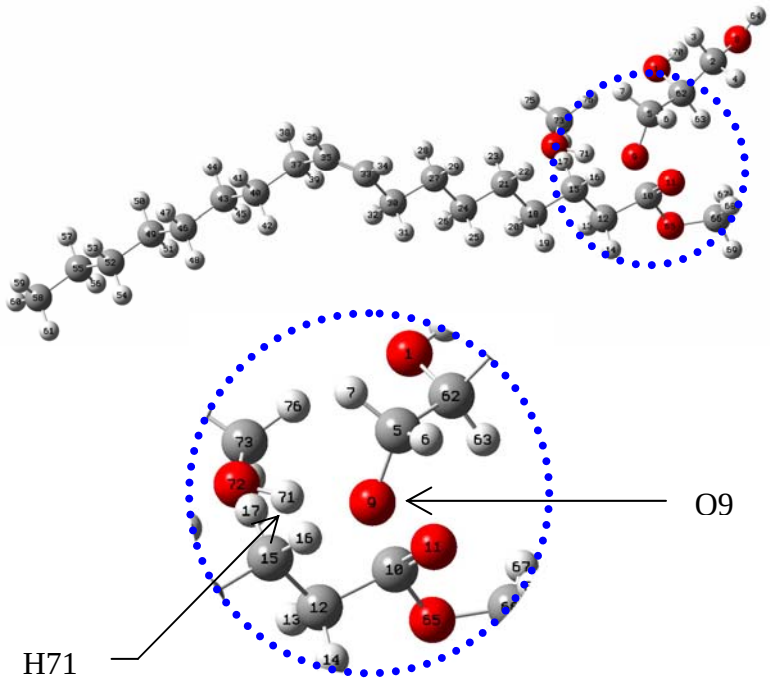
(b)

Figure39 The reaction structure of monoolein and methoxide in transesterification of monoolein: (a) input and (b) output.

The sixth simulation from Fig. 10 (c.2) is the reaction of the product in the first simulation (intermediate1) and methanol in transesterification of monoolein. The amount of atoms in the input file was 76. The reaction between O9 of triolein and H71 of methanol was calculated based on HF6-31G. The result found that the product structure wasn't intermediate2 as shown in Fig. 10 (c.2) and weren't ester and glycerol as shown in Fig. 10 (c.3). So, the method was changed to HF3-21G. The result showed that the final products were ester and glycerol. The relative energy between input structures and output structures of the reaction is 4091.37 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 40.



(a)

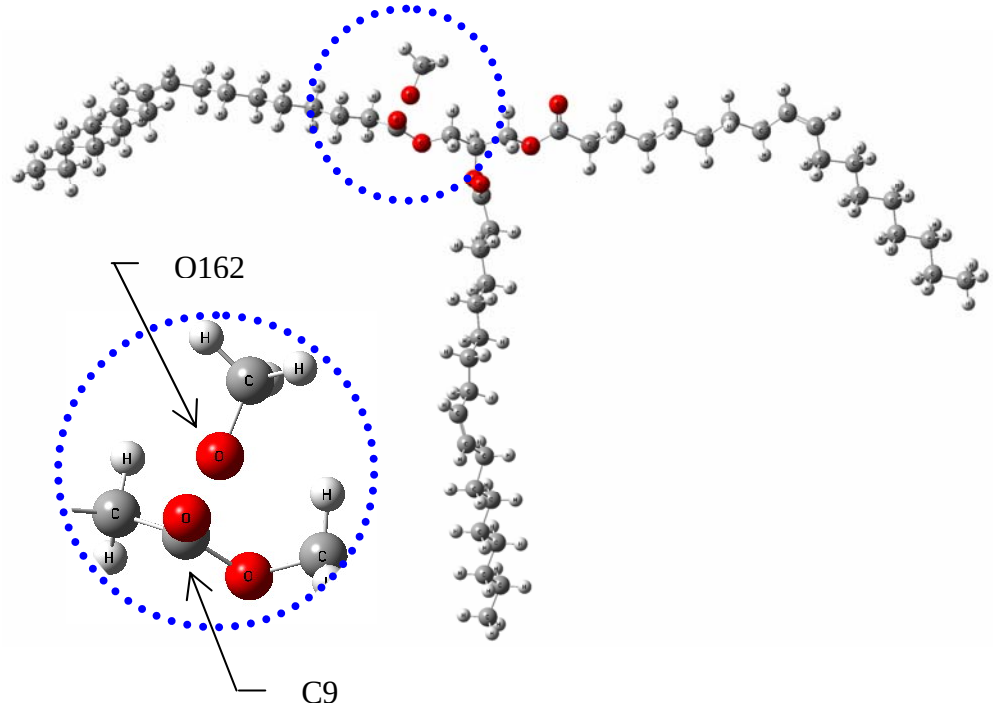


(b)

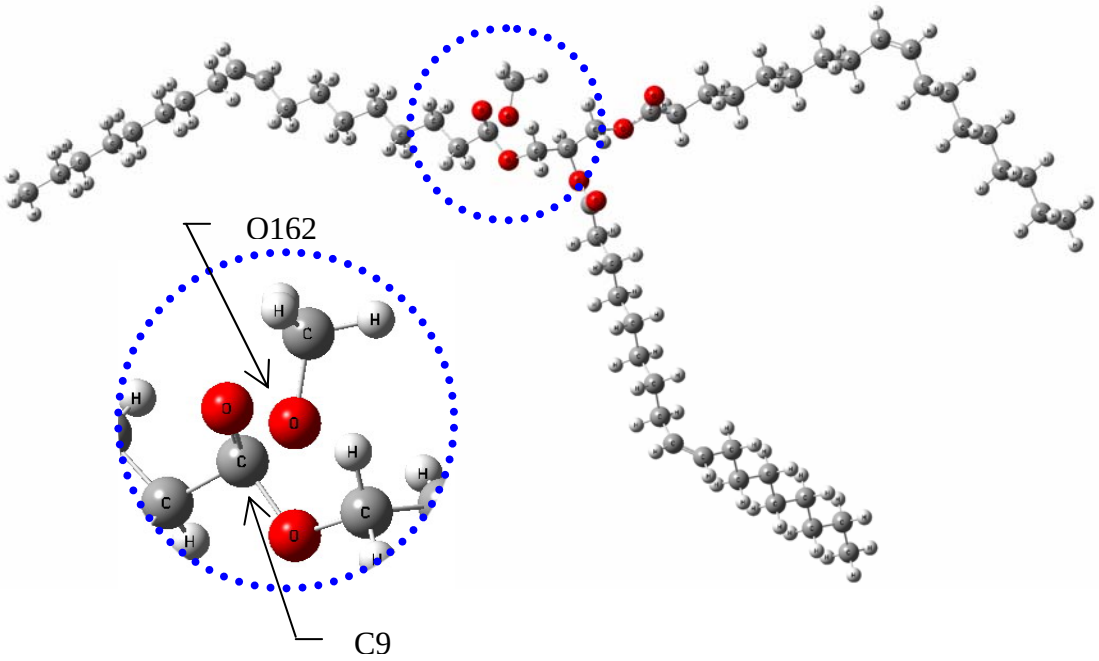
Figure40 The reaction structure of intermediate1 and methanol in transesterification of monoolein: (a) input and (b) output.

Transesterification mechanism Type 5

The first simulation from Fig. 11 (a.1) is the reaction of triolein and methoxide. The amount of atoms in the input file was 172. The reaction between C9 in carbonyl group of triolein (C=O) and O162 of methoxide was calculated based on HF6-31G method. The result found that the product structure wasn't intermediate1 in transesterification of diolein. So, the method was changed to HF3-21G. And the result showed that the product was intermediate1. And intermediate1 appeared in the 76th of the simulation cycles. Hence, this simulation is a reversible reaction. The relative energy between input structures and output structures of the reaction is 196.65 kcal/mol. The input and output structure were shown in Fig. 41.



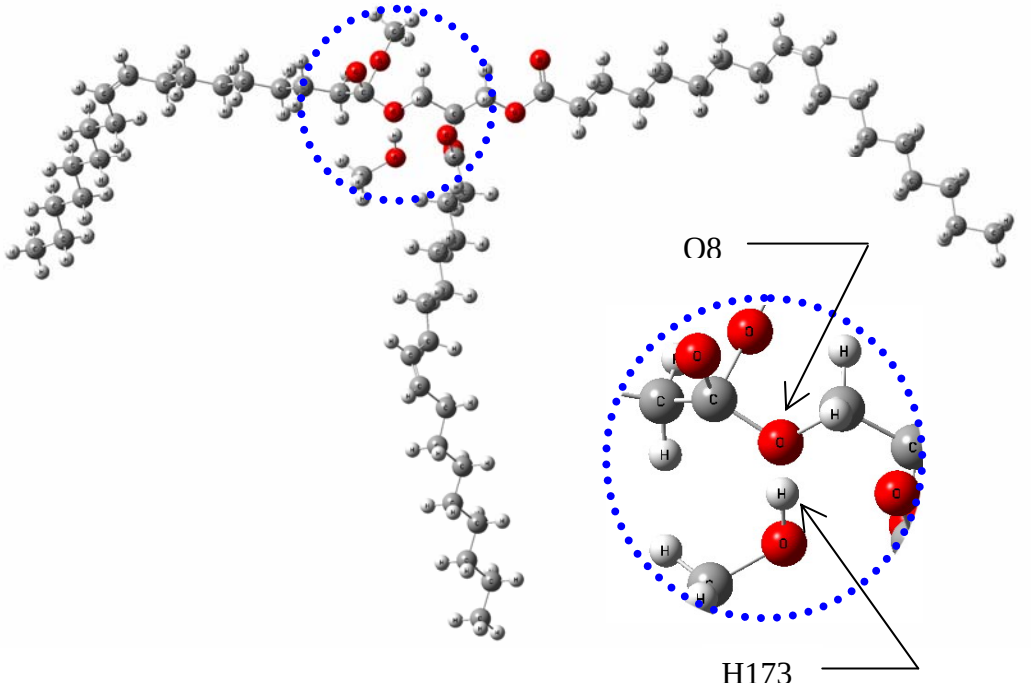
(a)



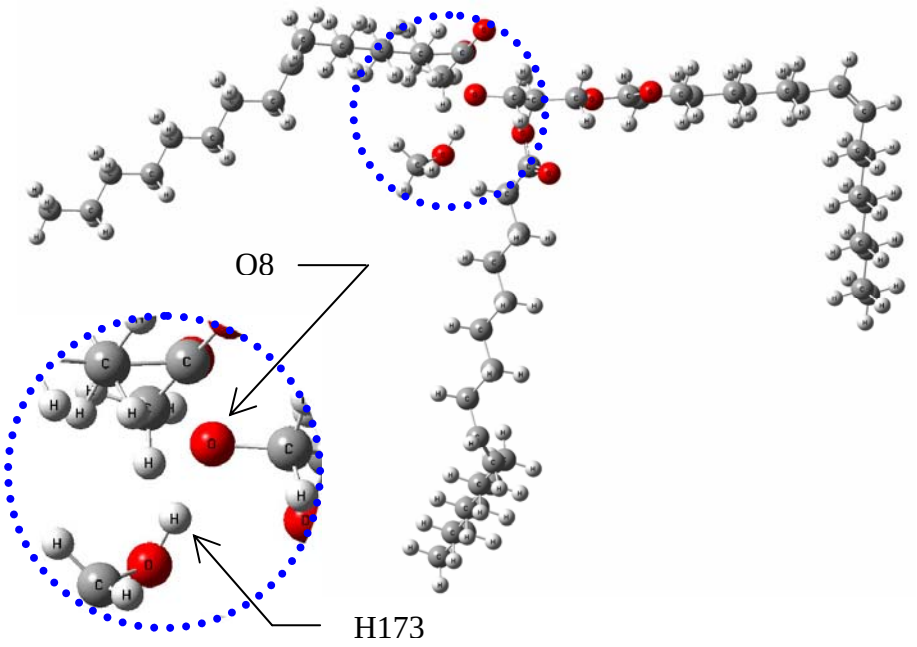
(b)

Figure41 The reaction structure of triolein and methoxide in transesterification of triolein: (a) input and (b) output.

The second simulation from Fig. 11 (a.2) is the reaction of the product in the first simulation (intermediate1) and methanol in transesterification of triolein. The amount of atoms in the input file was 178. The reaction between O8 of triolein and H173 of methanol was calculated based on HF6-31G method. The result found that the product structure wasn't intermediate2 as shown in Fig. 11 (a.2) and weren't ester and diolein as shown in Fig. 11 (a.3). So, the method was changed to HF3-21G. And the result found that the final products are ester and diolein. The relative energy between input structures and output structures of the reaction is 243.79 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 42.



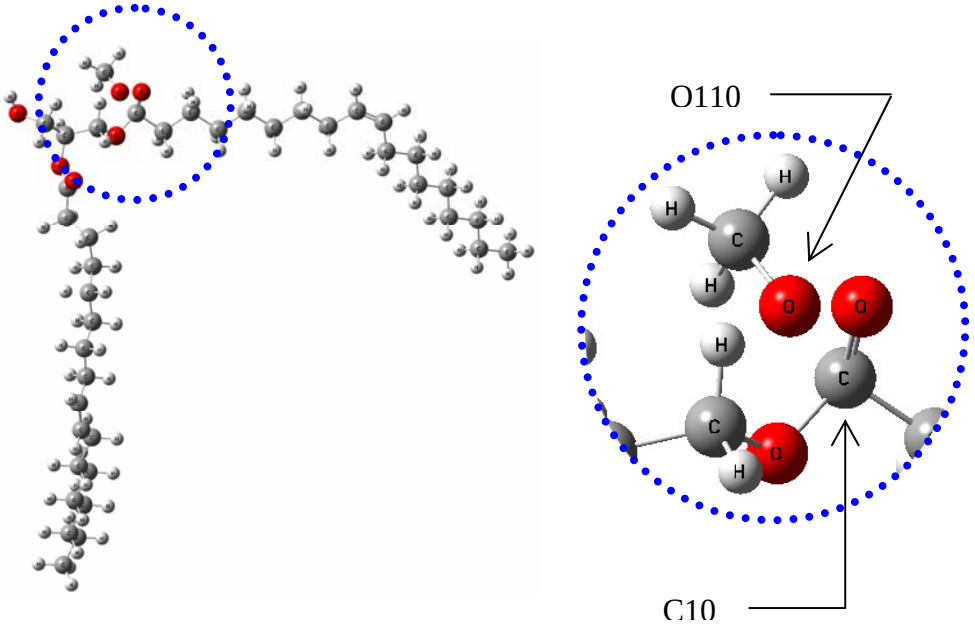
(a)



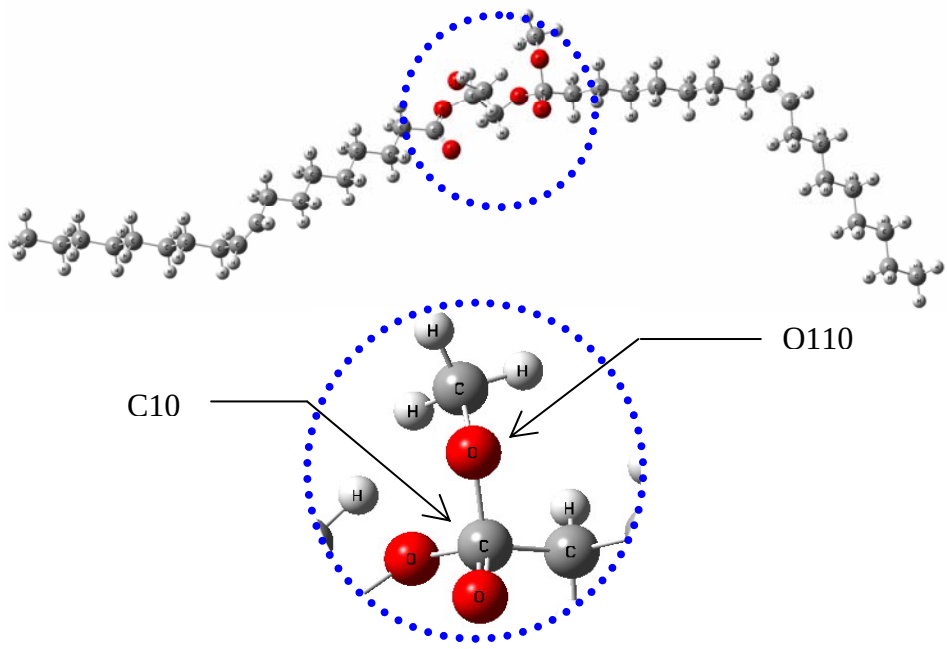
(b)

Figure42 The reaction structure of intermediate1 and methanol in transesterification of triolein: (a) input and (b) output.

The third simulation from Fig. 11 (b.1) is the reaction of diolein and methoxide. The amount of atoms in the input file was 121. The reaction between C10 in carbonyl group of diolein (C=O) and O110 of methoxide was calculated based on HF6-31G method. The result found that the product structure was intermediate1 as the product of step 1 in transesterification of diolein. And intermediate1 appeared in the 47^{th} - 49^{th} of the simulation cycles. Hence, this simulation is a reversible reaction. The relative energy between input structures and output structures of the reaction is 141.94 kcal/mol. The input and output structure were shown in Fig. 43.



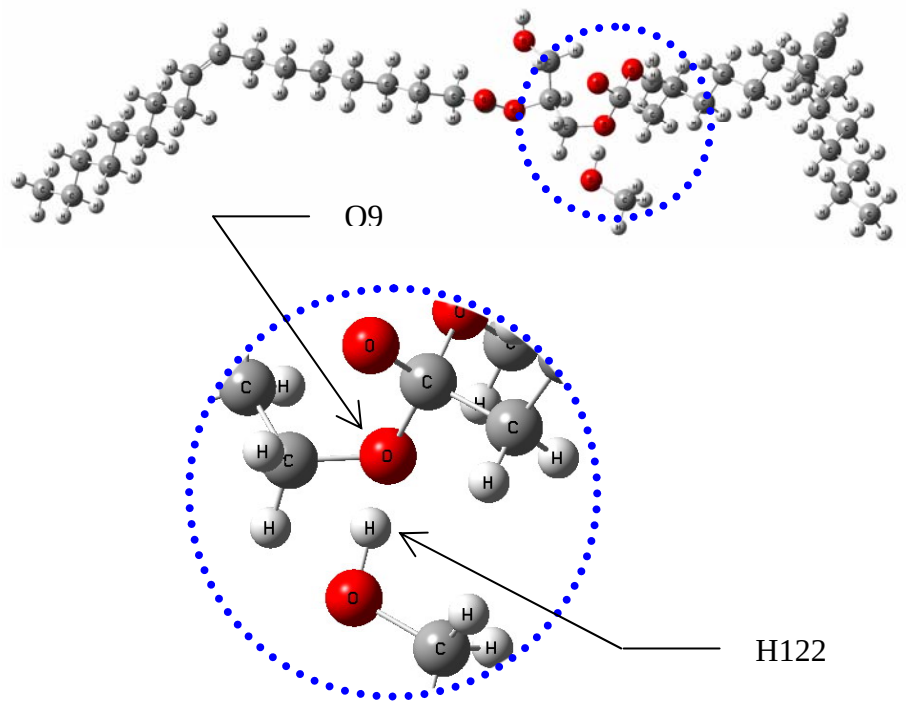
(a)



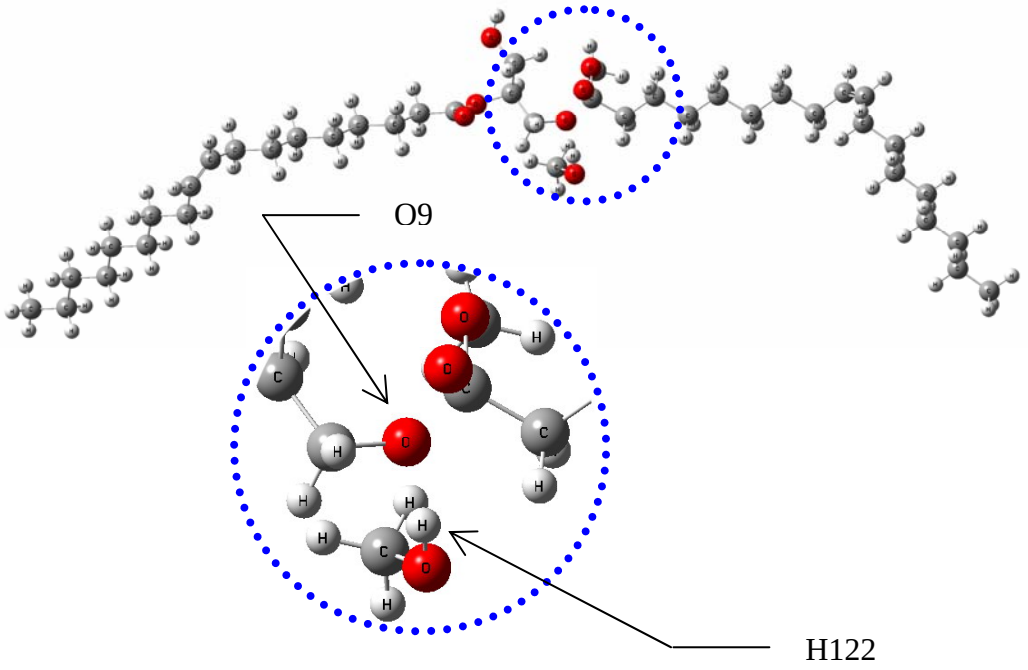
(b)

Figure43 The reaction structure of diolein and methoxide in transesterification of diolein: (a) input and (b) output.

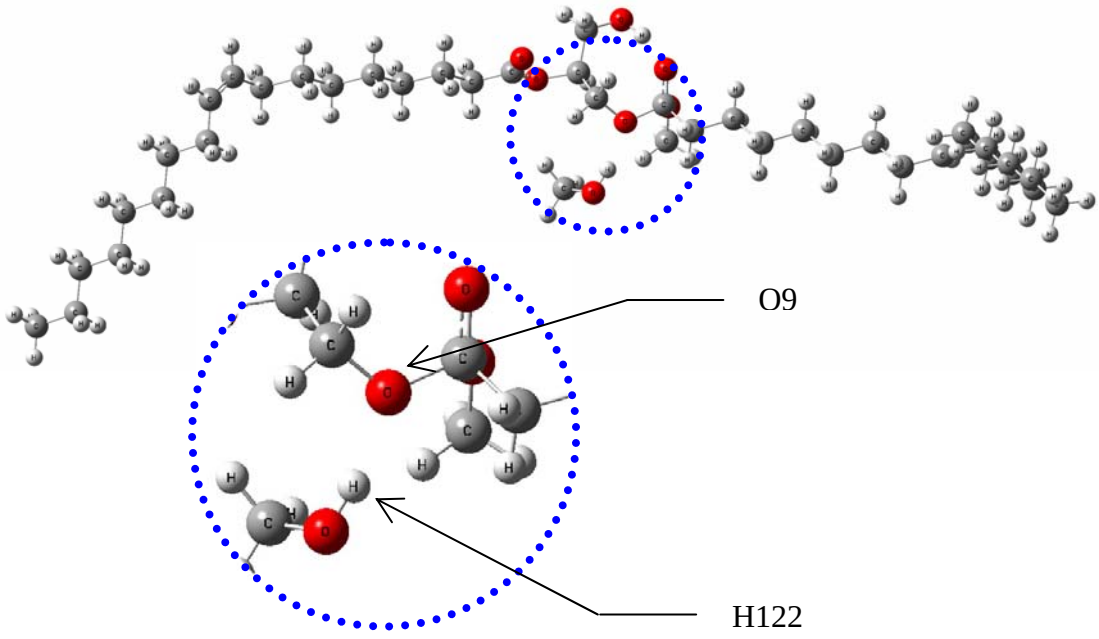
The forth simulation from Fig. 11 (b.2) is the reaction of the product in the third simulation (intermediate1) and methanol in transesterification of diolein. The amount of atoms in the input file was 127. The reaction between O9 of diolein and H122 of methanol was calculated based on HF6-31G method. The result found that the product structure wasn't intermediate2 as shown in Fig. 11 (b.2) and weren't ester and monoolein as shown in Fig. 11 (b.3). The final products were intermediate1 and methanol as the reactant in this simulation. The final products, ester and monoolein, appeared in the 3rd - 13th, 17th - 24th, 27th, 29th - 35th, and 37th – 52nd of the simulation cycles. Hence, this simulation is a reversible reaction. The relative energy between input structures and output structures of the reaction is 87.85 kcal/mol. The input, structure of 3rd cycle and output structure were shown in Fig. 44.



(a)



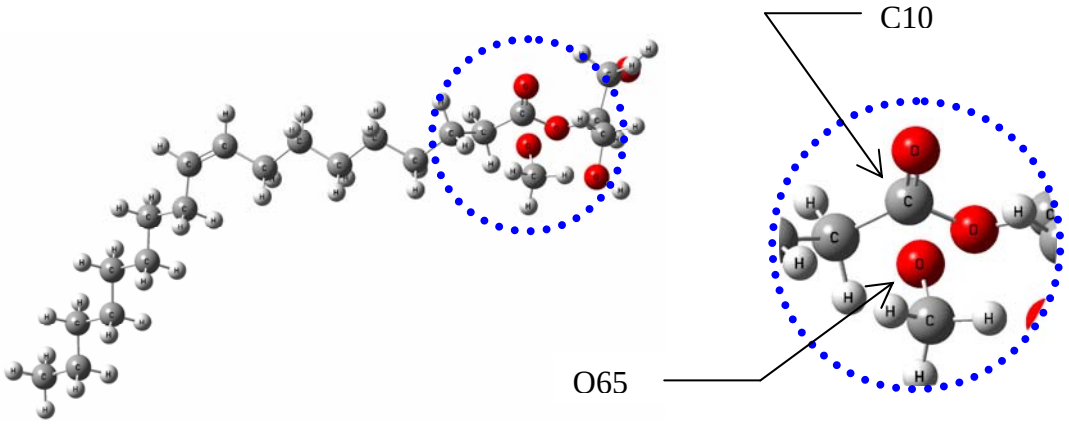
(b)



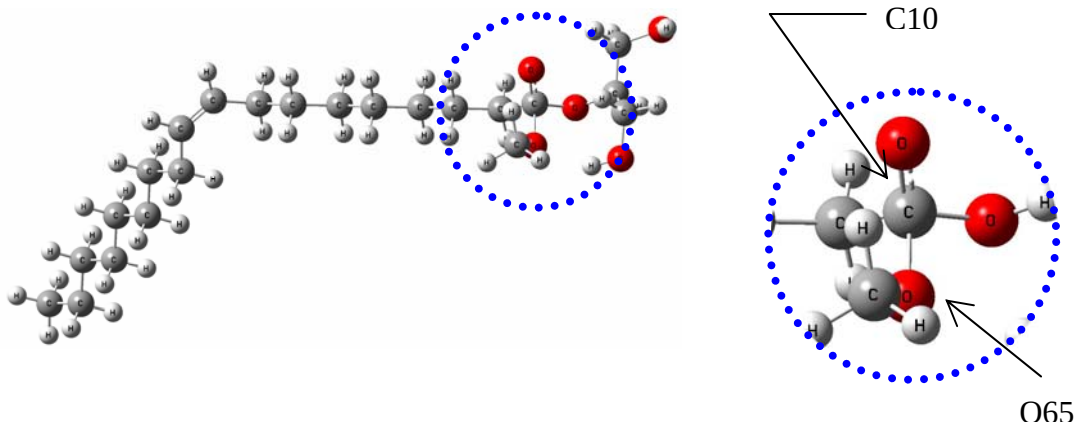
(c)

Figure44 The reaction structure of intermediate1 and methanol in transesterification of diolein: (a) input, (b) structure of 3rd cycle, and (c) output.

The fifth simulation from Fig. 11 (c.1) is the reaction of monoolein and methoxide. The amount of atoms in the input file was 70. The reaction between C10 in carbonyl group of monoolein (C=O) and O65 of methoxide was calculated based on HF6-31G. The result found that the product structure was intermediate1 as the product of step 1 in transesterification of triolein. The relative energy between input structures and output structures of the reaction is 163.15 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 45.



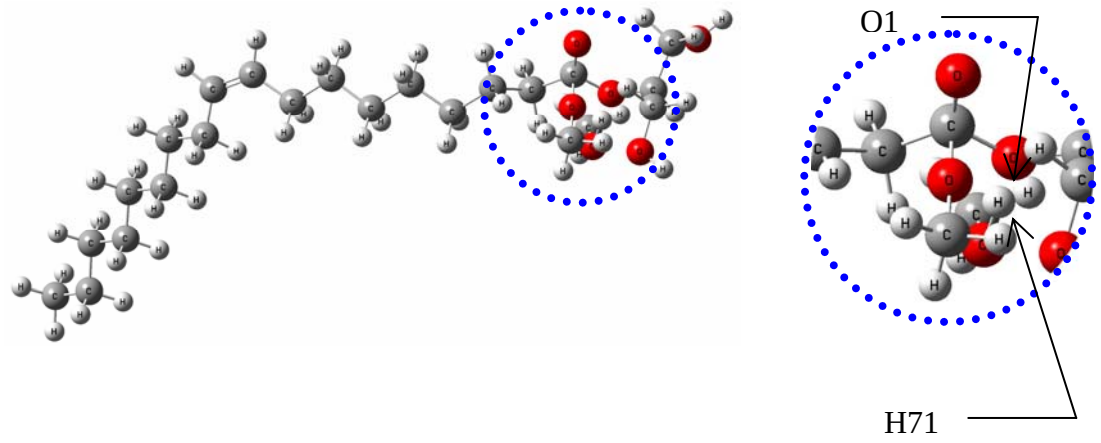
(a)



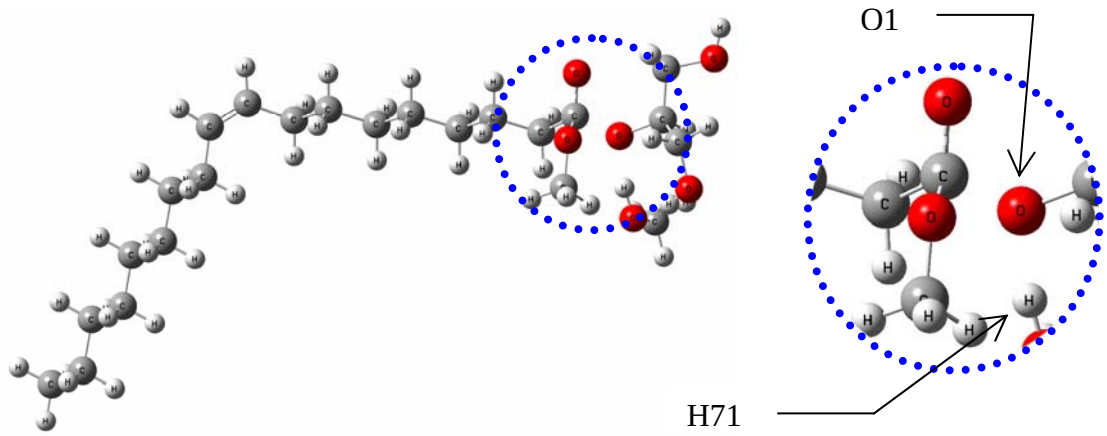
(b)

Figure45 The reaction structure of monoolein and methoxide in transesterification of monoolein: (a) input, and (b) output.

The sixth simulation from Fig. 11 (c.2) is the reaction of the product in the first simulation (intermediate1) and methanol in transesterification of monoolein. The amount of atoms in the input file was 76. The reaction between O1 of triolein and H71 of methanol was calculated based on HF6-31G. The result found that the product structure was ester and monoolein as shown in Fig. 11 (b.3) instead of intermediate2 as shown in Fig. 11 (b.2). The final products, ester and monoolein, appeared in the 7^{th} – 10^{th} of the simulation cycles. Hence, this simulation is a reversible reaction. The relative energy between input structures and output structures of the reaction is 282.38 kcal/mol. The input and output structure were shown in Fig. 46.



(a)

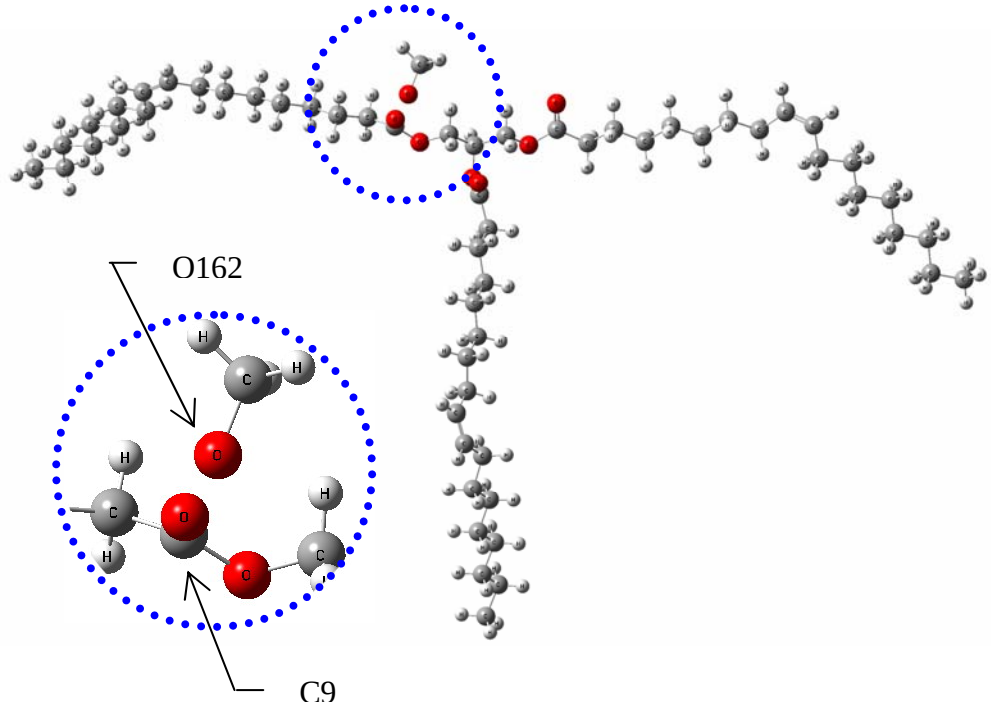


(b)

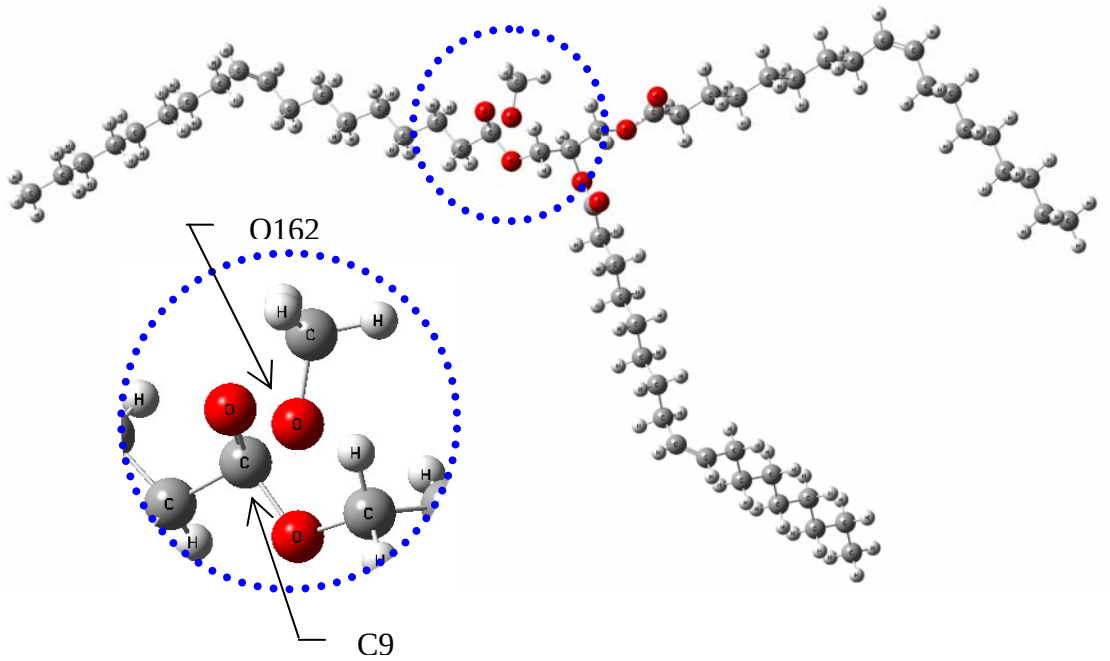
Figure46 The reaction structure of monoolein and methoxide in transesterification of monoolein: (a) input and (b) output.

Transesterification mechanism Type 6

The first simulation from Fig. 12 (a.1) is the reaction of triolein and methoxide. The amount of atoms in the input file was 172. The reaction between C9 in carbonyl group of triolein (C=O) and O162 of methoxide was calculated based on HF6-31G method. The result found that the product structure wasn't intermediate1 in transesterification of diolein. So, the method was changed to HF3-21G. And the result showed that the final product was the intermedaite1. The final products, intermediate1, appeared in the 76th of the simulation cycles. Hence, this simulation is a reversible reaction. The relative energy between input structures and output structures of the reaction is 196.65 kcal/mol. The input and output structure were shown in Fig. 47.



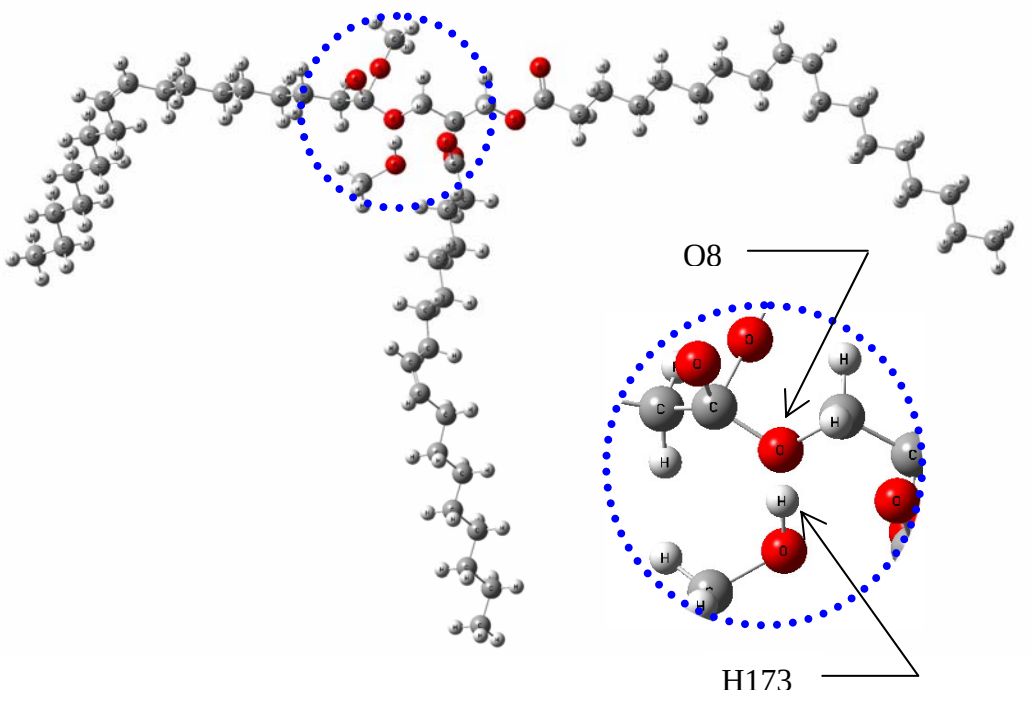
(a)



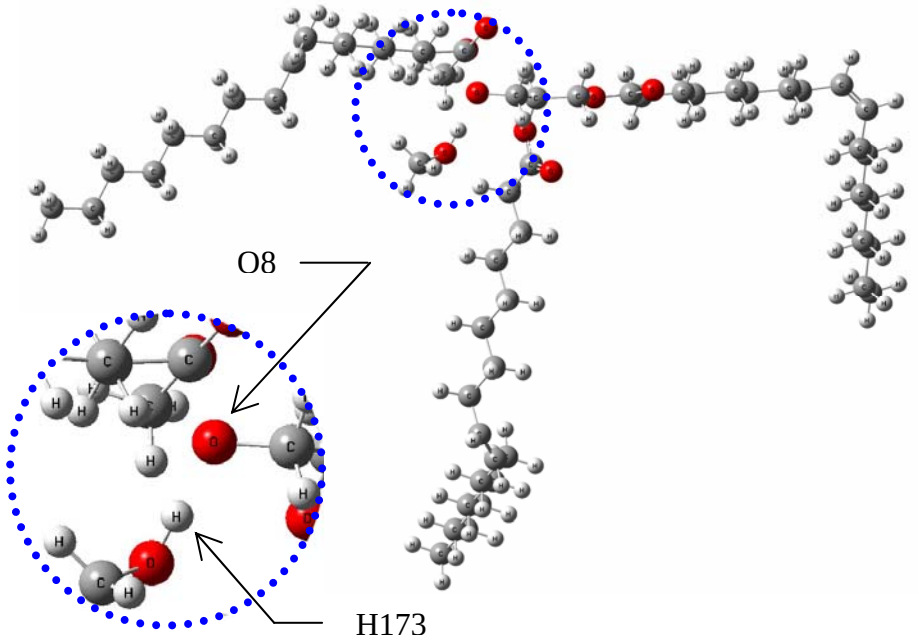
(b)

Figure47 The reaction structure of triolein and methoxide in transesterification of triolein: (a) input and (b) output.

The second simulation from Fig. 12 (a.2) is the reaction of the product in the first simulation (intermediate1) and methanol in transesterification of triolein. The amount of atoms in the input file was 178. The reaction between O8 of triolein and H173 of methanol was calculated based on HF6-31G method. The result found that the product structure wasn't intermediate2as shown in Fig. 12 (a.2) and weren't ester and diolein as shown in Fig. 12 (a.3). So, the method was changed to HF3-21G. And the result showed that the final products are ester and diolein. The relative energy between input structures and output structures of the reaction is 243.79 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 48.



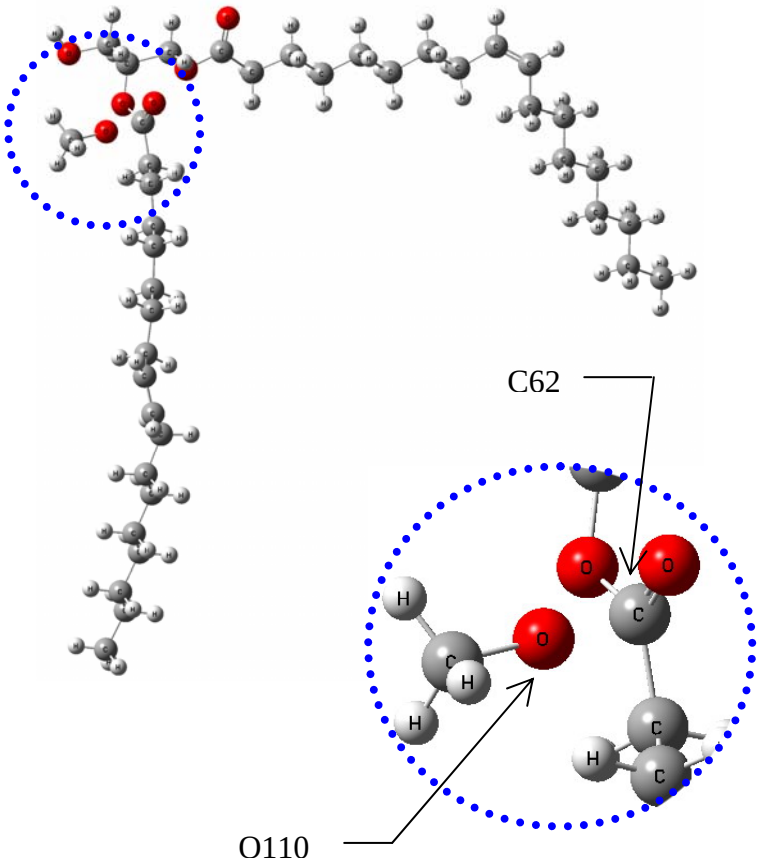
(a)



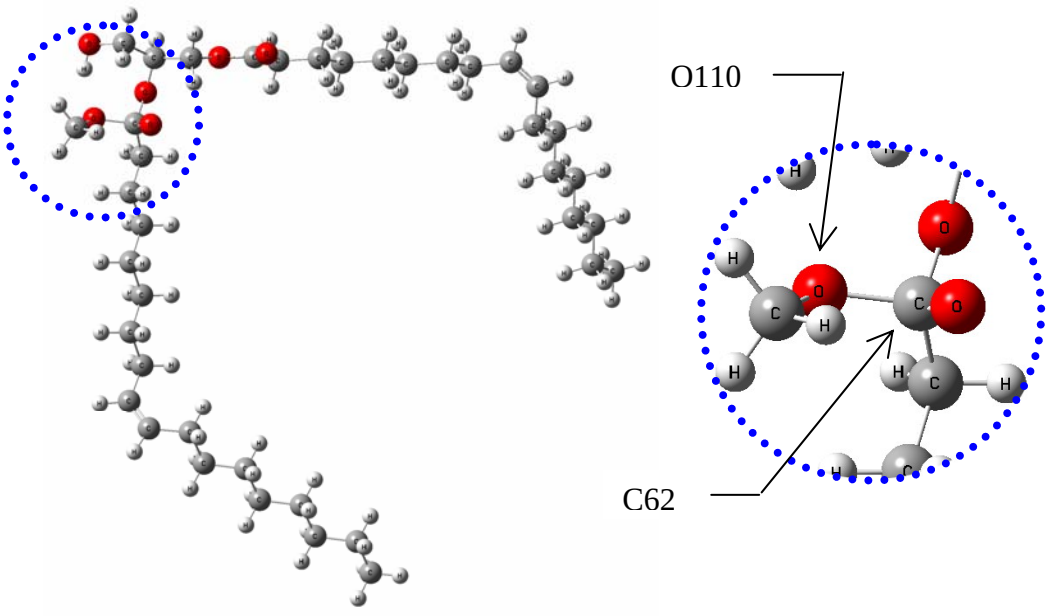
(b)

Figure48 The reaction structure of intermediate1 and methanol in transesterification of triolein: (a) input and (b) output.

The third simulation from Fig. 12 (b.1) is the reaction of diolein and methoxide. The amount of atoms in the input file was 121. The reaction between C62 in carbonyl group of diolein (C=O) and O110 of methoxide was calculated based on HF6-31G method. The result found that the product structure was intermediate1 as the product of step 1 in transesterification of diolein. The final products, intermedaite1, appeared in the 17th – 42nd of the simulation cycles. Hence, this simulation is a reversible reaction. The relative energy between input structures and output structures of the reaction is 181.98 kcal/mol. The input and output structure were shown in Fig. 49.



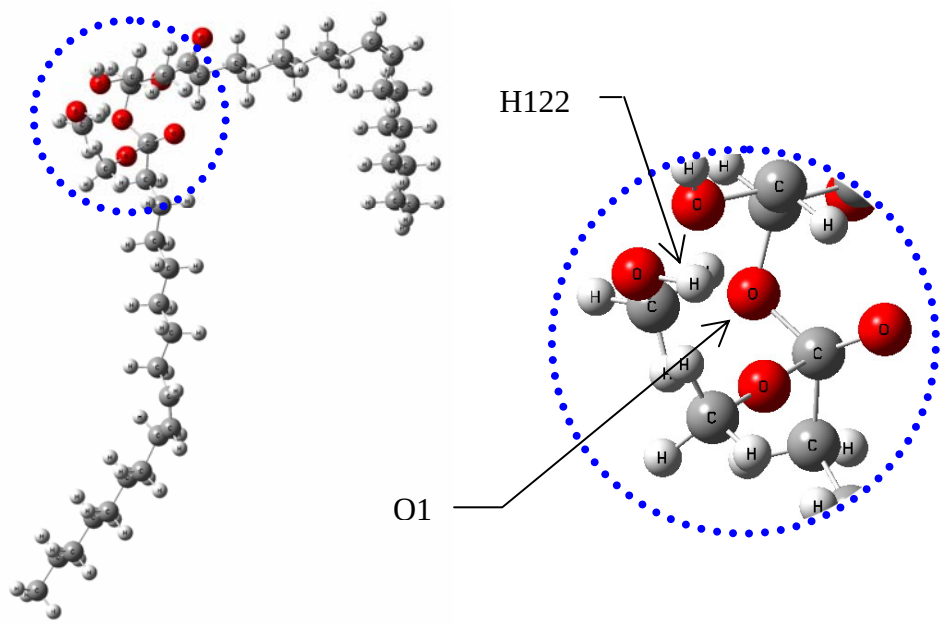
(a)



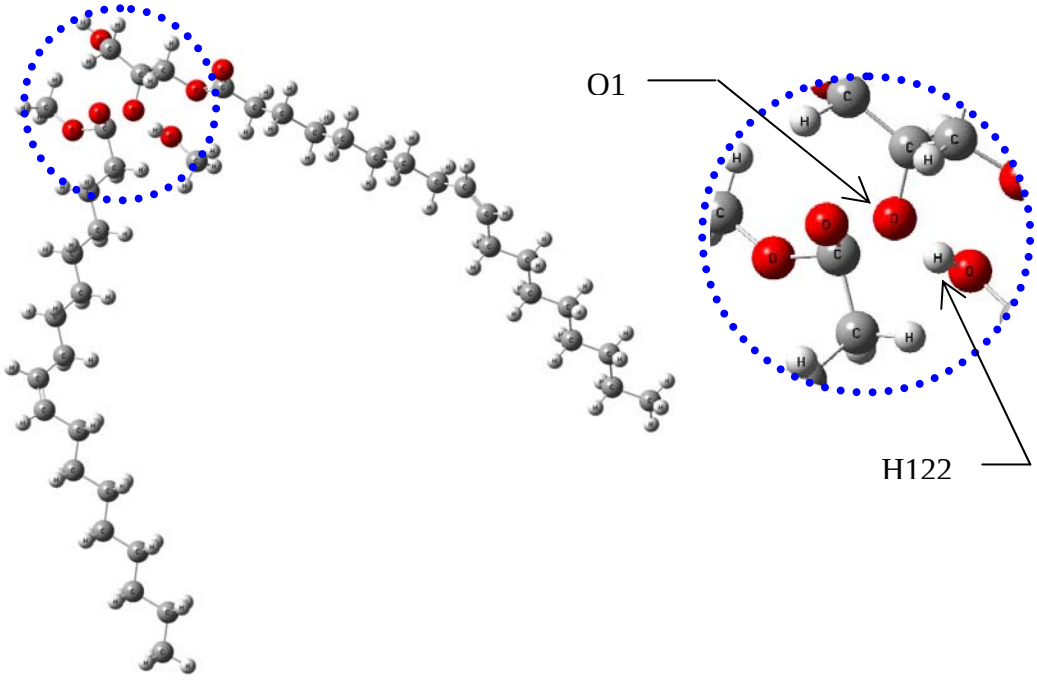
(b)

Figure49 The reaction structure of diolein and methoxide in transesterification of diolein: (a) input and (b) output.

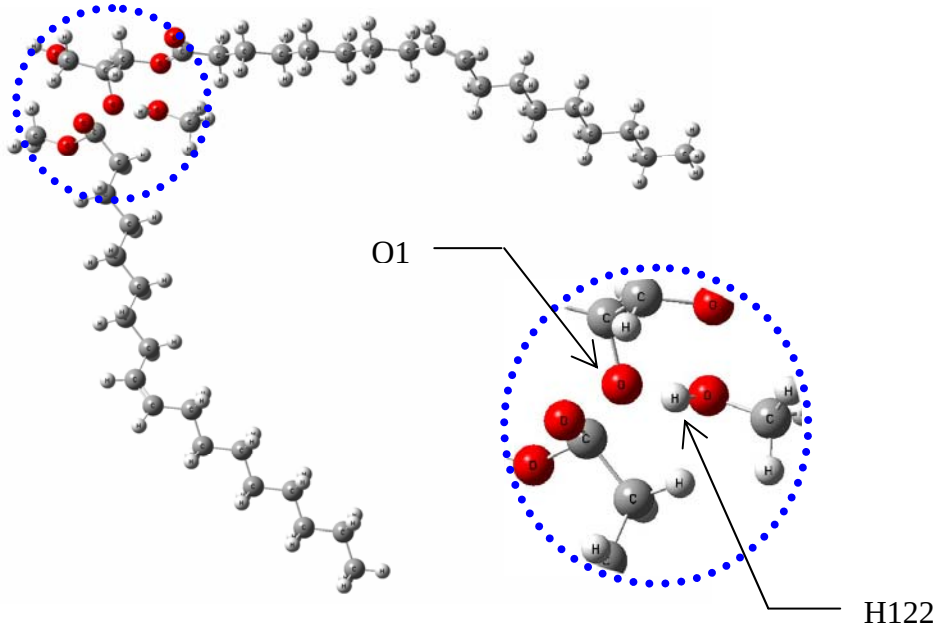
The forth simulation from Fig. 12 (b.2) is the reaction of the product in the third simulation (intermediate1) and methanol in transesterification of diolein. The amount of atoms in the input file was 127. The reaction between O1 of diolein and H122 of methanol was calculated based on HF6-31G method. The result found that the product structure wasn't intermediate2 as shown in Fig. 12 (b.2) and weren't ester and monoolein as shown in Fig. 12 (b.3). The final products were intermediate1 and methanol as the reactant in this simulation. But ester and monoolein appeared in the 9^{th}, 10^{th}, 12^{th} – 41^{st}, and 46^{th} of the simulation cycles. Hence, this simulation is a reversible reaction. The relative energy between input structures and output structures of the reaction is 219.63 kcal/mol. The input, structure of 9^{th} cycle and output structure were shown in Fig. 50.



(a)



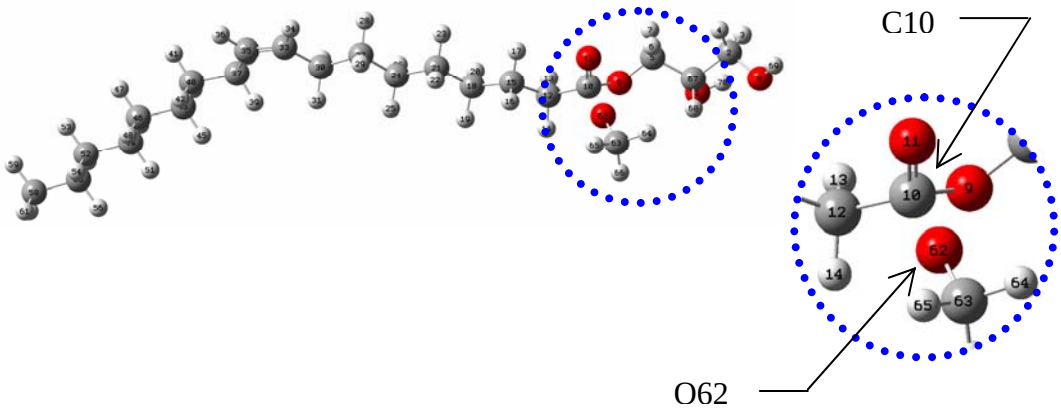
(b)



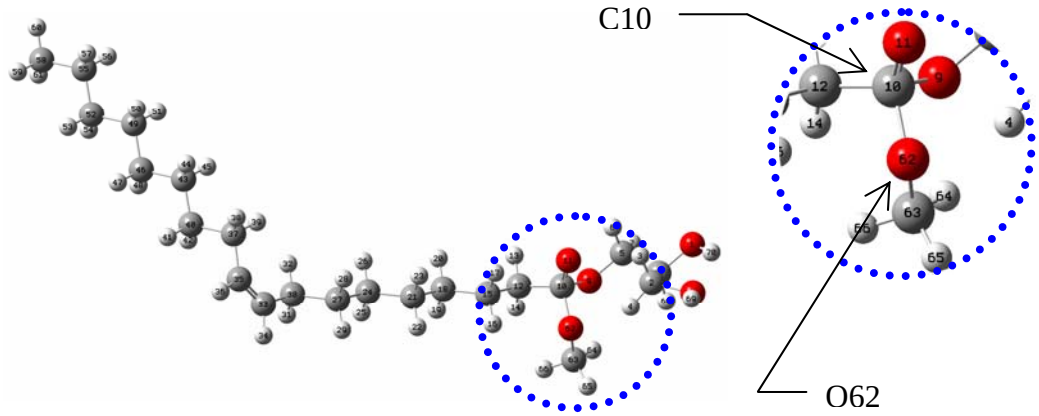
(c)

Figure50 The reaction structure of intermediate1 and methanol in transesterification of diolein: (a) input, (b) structure of 9th cycle and (c) output.

The fifth simulation from Fig. 12 (c.1) is the reaction of monoolein and methoxide. The amount of atoms in the input file was 70. The reaction between C10 in carbonyl group of monoolein (C=O) and O62 of methoxide was calculated based on HF6-31G. The result found that the product structure wasn't intermediate1 as shown in Fig. 12 (c.1) in transesterification of monoolein. So, the method was changed to HF3-21G. And the result showed that the product was intermediate1. The relative energy between input structures and output structures of the reaction is 125.50 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 51.



(a)

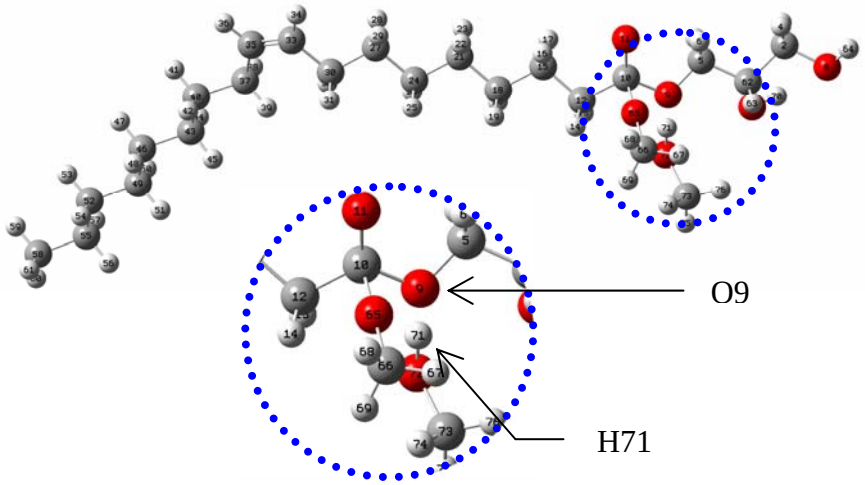


(b)

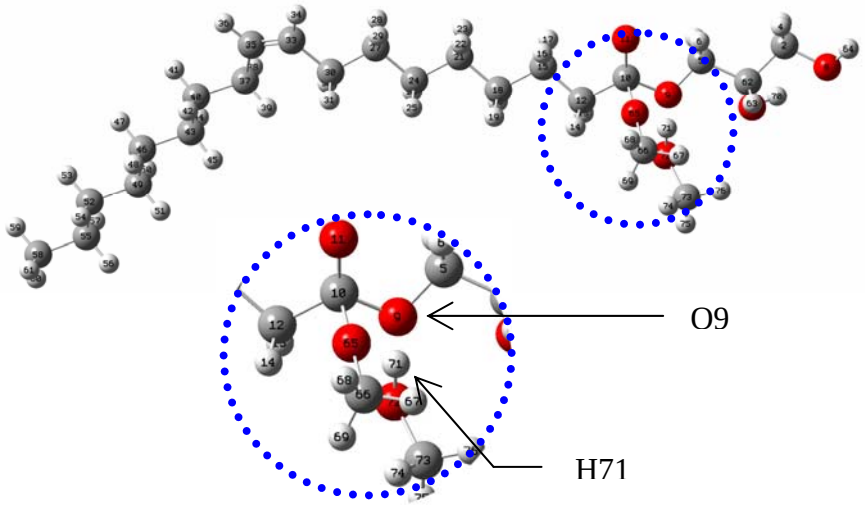
Figure49 The reaction structure of monoolein and methoxide in transesterification of monoolein: (a) input and (b) output.

The sixth simulation from Fig. 12 (c.2) is the reaction of the product in the first simulation (intermediate1) and methanol in transesterification of monoolein. The amount of atoms in the input file was 76. The reaction between O9 of triolein and H71 of methanol was calculated based on HF6-31G. The result found that the product structure wasn't intermediate2 as shown in Fig. 12 (c.2) and weren't ester and glycerol as shown in Fig. 12 (c.3). So, the method was changed to HF3-21G. The

result showed that the final products were ester and glycerol. The relative energy between input structures and output structures of the reaction is 4091.37 kcal/mol. There was no evident to have the reverse action from this simulation. The input and output structure were shown in Fig. 52.



(a)



(b)

Figure52 The reaction structure of intermediate1 and methanol in transesterification of monoolein: (a) input and (b) output.