

A Quantum Mechanics Approach to Biofuel Synthesis

George Marton*, Valentin Pleșu, Anca Marton, Marius Titus Bercaru
University POLITEHNICA of Bucharest, Centre for Technology Transfer in Process
Industries (CTTPI), 1, Gh. Polizu Str., 011061 Bucharest, Romania
cttip@chim.upb.ro

The paper presents the computational data concerning the trans-esterification of triglycerides for biofuel production. The mechanism of the methoxyide promoted trans-esterification was studied to establish the most probable reaction pathway and the most favoured intermediates with the aid of quantum computational methods. Attempts of correlating the structure parameters of eight triglycerides as raw materials with their properties are also presented, for finding the best compromise for the computation effort. It was found that triglycerides can be modelled by quantum computation on relatively inexpensive computer clusters using a good level of theory and basis-set. For eight triglycerides the geometry and the energy of ground state was calculated.

1. Introduction

The goal of the present paper is to simulate and analyse biodiesel synthesis process in order to continue previous studies on the starting materials evaluation (Pleșu et al., 2009), as the continuously increasing importance of molecular modelling succeeds to determine the compounds properties by computational methods. Among such methods, starting with “Molecular mechanics”, semi-empirical methods and ending with ab-initio methods, the DFT (Density Functional Theory) is probably the most used method. DFT is considered by some authors as an ab-initio method, and by others as a semi-empirical one. Another important factor for the level of theory is the basis set used in calculations. More complex and state-of-art basis sets are continuously published, but they require more computing power. In our research we focus on two targets: the quantum computation study of the trans-esterification reaction and finding the best compromise for the performance – computing demands. In order to correlate the structural elements with the properties of the compounds by QSPR methods it is necessary to build a very good ground structure as close as possible to reality and molecular properties like internal parameters. The distances between atoms, bonded and non-bonded, angles between bonds and dihedral angles, the formation energy, charge distribution, dipole moment, molecular surface and molecular volume are of major importance.

2. Results and Discussion

For the ground state geometry of the triglycerides a number of eight representative examples were simulated using GAMESS-US (Schmidt et al., 1993). The choice of

GAMESS is determined by the fact that it is free software and that for Linux the binaries are personalised by user to particular computer hardware. The Linux distribution is able to run in parallel mode on many nodes and processors thanks to the built-in parallel interface. In Figure 1 it is shown the initial conformation of a triglyceride **1** ((9Z,12Z)-1-((Z)-12-hydroxyoctadec-9-enoyloxy)-3-(palmitoyloxy) propan-2-yl octadeca -9,12-dienoate, i.e. glyceryl-1-palmito-2-linoleoyl-3-ricinoleate) after a first optimisation of geometry using a semi-empirical method (AM1). The initial optimisation with a semi-empirical method is a must, especially for large molecules, as the optimisation time is significantly reduced.

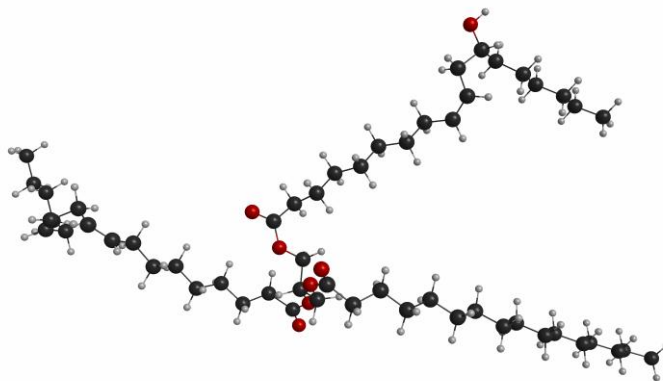


Figure 1: Initial conformation of triglyceride 1

Figure 2 presents the final conformation of the same molecule after optimisation using DFT B3LYP level of theory and 6-31G(d) basis set.

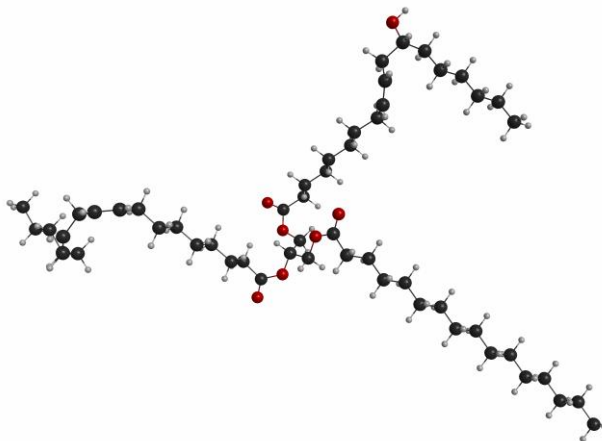


Figure 2: Final geometry of triglyceride 1

Figure 3 shows the variation of energy and energy gradient during the entire optimisation, while Figure 4 refers to the last 75 steps of optimisation.

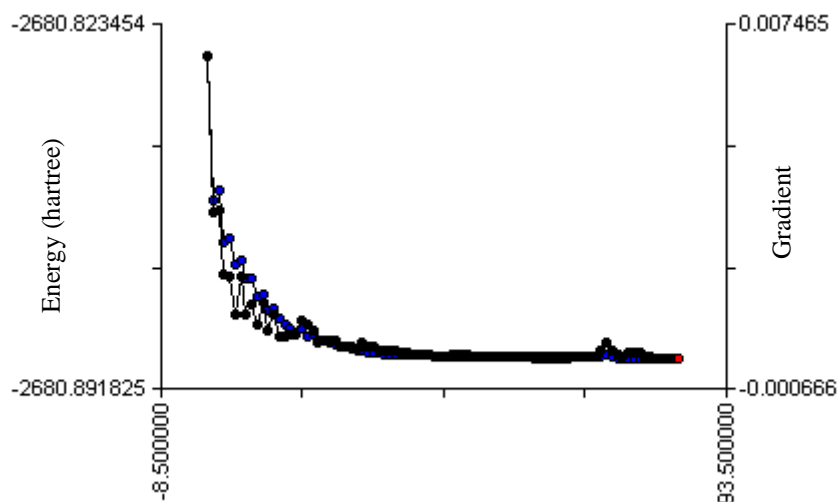


Figure 3: Variation of energy and energy gradient during the optimisation of triglyceride **1**

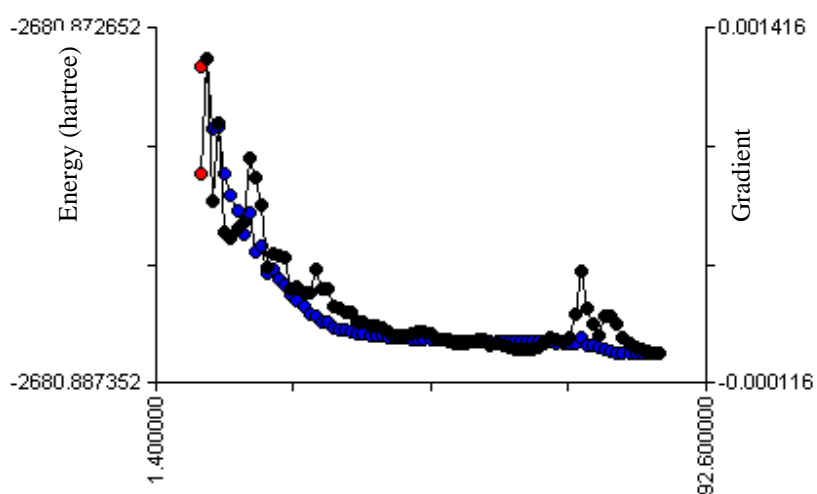


Figure 4: The variation of energy and energy gradient during the last 75 steps of optimisation triglyceride **1**

It is remarkable that near the end of the optimisation (around the 63rd step of a total of 86) the energy variation is very small, and the gradient close to the set limit. This is imposing a low gradient limit (0.0001), otherwise the final geometry and energy would be quite far from optimal ones.

Another interesting fact is the conformation of the long saturated chain, which in some triglycerides is not straight, but bent towards the unsaturated fatty acid radical (Figure 5).

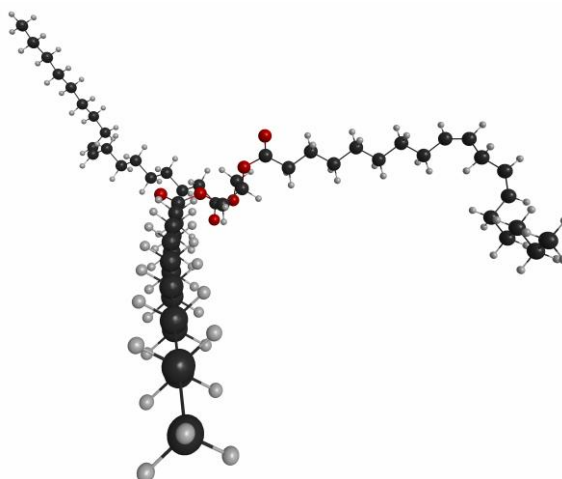


Figure 5: Conformation of the long saturated chain

Another important factor is the type of coordinates used during the optimisation. There are three choices – Cartesian, Z-matrix internals and delocalized internal coordinates (DLC) (Baker et al., 1996). The difference is in the total time necessary for the optimisation. The slowest method is to use Cartesian coordinates and the fastest is to use delocalized internal coordinates. Also DLC gives a better value for the energy of the ground state. Using DLC is a problem in GAMESS as the internal routine is not working right if the number of atoms is over 140, and practically all triglycerides with fatty acids are larger than that. A manual construction of the coordinates is not possible since there are $3n-6$ of them (n is the number of atoms in the molecule). In this study we used Z-matrix internals and the computer time for optimisation of triglyceride **1** was 55200 min (920 h). Due to the parallelisation, the optimisation was run on a computer cluster containing ten nodes and 40 cores, so there were 40 processes running in parallel. The resulting processor time was 1380 min (23 hours) and a total wall-time of 1584 min. Processor utilisation capacity was 87.12%, which is good for a cluster of this dimension.

The optimisation of other triglycerides showed that there is a high possibility to end in a local minimum, so it is compulsory to check the final structure and to perform manual corrections of the geometry and an optimisation of the new geometry in order to check that obtained energy is a general minimum. This is greatly increasing the computer time. Also optimisation of larger molecules (triglyceride **1** has 162 atoms) is further increasing the computer time. A molecule with 187 atoms doubles the required time. In order to compute the formation energy the necessary vibration energy computation is also a time consuming step. Table 1 presents ground state energies of some triglycerides calculated by DFT B3LYP 6-31G(d) level of theory.

Table 1 Total ground state energies of some triglycerides

acid1	acid 2	acid 3	Molecular formula	Energy (hartree)
Palmitic	Erucic	Erucic	C ₆₃ H ₁₁₈ O ₆	-2903.6410
Palmitic	Erucic	Oleic	C ₅₉ H ₁₁₀ O ₆	-2764.0992
Palmitic	Erucic	Ricinoleic	C ₅₉ H ₁₁₀ O ₇	-2839.2389
Palmitic	Linoleic	Erucic	C ₅₉ H ₁₀₈ O ₆	-2762.8351
Palmitic	Linoleic	Linoleic	C ₅₅ H ₉₈ O ₆	-2604.4680
Palmitic	Linoleic	Linolenic	C ₅₅ H ₉₆ O ₆	-2603.2579
Palmitic	Linoleic	Oleic	C ₅₅ H ₁₀₀ O ₆	-2605.7136
Palmitic	Linoleic	Ricinoleic	C ₅₅ H ₁₀₀ O ₇	-2680.8861

3. The Trans-esterification Mechanism

Another goal was the quantum computation study of the trans-esterification reaction mechanism. The classical mechanism implies as a first step the formation of a tetrahedral intermediate **2**. Quantum computations shows that the alkoxy anion attack occurs to the acyl bonded to the middle carbon of glycerol (Asakuma et al., 2009), followed by the elimination of the glycerolate anion and formation of the methyl ester of the fatty acid from the 2-position in the initial glycerol triester.

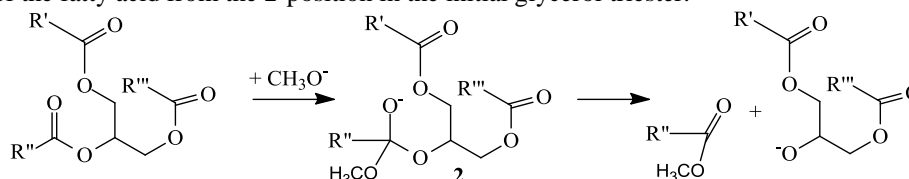


Figure 6 First step in the reaction mechanism of trans-esterification

Another possibility is the extraction of a proton from the α -carbon of the fatty acid. The resulted anion **3**, eliminates the glycerolate anion and a ketene **4** is formed.

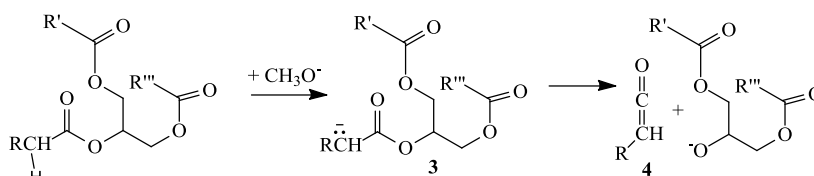


Figure 7: Formation of a ketene as an intermediate in trans-esterification

The resulted ketene reacts with methanol to generate the methyl ester. The ketene

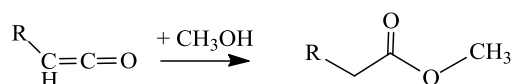


Figure 8: Formation of methyl ester out of the ketene

mechanism, proposed for alkali catalyzed reactions of some types of aromatic esters was theoretically demonstrated by quantum computations (Pratt and Bruce, 1970) and by caption of the intermediate ketene (Badea et al., 2001). Due to very long computer

time necessary for triglycerides modelling, trans-esterification reaction between a smaller ester (ethyl propionate) and methanol (Figure 9), generating methylketene as intermediate was modelled (Figure 10).

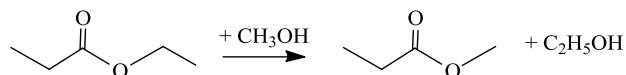


Figure 9: The modelled trans-esterification reaction

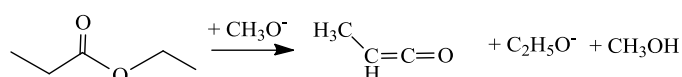


Figure 10: Proposed intermediate ketene step in ethyl propionate trans-esterification

Energy quantum computation for intermediates involved in this reaction shows that the tetrahedral intermediate is more stable than the ketene intermediate with about 72 kcal/mol. Even if the quantum computation shows that in the trans-esterification of ethyl propionate with methanol the tetrahedral intermediate is the one involved, still this result cannot be extended to trans-esterification of triglycerides without further investigation. The neighbouring effect of carboxyl groups and of the long chains in the fatty acids might strongly influence the energies of the involved intermediates.

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