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Research paper

Unravelling the chemical reactions of fatty acids and triacylglycerides under hydrodeoxygenation conditions based on a comprehensive thermodynamic analysis

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ABSTRACT

Triacylglycerides (TAGs) and their related fatty acids (FAs) are abundant in biomass (vegetal oils and animal fats). Here, we studied by theoretical calculations the most representative FAs and their chemical reactions under hydrogen atmosphere to produce O-free hydrocarbon molecules. In general, the ΔH_r^0 and ΔG_r^0 do not vary due to the size of the molecule. Selected TAGs were also studied by theoretical calculations. Similar as FAs, the overall reaction energies do not depend on the size of the molecules. Possible reaction networks for the hydrogenation and hydrogenolysis processes are proposed for such biomolecules under hydrogen environments. We also studied the profiles of the enthalpy and Gibbs energy of reaction for TAGs at typical operating conditions of temperature or pressure. This self-consistent study is willing to contribute for a better understanding of the reactions of the biomass that take place under hydrogen atmosphere.

1. Introduction

Interest for renewable energies is growing for their potential alternatives to bring similar raw materials or energy than those obtained from fossil oils [1,2]. The generation of bio- or green fuels since early this decade has become a major research and industrial topic [3-5]. Vegetable oils, especially palm oil, have been good candidates to develop environmental friendly and high quality fuels [6] if we keep in mind sustainable production techniques. However, these vegetable oils cannot be used immediately as fuels due to their high oxygen content, which leads to low heating value, immiscibility with fossil fuels, a tendency for polymerization, thermal instability and high viscosity [7]. Catalytic hydrotreating (HDT) is a promising technology for the conversion of biomass to liquid biofuels. Hydrodeoxygenation (HDO) is the main catalytic process to eliminate oxygen contained in the organic molecules by hydrogenation and hydrogenolysis reactions [8-10] Nowadays, several research efforts are trying to eliminate oxygen from the vegetable oils by their chemical reactions under hydrogen atmosphere [11,12]. Those have faced several challenges and future opportunities about chemistry, catalytic processes, biorefinery concepts, engineering changes and solutions are emerging [13].

Target molecules in vegetable oils for biofuels production are triacylglycerides (TAGs) that are meant to be converted into fatty acids (FAs). After their reaction under hydrogen atmosphere, TAGs and FAs are transformed into hydrocarbon chains that are able to be used as fuel or incorporated in existing refinery infrastructure [14,15]. Their conversion is complicated since the typical catalyst used for HDT processes is poisoned by coke deposition and unstable in the presence of water [16]. On the other hand, detailed steps of chemical reaction of the TAG or FAs under hydrogen atmosphere to produce O-free hydrocarbons are almost scarce in the literature. There are studies of the chemical reactions of TAGs for the production of biodiesel, but in this process TAGs react with H₂O or alcohols to produce FAs or esthers [17]. It is wellknown that FAs under hydrogen atmosphere can react towards three main routes, namely deoxygenation, decarbonylation or decarboxylation.

Detailed thermochemical data is necessary for a better understanding of the factors that affect the elimination of oxygen from biomass molecules. Thermodynamic properties such as Δ H or Δ G have been reported for selected FAs and some of them showed discrepancies [18–20]. Those values were calculated by different approaches, in some cases based on very rough models or adapting engineering data of

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estimated energy for the bonds within the FAs. For instance, decarboxylation and hydrodeoxygenation are reported at certain temperature or pressure and sometimes the values do not agree well between different reports. To the best of our knowledge, full thermochemical data for the reactions of TAGs under hydrogen atmosphere have not been reported yet and those values are very much needed to understand their conversion into green fuels. Moreover, reaction steps and intermediate structures are necessary to draw a clear reaction scheme for the TAGs under HDO conditions. Those studies are very difficult to conduct by experimental methods. On the other hand, accurate theoretical calculations are currently possible with the existing supercomputer infrastructures, for which these biomolecules are very attractive. Therefore, we are presenting a detailed and consistent theoretical study about the chemical reactions and their energies for FAs and TAGs under hydrogen atmosphere.

2. Computational details

FAs were chosen as they are found in the nature and are relevant for the production of green fuels (C_8 to C_{18}) such as caprylic, capric, lauric, palmitic, stearic acids and others with unsaturation in the aliphatic chain. Ground state structures of the molecules were obtained by means of Density Functional Theory (DFT) calculations. The optimized geometry for each compound was obtained using the hybrid meta GGA density functional M06 [21] with the 6-31 + G(d,p) standard basis set. We obtained the optimized geometry of tricaprylin and related products at the same level of theory. However, TAGs bigger than caprylin were studied at M06/6-31G(d,p) level due to the size of the system. It was not computationally possible to get geometry optimization at higher level of theory for TAGs larger than C_{10} , due to the diffuse function makes the calculation complicated for its convergence. Thus, we chose the M06/6-31G(d,p) level to get the optimized geometry of TAGs and then single point calculation were done at the same level of theory than FAs for a proper comparison of the energy values varying the size of the TAG. All harmonic vibrational frequencies were real; therefore the structures are minima on the potential energy surface.

We chose the M06 functional because it has shown its excellent performance to get accurate thermodynamic properties [22]. The thermal correction to the total energy was obtained with the contribution of the translation, electronic, rotational and vibrational motions. Then Δ H and Δ G were computed for the chemical processes that have been described experimentally for the FAs and for a proposed network of TAGs under H₂ atmosphere. We also conducted a thermochemical study by varying temperature and pressure for the HDO, decarbonylation and decarboxylation processes of selected FA. On the other hand, we proposed a reaction network for the partial FA elimination from the TAGs and its partial reduction under H₂ environments. Δ H and Δ G as a function of *T* and *P* were also calculated for the TAGs chemical reactions under H₂ atmosphere. Enthalpy and Gibbs energy were calculated at M06/6-31 + G(d,p).

All the calculations were carried out with Gaussian 09 [23], considering all electron and closed shell systems.

3. Results and discussion

3.1. Fatty acids

We studied the most abundant FAs in biomass ranging from C_8 to C_{18} and including those with unsaturations. Fig. 1 showed the optimized geometries for selected FAs, namely stearic (18:0), oleic (18:1) and linoleic (18:2) acids. Those molecules contain the same number of carbon and oxygen atoms, but they have a different number of unsaturated C=C bonds within their structures. Stearic acid is a linear molecule with sp^3 hybridization of all its carbon atoms, while oleic and linoleic acids contain one and two C=C bond, respectively, with a *cis* configuration. It produces fatty acids with nonlinear structure. The



Fig. 1. Optimized geometries of fatty acids: (a) stearic acid, (b) oleic acid, and (c) linoleic acid.

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IOMO (ϵ_{HOMO}), LUMO (ϵ_{LUMO}) energies and their gap for fatty acid	ls.

Name (C:D)	€ _{HOMO}	ε _{LUMO}	$\Delta_{\text{H-L}}$
_	(eV)	(eV)	(eV)
Caprylic acid (8:0)	-8.27	-0.65	7.62
Capric acid (10:0)	-8.27	-0.66	7.61
Lauric acid (12:0)	-8.26	-0.66	7.60
Myristic acid (14:0)	-8.26	-0.66	7.60
Palmitic acid (16:0)	-8.25	-0.66	7.59
Stearic acid (18:0)	-8.23	-0.66	7.57
Palmitoleic acid (16:1)	-6.83	-0.67	6.16
Oleic acid (18:1)	-6.83	-0.67	6.16
Linoleic acid (18:2)	-6.78	-0.76	6.01

electronic properties of those molecules are shown in Table 1. The FAs from caprylic (C_8) to stearic acid (C_{18}) showed slight changes in their average values for HOMO (-8.25 eV) and LUMO (-0.66 eV) energies, which pointed out that the size of the aliphatic chain does not have a significant influence on the electronic structure of those FAs. The band gap of the linear molecules slightly decreases as the number of carbon atoms increase, caprylic acid 7.62 eV and stearic acid 7.57 eV. Oleic acid (C18:1 Δ 9) exhibited a change in its HOMO and LUMO energy values respect to its saturated counterpart. The gap was decreased to 6.16 eV. However, a comparison with palmitoleic acid (C16:1 Δ 9) showed the same values than the ones for oleic acid. The addition of another C=C bond (linoleic acid) also decreased the values of the frontier MOs. Naturally, the number of the unsaturation is more important on their electronic properties than the total number of carbon atoms.

Chemical reactions of FAs under HDO conditions are depicted in Fig. 2. We studied the consecutive reduction reactions of the -COOH groups from the FAs to form the corresponding fatty alcohol (R1-R3), its final reduction to hydrocarbon (R4) and the overall reaction from the FA to the O-free hydrocarbon (R5). Other two reactions that take place under HDO conditions are their thermal decomposition namely decarbonylation (R6) or decarboxylation (R7) reactions. We studied the thermochemical data of those chemical reactions for the most representative FAs present in biomass. ΔH_r^0 and ΔG_r^0 values are shown in Table 2. Reduction of the fatty acid moiety to produce the first hydrogenated product namely its aldehyde species showed positive values for both thermodynamic quantities. This value agrees with previous studies where the first reduction reaction is not well promoted at standard conditions (ΔH^0 and $\Delta G^0 > 0$) [19]. The ΔS^0 of this process is positive (39.26 JK^{-1} mol⁻¹), therefore it is a spontaneous reaction. We could state that this reaction limits all the HDO process through the

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