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DFT INSIGHTS INTO NANO-GRAPHENE OXIDE-CATALYSED TRANSESTERIFICATION OF JATROPHA CURCAS OIL: CONFORMATIONAL PREFERENCE AND ACTIVE SITES

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Abstract. The mechanism of biodiesel formation from Jatropha curcas oil and methanol over nano-graphene oxide (NGO) was investigated by quantum-chemical modelling at the B3LYP/6-31++G** level. The trans configuration of the double bonds in the triglyceride was found to be thermodynamically more stable on the NGO surface than the cis configuration. A five-step pathway was examined for each of the three NGO active sites (carboxyl, hydroxyl and epoxy groups). In all cases, the third step, in which electron density is redistributed and the key complex forms, was identified as decisive. The hydroxyl-mediated route showed the lowest activation energy (72.82 kJ·mol^{-1}) and the lowest activation Gibbs energy, whereas the epoxy-mediated route was the least favourable.

Keywords: Jatropha curcas oil; biodiesel; nano-graphene oxide; transesterification mechanism; DFT; activation energy.

Introduction. Jatropha curcas is a perennial, drought-tolerant crop that can grow on degraded land unsuitable for food crops. Its seed oil is non-edible owing to toxic constituents such as phorbol esters, which makes it a promising feedstock for biodiesel that does not compete with food production. Biodiesel is most widely produced by transesterification, in which triglycerides react with a low-molecular-weight alcohol to give fatty acid alkyl esters and glycerol. Homogeneous catalysts, however, complicate product separation and generate liquid waste, which motivates the use of heterogeneous nanocatalysts with a high specific surface area and abundant active sites. The kinetics and thermodynamics of transesterification have been studied experimentally [1], whereas DFT calculations make it possible to examine reaction mechanisms at the molecular level [2].

Nano-graphene oxide carries carboxyl, hydroxyl and epoxy groups, each of which may act as a catalytic centre. Which of these sites controls the reaction, and how the spatial configuration of the unsaturated oil molecule affects adsorption on NGO, remains insufficiently understood at the molecular level. The aim of this work is to clarify these questions by quantum-chemical modelling of the NGO-catalysed reaction between Jatropha oil and methanol.

Computational methodology. The Jatropha oil molecule was represented as a triglyceride ($C_{57}H_{104}O_6$) bearing one doubly unsaturated ($C_{17}H_{31}$), one monounsaturated ($C_{17}H_{33}$) and one saturated ($C_{17}H_{35}$) chain. The geometries of NGO, oil, methanol, biodiesel (fatty acid methyl esters) and glycerol were optimised, and thermodynamic parameters (total energy ΔE_{total}, enthalpy ΔH, Gibbs energy ΔG and dipole moment μ) were calculated at the B3LYP/6-31++G** level. The reaction was modelled as a five-step pathway P_i–S1…S5 (i = I, II, III) for each active site of NGO: carboxyl (path I), hydroxyl (path II) and epoxy (path III). Activation enthalpies, Gibbs energies and rate-related parameters were evaluated at 348.15 K within transition-state theory [2], and the activation energy E_a was obtained from the Arrhenius relation.

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Results and discussion. Conformational preference. The configuration of the C=C bonds determines how the oil molecule lies on the NGO surface. The elongated trans form gives a larger contact area with the surface than the bent cis form. As shown in Table 1, the trans configuration is lower in total energy, enthalpy and Gibbs energy and has a higher dipole moment, which favours interaction with polar methanol. Hence, the trans configuration is the preferred one in the NGO-catalysed process.

Table 1. Calculated parameters of the cis and trans configurations of Jatropha oil with methanol on NGO

Configuration	ΔE_{total}, kJ·mol^{-1}	μ, D	ΔH, kJ·mol^{-1}	ΔG, kJ·mol^{-1}
cis	−691.89	7.57	−453.76	−457.19
trans	−692.91	9.85	−464.01	−467.74

Rate-determining step. On all three pathways, steps S1–S2 correspond mainly to physical adsorption of oil and methanol on NGO without substantial rearrangement of chemical bonds, so the energy changes are small. In the third step (P_i–S3), bond lengths change, intermediate complexes form and the dipole moment reaches its maximum (12.79–15.49 D, Table 2), indicating intense redistribution of electron density; biodiesel and glycerol are then released from the surface in steps S4–S5. Therefore, S3 is the decisive step of the mechanism. The calculated process is endothermic and endergonic ($\Delta H^{\ddagger} > 0$, $\Delta G^{\ddagger} > 0$), which is consistent with the practice of heating the reaction mixture to 60–80 °C.

Table 2. Parameters of the third step (P_i–S3) for the three active sites of NGO

Active site (path)	ΔE_{total}, kJ·mol^{-1}	μ, D	$\Delta G^{\ddagger}$, kJ·mol^{-1}	E_a, kJ·mol^{-1}
Carboxyl (I)	−692.50	15.49	156.61	74.02
Hydroxyl (II)	−692.68	12.79	154.07	72.82
Epoxy (III)	−692.15	13.45	171.51	73.01

Role of the active sites. The hydroxyl route has the lowest total energy at the decisive step, the lowest activation Gibbs energy and the lowest activation energy (72.82 kJ·mol^{-1}). This is attributed to the ability of the –OH group to act as both proton donor and acceptor and to form strong hydrogen bonds that stabilise the transition state. In the carboxyl route, part of the energy is spent on deformation of the C=O bond, which raises the requirement relative to the hydroxyl group. The epoxy route, located on the basal plane of the graphene layer, has the highest activation Gibbs energy (171.51 kJ·mol^{-1}) and is therefore the least probable. Thus, the three NGO sites contribute unequally, and the –OH groups are the most efficient catalytic centres in the modelled transesterification.

Conclusions. Modelling at the B3LYP/6-31++G** level shows that (i) the trans configuration of Jatropha oil is more stable than the cis configuration on the NGO surface; (ii) the reaction proceeds through a five-step pathway whose third step is decisive for all active sites; (iii) the calculated activation energies lie within 72.82–74.02 kJ·mol^{-1}; and (iv) the hydroxyl groups of NGO are the most favourable catalytic centres, whereas the epoxy groups are the least favourable. These findings provide a molecular-level basis for the targeted design of NGO-based nanocatalysts for biodiesel production; experimental verification of the predicted site preference is the logical next step.

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