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Acid hydrolysis of tripalmitin and triolein. Preliminary thermodynamic study

Hidrólisis ácida de tripalmitina y trioleína. Estudio termodinámico preliminar

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Abstract

Hydrolysis reactions can be carried out using triglycerides with different carbon chain sizes, with acetic acid and ethanoic acid being the most common products, in addition to glycerol which would be the common product in any hydrolysis reaction in the production of biodiesel. In the case of Macaúba oil, it is suspected that when undergoing a hydrolysis reaction, as a mixture, the triglycerides, oleic, palmitic and stearic are likely to be the most important reagents and consumption in the reactions.

According to the literature, there is a shortage of information concerning the compounds involved in the hydrolysis of the reactions of vegetable oils, so the availability of experimental data on the molecules involved in the production of the fatty acids and glycerol reactions is scarce in literature. In many studies, methods of group contributions or empirical correlations are used to predict the properties of molecules. Thus, in this work, an initial thermodynamic analysis of the reactions occurring in the hydrolysis of Macaúba oil, especially of tripalmitin and triolein, was performed in a temperature range from 300 to 700 K. The thermodynamic parameters employed in this work, for some compounds, were estimated by methods available in the literature. The calculation of the Gibbs energy of the reactions was done by employing the results of the enthalpy of reactions found in previous works. Finally, from the possession of the set of these parameters, for the possible hydrolysis reactions to be studied, it was possible to estimate the reactionary Gibbs energy of the same, which allowed adding more information in this field of study.

Keywords: Hydrolysis; Reaction; Gibbs energy; Enthalpy.

Resumen

Las reacciones de hidrólisis pueden ser conducidas utilizando triglicéridos con diferentes tamaños de cadena carbónica, siendo el ácido acético y etanoico los productos más comunes, además del glicerol que sería el producto común en cualquier reacción de hidrólisis en la producción de biodiesel. En el caso del aceite de Macaúba, se sospecha que cuando se somete a una reacción de hidrólisis, por ser una mezcla, los triglicéridos, oleico, palmítico y esteárico probablemente serán los reactivos de mayor importancia y consumo en las reacciones. De acuerdo con la literatura, se nota una escasez de información acerca de los compuestos involucrados en la hidrólisis de las reacciones de aceites vegetales, por lo que la disponibilidad de datos experimentales de las moléculas implicadas en las reacciones de producción de los ácidos grasos y glicerol es escasa en la literatura. En muchos estudios se utilizan métodos de contribución de grupos o correlaciones empíricas para predecir las propiedades de las moléculas. Así, en este trabajo, se realizó un análisis termodinámico inicial de las reacciones que ocurren en la hidrólisis del aceite de Macaúba, en especial de la tripalmitina y de la trioleína, en un rango de temperatura de 300 a 700 K. Los parámetros termodinámicos empleados en este trabajo, para algunos compuestos, fueron estimados por métodos disponibles en la literatura. El cálculo de la energía de Gibbs de las reacciones se realizó empleando resultados de entalpía de reacciones encontradas en trabajos anteriores. Finalmente, de posesión del conjunto de estos parámetros, para las posibles reacciones de hidrólisis a ser estudiadas, fue posible estimar la energía de Gibbs reaccionaria de las mismas, lo que permitió agregar más información en esta área de estudio.

Palabras clave: Hidrólisis; Reacción; Energía de Gibbs; Entalpía.

Introduction

Acid hydrolysis and transesterification are the main processes used to obtain biodiesel. Both can occur when a reaction between a triacylglycerol (fat or oil) and a molecule of water or an alcohol produces fatty acid alkyl esters (biodiesel) and glycerol as sub-product. These reactions of vegetable oils are catalyzed by acid/base catalysts to increase the reaction rate and its yield. It is known that for the transesterification an excess of alcohol is required to shift the equilibrium of the reaction [1,2] substance based on known parameters of similar substances; however, for acid hydrolysis there is no study about the thermodynamic equilibrium for the reactions at this moment. It is well-known that the prediction of chemical and phase equilibrium has a remarkable application in many industrial processes, such as biodiesel production and more specifically at the separation stage. For this reason, several optimization techniques have been proposed in many studies [3-6] to solve the problem of simultaneous chemical and phase equilibrium calculation by direct Gibbs energy minimization. On the other hand, for the preliminary studies, the use of classical equations can be employed to have a general idea about the reactions, such as hydrolysis of Macaúba oil that have never been thermodynamically studied. Classically, two methods are used to calculate the thermodynamic equilibrium. The “law of mass action” can be implemented, according to which the concentrations of the reactants and products are related by a constant, provided that the stoichiometric coefficients of the reaction are known. Several reactions can be chained. The method is reasonable, appealing and, at least conceptually, simple. But it is very dependent on the chosen chemical reactions and the values of the equilibrium constants [7-9]. Besides, it is not suited to very complex problems where the details of the chemistry are not known. The second method involves the well-established concept formulated by Gibbs [10] according to which the “Gibbs free energy” (free enthalpy, ΔG_r^0) of the reactive system reaches a minimum at the thermodynamic equilibrium. There is no need to know the process of the chemical reactions, only the energy and molecular composition of the reactants and the chemicals likely to be present in the final products. Greinert *et al.*, 2020 have published a recent work that focuses on determining an activity-based ΔG_r^0 value for the glyceraldehyde 3-phosphate dehydrogenase (GDH) reaction [11]. GDH is the first reaction of the pay off phase of glycolysis, which is connected to a production of ATP and NADH.

In addition to NADH production and the resulting importance of this reaction, the GDH reaction represents a crucial bottleneck for glycolysis [12] meaning that a correct thermodynamic interpretation of glycolysis strongly depends on the fundamental understanding of this reaction.

Thus, the observed concentration-based ΔG_r^{0obs}

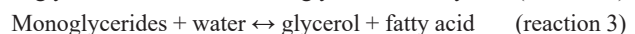
values available from literature, which differ by up to 5 kJ mol⁻¹ from each other for the GDH reaction [12-14], will be compared to a new activity-based value from this work in order to find a reliable ΔG_r^0 for the usage in any future work that is connected to this reaction.

In this work, all investigations and calculations are based on the van 't Hoff equation [15-17] considering a temperature-independent enthalpy of reaction (ΔG_r^0). The Gibbs energy of reaction (ΔG_r^0) explains whether a single hydrolysis reaction occurs under prevailing reaction conditions. Negative values indicate that reactions are thermodynamically feasible, while others with positive values are not. Especially, in this work, the equilibrium constant of the reaction (K) will be calculated, taking as a basis the value of the Gibbs energy of the reaction.

Similarly, based on the relationship between K and ΔG_r^0 , K values greater than one mean thermodynamically feasible reaction, while others smaller than one are not favored.

Methodology

The exploration of vegetable oil is a typical line of research in Brazil [17,18] and other countries [19]; however, few works are directed to the reactionary field. Rabelo, 2024 has presented a scheme of the reactions involving the hydrolysis of a triglyceride. In this way, the hydrolysis reactions (1,2 and 3) of vegetable oils can be described as follows:

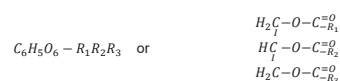


Adding the three equations, comes the global reaction (reaction 4) which is given by:

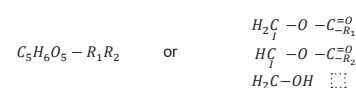


Considering that R₁, R₂ and R₃ are organic radicals of the type of methyl, ethyl, propyl etc., the representation of glycerides is as follows:

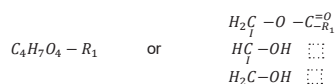
Triglyceride



Diglyceride



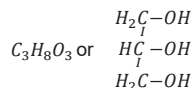
Monoglyceride



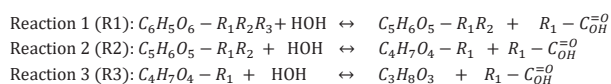
The representation of the fatty acid is



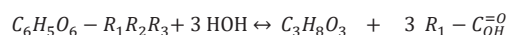
The glycerol can be represented as



Thus, the generic reactions suffered by a triglyceride, with a general formula previously mentioned, are as follows:



The sum of the three reactions produces the global reaction is:



If $R_1=R_2=R_3$ is equal to the radical $(CH_2)_{14}CH_3$, the reactions lead to the formation of palmitic acid from the triglyceride tripalmitin, $C_{51}H_{98}O_6$.

If $R_1=R_2=R_3$ is equal to the $(CH_2)_{14}(CH)_2CH_3$ the reactions lead to the formation oleic acid from the triglyceride triolein, $C_{57}H_{104}O_6$.

The enthalpy of the 1-3 reactions and the R_4 (global reaction) for both tripalmitin and triolein were determined in the TCC (Trabalho de Conclusão de Curso) of Rabelo, 2024 for the temperature range from 298.15 to 700K.

These values will be used in this work to obtain the behavior of the thermodynamic equilibrium of both the partial reactions and the overall reaction involving the two triglycerides mentioned. The choice of these compounds is due to their greater abundance of the oil in the mesocarp of Macaúba.

The study of thermodynamics requests parameters that are sometimes not yet available in literature, an example of this would be the Gibbs energy of formation of compounds. The estimate of the Gibbs energy of formation of the compounds, at 298.15K, present in the reactions was made using the Joback's method in which:

$$\Delta G_{f,298,15K}^0 = 53,88 + \sum_k N_k \Delta G_{fk} \quad (1)$$

In the case of gaseous water this value was collected in Reid *et al.*, 1987[20] being -228.42 kJ/mol and was used in the calculations. Table 1 contains the results of the $\Delta G_{f,298,15K}^0$ of the compounds of this work, estimated by the Joback's method.

Table 1: Gibbs formation energy values (ΔG_f^0 , kJ/mol) of compounds at 298.15 K estimated by the Joback method.

Chemical	Glycerol	Triolein	Diolein	Monoolein
$\Delta G_{f,298,15K}^0$	-543,28	-189,78	-112,80	-35,82

Tripalmitin	Dipalmitin	Mono palmitin	Oleic acid	Palmitic acid
-520,45	-326,58	-142,71	-197,14	-304,03

From the literature it has been found that the Gibbs energy of a reaction ($\Delta G_{r,T}^0$) at a given temperature can be written as follows:

$$\Delta G_{r,T}^0 = -RT \ln K \quad (2)$$

where R is the constant of perfect gases, T is the temperature and K is the equilibrium constant of the reaction to the temperature of the system.

Considering a temperature range of T_1 and T_2 less than 30 °C it can be assumed that the reaction enthalpy (ΔH_r^0) [18] is practically constant and the equation defining the equilibrium constant can be integrated into these limits resulting in:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H_r^0}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad (3)$$

In which it is necessary to know the constant K_1 at the temperature T_1 which becomes the reference for the other calculations of the equilibrium constant of the reaction at the other temperatures.

Results and Discussions

Thus, the equation 3 was applied to all the reactions of this work resulting in Tables 2 and 3 below.

Table 2: Values of the Neperian Logarithm of the equilibrium constant (lnK) of the reactions involving tripalmitin for the temperature range of 298.15 to 700 K.

Reaction	Temperature							
	298.15	300	350	400	450	500	600	700
R1	-43.67	-43.18	-31.8	-23.04	-16.01	-10.11	0.262	9.95
R2	-43.67	-43.18	-31.8	-23.03	-15.81	-9.52	2.84	15.8
R3	192.1	190.8	160.8	138.0	119.8	104.7	79.56	58.4
Global	104.8	104.46	97.3	92.05	88.1	85.21	82.82	81.32

Table 3: Values of the Neperian Logarithm of the equilibrium constant (lnK) of the reactions involving triolein for the temperature range of 298.15 to 700 K.

Reaction	Temperature								
	298.15	300	350	400	450	500	550	600	700
R1	-43.67	-43.11	-30.25	-20.53	-12.87	-6.59	-1.27	3.42	11.39
R2	-43.67	-43.11	-30.25	-20.63	-13.12	-7.00	-1.82	2.78	15.8
R3	192.1	190.9	163.1	142.1	125.7	112.4	101.4	92.1	76.93
Global	104.8	104.7	102.6	100.96	99.7	98.9	98.4	98.3	99.01

An analysis of Tables 2 and 3 allows to observe that the three reactions (R1, R2 and R3) that combined generate the overall reaction (R4) or global, behave in a similar way, both for the initial reagent triolein and for tripalmitin.

Reactions 1 and 2 are thermodynamically unfavorable up to 550 K, and from 600 K they become favorable. On the other hand, reaction 3 is thermodynamically favored in every temperature range studied and seems to be the one that commands the favorability of the process. However, although crucial to the reactionary process, reaction 3 is favored at lower temperatures, however, in these ranges, the reactional system is kinetically LOW, because the two initial reactions are disadvantaged.

Conclusions

The preliminary thermodynamic study has shown the difficulties to obtain results for two systems especially in relation to the parameters requested, which are sometimes not yet available in literature, an example of this would be the Gibbs energy of formation of compounds. Although it is recognized that all these systems need further study, it is suggested that the reactionary process should be initiated at higher temperatures and subsequently the reactor temperature should be lowered to accelerate the reaction.

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