MODELING AND SIMULATION OF THE SAPONIFICATION PROCESS OF MICROALGAL BIOMASS FOR FATTY ACIDS PRODUCTION

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Abstract. *Different studies show that the use of microalgae as a source of oil has a high efficiency, making it an excellent alternative with respect to the production of biofuel. However, the extraction of fatty materials is a topic not yet consolidated, because the processes commonly used are expensive, making it difficult to achieve a sustainable production of biodiesel. This paper proposes the modeling of extraction of fatty acids by saponification of wet biomass of microalgae, showing the influence of the reactants in the process. Based on the modeling, it is found that chemical processes with microalgae can be performed without requiring a drying step for the extraction of oil. For that, triglyceride saponification was carried out with an alcoholic solution of NaOH in ethanol, varying concentrations of NaOH in a Fortran program. The numerical simulations show that the production of fatty acids with the process is highly effective, indicating that the methodology has potential to be scaled up for industrial microalgae biomass oil extraction.*

Keywords*: Modeling, microalgae, fatty acid, hydrolysis, NaOH*

1. INTRODUCTION

Through analysis of the literature related to the production of biodiesel and the numerical simulation of equipment components, there is the existence of numerous studies to develop methods of correlating physical quantities with biology and physical chemistry. Given the importance of the subject, a lot of scientific research and effort have been conducted to study the possible techniques and methods that will correlate quantitatively accurately distributional effects of temperature, light, flows, velocities, concentrations, pH, etc., in productivity of microalgae.

Several lines of research have been developed in search for alternative fuels that are economically competitive, environmentally friendly and easily available. Among the various proposed sources for the production of biodiesel, microalgae stand out due to the high fat content compared to other oil sources, but there are some problems regarding the high cost of production of biodiesel from microalgae. Given that, a new line of work is proposed to seek to resolve the recognized bottleneck in the production of biodiesel from microalgae, which is the removal of water from biomass microalgae and oil extraction (Uduman *et al*, 2010). Therefore, the proposition is that fatty acids could be obtained via saponification of the humid microalgae biomass directly without the need for separation and drying.

This work is based on experimental work and therefore was performed simulations varying concentrations of NaOH, where the kinetic modeling of the hydrolysis reaction in the extraction of fatty acids of microalgae has been implemented and developed computationally with the objective of estimating parameters for the reaction. information about the conditions under which occurs are the reaction given the input data, which results in variations in the concentrations of reactants and the reaction products during formation, so that the parametric analysis is performed. In a next step, the model developed to simulate the varying concentrations of NaOH from the experiment, as can be experimentally validated data used in mathematical simulation.

2. MATERIALS AND METHODS

To obtain the experimental work and the microalgae biomass, we used the species *Scenedesmus sp*. Was grown in a tubular fotobiorreator (10 m^3 on a 10 m^2 surface, with 3.5 km of transparent PVC pipes). After the biomass production the material was flocculated in the presence of NaOH and $FeSO_4$. Following flocculation, the thickened material passed through a filter press, resulting in approximately 10 kg of biomass with 80% humidity. The pilot plant used the moist biomass obtained with the technique of saponification (alkaline hydrolysis) for the extraction of fatty material, followed by fatty acids formation through acidification with HCl, and recovery with hexane.

The alkaline hydrolysis of triglycerides and free fatty acids occurs in presence of NaOH and ethanol in a jacketed reactor mixture at a temperature of 60 °C for 1 hour. Then the material is sent to an acidification tank where there is the addition of HCl down to pH 1.0 in order to escalate the salt formed and free fatty acids. Then there is the liquid-liquid

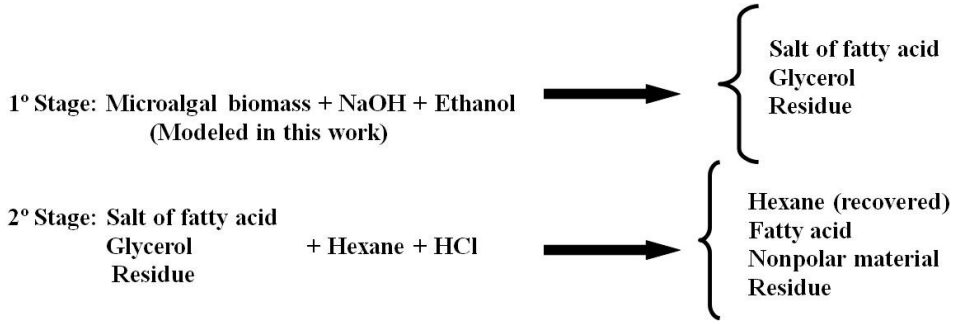
extraction with hexane PA. Since the solvent phase contains fatty acids and apolar fractions, it is finally distilled in a distillation column in order to obtain the fatty acids.

For the numerical simulation was used some hypotheses, as described in Section 2.1, and Fortran software was used with the Runge-Kutta method to simulate ordinary differential equations

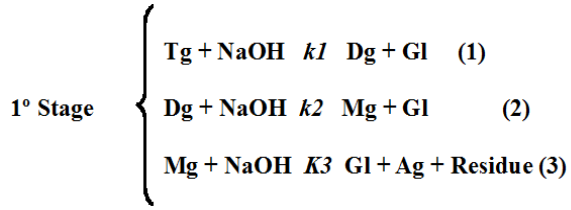
2.1. Assumptions for modeling

In this work, the developed modeling part considered that: 1) The reaction is 1st order, 2) occurs in a reactor of perfect mix, 3) The system is considered closed, i.e., excluding mass exchanges with the environment, and 4) The reaction is considered irreversible.

* Scheme of the reaction of alkaline hydrolysis (saponification):



The alkaline hydrolysis reaction step is divided into two stages: 1st reaction step of breaking the carbonic chain, followed by extraction with hexane called 2nd step. In step (1), triglyceride (Tg) reacts with the hydroxide (NaOH - sodium hydroxide) and ethanol resulting in the formation of one molecule of diglyceride (Dg). Then step (2), the diglyceride hydroxide reacts with the formed ethanol, leading to the formation of monoglyceride (MG), and in turn the monoglyceride is converted in step (3) to glycerol (Gl), and fatty acid residue.



K1 = one step direct rate constant – step 1;
K2 = one step direct rate constant – step 2;
K3 = direct kinetic constant – step 3;
Tg = initial concentration of triglycerides (mol/L);
NaOH = initial concentration of NaOH (mol/L);
Ag = fatty acid.

2.2. Mathematical Equations used for modeling the 1st stage

$$dCTg/dt = - K1.CTg.CNaOH \quad (1)$$
$$dCDg/dt = K1.CTg.CNaOH - K2.CDg.CNaOH \quad (2)$$
$$dCMg/dt = K2.CDg.CNaOH – k3.CMg.CNaOH \quad (3)$$
$$dCAg/dt = K1.CTg.CNaOH + K2.CDg.CNaOH + k3.CMg.CNaOH \quad (4)$$
$$dCNaOH/dt = - K1.CTg.CNaOH - K2.CDg.CNaOH – k3.CMg.CNaOH \quad (5)$$
$$dCGl/dt = K3.CMg.CNaOH \quad (6)$$

It was initially assumed only the presence of microalgal biomass and sodium hydroxide (NaOH). To simulate the behavior of the reaction kinetics, data rate constants were used from the literature, as listed in Tab. 1.

Table 1. Kinetic constants given by Noureddini and Zhu (1997).

Reaction		Constant	Value (mol/min)
TG	DG	K1	0,05
DG	MG	K2	0,22
MG	GL	K3	0,24

3. RESULTS AND DISCUSSION

The simulation results of Figs. 1 to 4 show the system mathematically predicted behavior. They describe the kinetics of the hydrolysis reaction of alkaline wet microalgal biomass with different concentrations of NaOH, obtained with parameter data from the literature (such as kinetic constants).

Figures 1 and 2 present the simulation of the irreversible reaction, with a reaction time of 60 minutes and initial concentration of NaOH of 2.5 mol/L. It may be noted that the reaction takes place almost completely within the first 15 minutes.

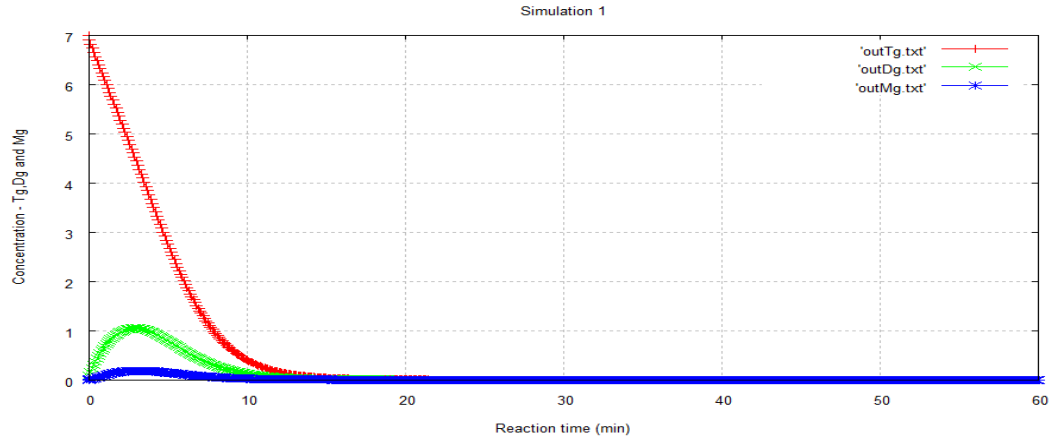


Figure 1. Simulation of the behavior of the reaction, showing the concentration of Tg, Dg and Mg using 2.5 mol/L NaOH.

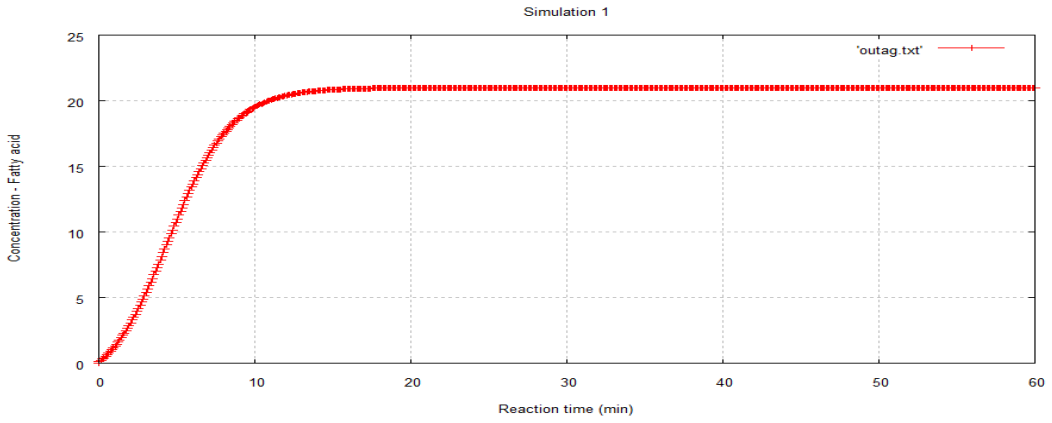


Figure 2. Simulation of the behavior of the formation of fatty acids during the reaction with initial concentration of 2.5 mol/L NaOH.

Note that to reduce the initial concentration of 50% NaOH, 2.5 mol/L to 1.25 mol/L, the reaction kinetics and the conversion of triglycerides, mono and di remains practically the same. After some time the reactants converge into products as shown in Fig. 3.

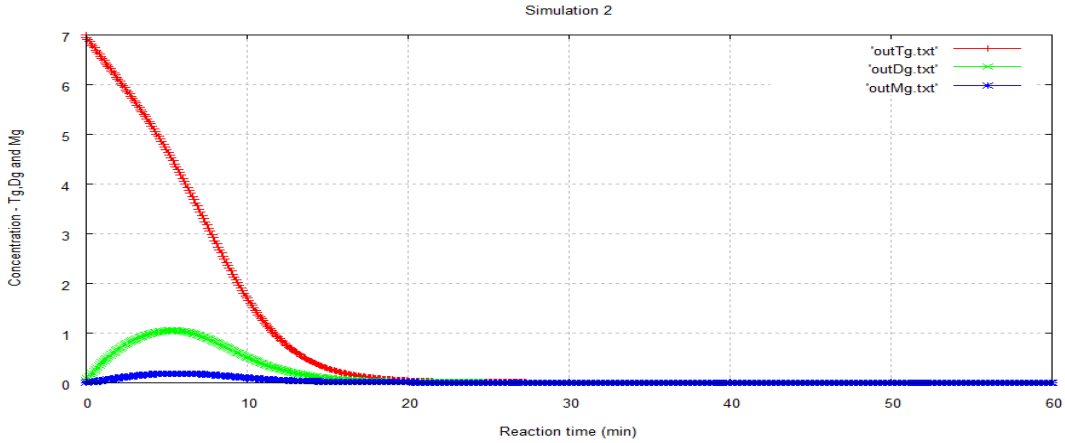


Figure 3. Simulation of the reaction, showing the concentration of Tg, Dg and Mg with 1.25 mol/L NaOH.

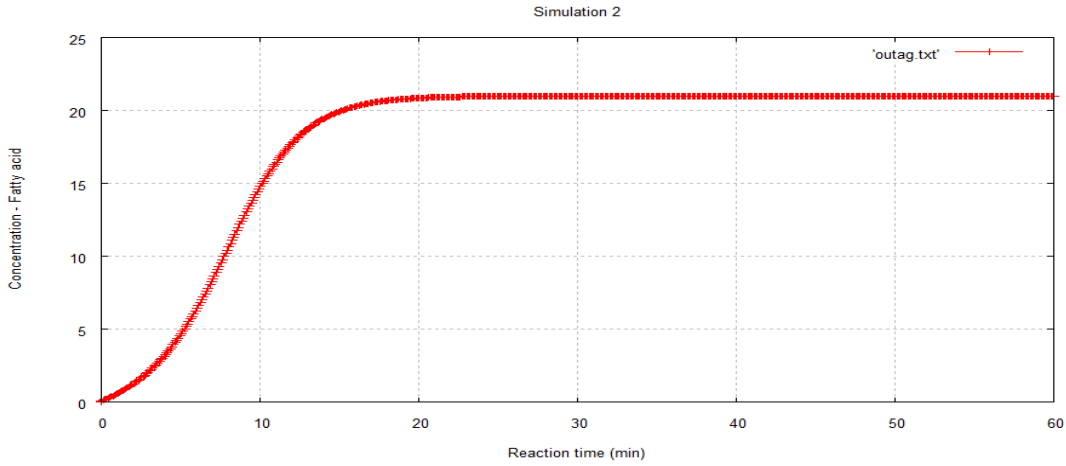


Figure 4. Simulation of the behavior of formation of fatty acids during the reaction by alkaline hydrolysis with 1.25 mol/L NaOH original.

We have seen the kinetic reaction by alkaline hydrolysis with two different concentrations of NaOH (2.5 mol/L and 1.25 mol/L) and used the Fortran program with the Runge-Kutta method to simulate ordinary differential equations for this model considered irreversible. It is concluded that by reducing the concentration of NaOH in 50%, the reaction has almost the same profile, but takes place more slowly.

According to Theodorou *et al* (2007), the velocity of a saponification reaction is changed by steric and electronic effects as well as the solvent due to specific interactions with solvent molecules reactants. Hydroxylic solvents, such as ethanol, strongly interact with anions and increase the energy barrier for reactions involving the approach of a negative charge to a neutral system (triglycerides). Changing the protonic reaction for saponification of other solvents which do not stabilize the reactants, the reaction may be faster, or as it was demonstrated in the simulation, the use of excess sodium hydroxide may cause the increase of speed.

The yield of the pilot process of saponification/extraction was 12.3% of fatty material in relation to dry biomass. However, this result demonstrates that throughout the process there was loss of material in transport and operation of equipment, estimated around 10% for calculating yield. Furthermore, there was observed the degree of degradation of the material at the time of flocculation, estimating the losses of biomass in the operation by 30%.

These results indicate the potential of the developed tool to simulate conditions of several chemical processes. It is also shown that the model reaction with lower concentrations of NaOH reduced cost in the production process on an industrial scale, since NaOH is available in the market.

The proposed methodology still needs energy analysis, but shows up as efficient as the classical fatty material in obtaining microalgae. Furthermore, it represents a viable alternative for producing satisfying results from a biomass still containing a considerable amount of moisture.

4. ACKNOWLEDGEMENTS

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6. RESPONSIBILITY NOTICE

The authors are the only responsible for written material in this paper.