



## Analysis of Macroalgae Oil Transesterification for Biodiesel Production

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In this research, the kinetic of the transesterification of algae oil with methanol in presence of sodium hydroxide was studied. The final conversion was determined using the acid value and it was obtained a conversion of 70 % at 8 h. The experimental results were found to fit a first-order kinetics. Finally, the kinetic constant was determined for the algae oil transesterification.

### 1. Introduction

Galicia (north eastern Spain) is a region with an abundance and wide diversity of marine species and has a deeply rooted seafaring tradition. Algae in Galicia have been traditionally used for agricultural uses. Coastal residents have always collected upon arrival at the coast after storms, to use such as fertilizer, correcting the soil pH, and even as food for livestock. There are a great number of different marine algae but only some species are being used as a food product. The other species are collected in the beaches and they are treated as a waste. Galician macroalgae from the Atlantic Ocean can be used (Maceiras et al., 2010a) for biodiesel production, fuel similar to that obtained from terrestrial plants or seeds. The use of this raw material can give a solution from an environmental and economic point of view. Moreover, this raw material does not compete with agricultural crops.

Biodiesel refers to any diesel-equivalent biofuel made from renewable biological materials such as vegetable oils or animal fats (Marchetti et al., 2007) by chemical reaction with a short-chain alcohol, such as methanol, ethanol, or butanol and a catalyst (Meher et al., 2006), called transesterification. This reaction involves the replacement of the alkyl group of an ester by another through interaction of the ester and alcohol. Generally, this reaction is catalyzed by a base or an acid catalyst. The basic catalysts are the most common since the process is faster and the reaction conditions are moderated. Many researchers have studied the vegetable oil transesterification reaction (Lapuerta et al., 2008; Sahoo and Das, 2009). In the transesterification of oils and fats, the triglycerides react with alcohols producing a mixture of alkyl esters of fatty acids (biodiesel) and glycerine as the main products of the reaction. The influence of these reactions is modified by the type of used catalyst and the characteristics of the raw material, especially the water content and free fatty acids of oils or fats. The three most common parallel reactions often affect transesterification results include neutralization, esterification and saponification. The base catalysis mechanism for triglycerides using alkali hydroxide as catalyst is shown in Figure 1 (Loterio et al., 2005). The first step (a) is a catalytic reaction with alcohol, producing an alkoxide. The nucleophilic attack of the alkoxide to the carbonyl group of the triglyceride generates a tetrahedral intermediate compound (b) from which the alkyl ester is formed and

the corresponding anion of triglyceride (c). Finally, the catalyst is deionized, resulting in the regeneration of the active compound (d), which allows that it can react with a new molecule of alcohol, beginning a new catalytic cycle. In the notation used, B is the base catalyst, R1, R2 and R3 are the carbonyl groups of fatty acids and R is the functional group of alcohol.

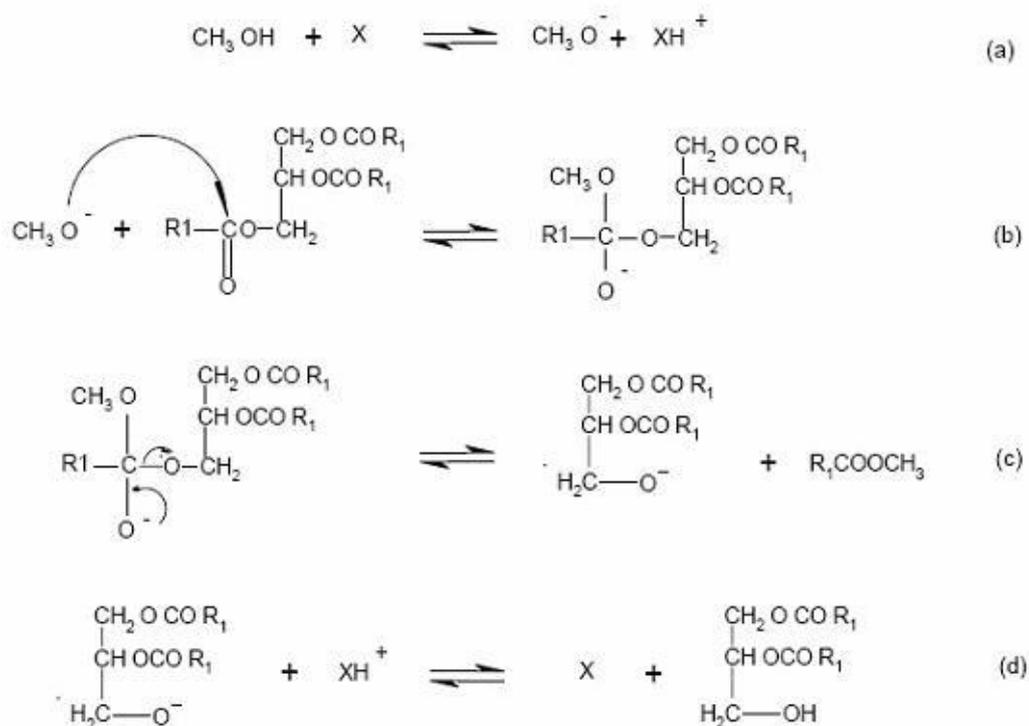


Figure 1: Mechanism of basic transesterification reaction

The mechanism of the transesterification reaction is well known. However, there is less information about the kinetic model of this reaction (Al-Zuhair et al., 2007; Vicente et al., 2005). Kinetic study of the algae transesterification is an important parameter for the reactor design. Due to the lack of data about this kinetic, the authors have analysed and discussed the kinetic of Galician macroalge oil with the aim of carrying out the transesterification in optima conditions.

## 2. Experimental

### 2.1 Materials

In this work two types of marine algae (*Fucus Spiralis* and *Pelvetia Canaliculata*) were collected from the Galician beaches. These macroalgae have been chosen based on the results of a previous work (Maceiras et al., 2010b). The algae were washed with water and sun-dried for a few days, since water inhibits transesterification. After that, the dried algae were crush in two steps in order to obtain small solid particles.

## 2.2 Oil extraction

Three hundred mL of n-hexane was used for 50 g of dried for the oil extraction. The extraction was carried out in a Soxhlet apparatus for 4 h according to UNE-EN 734-1:2006. The extraction was carried out in order to determine the algae oil content and its acid value.

All of the experiments were carried out using a 0.5 L round-bottomed glass flask. The resultant solution was separated from solvent by distillation. The solvent was reused in the next batch of extraction. Finally, the sample was dried in an oven (100 °C) until constant weight.

## 2.3 Reaction procedure

The transesterification process was conducted simultaneously with the extraction in order to avoid the previous step of oil extraction and purification of obtained oil. Then, 10 g of dry algae and crushed (5 g of *Pelvetia Canaliculata* and 5 g of *Fucus Spiralis*) was mixed with 30 mL of methanol in which sodium hydroxide (1 wt % dry basis) had been previously dissolved. It has been employed a methanol excess of about 50 times more methanol than the optimum ratio used as oil-methanol 1:6 to obtain a high degree of conversion of monoalkyl esters which is achieved by adding excess alcohol with respect to the stoichiometric reaction (Hass et al., 2003). The reaction mixture takes place in flasks with 0.1 L and reaction was conducted at 60 °C for four and eight hours with constant stirring of 150 rpm. In the reaction mixture the solid phase was separated by filtration using a Buckner funnel under vacuum. To obtain the crude biodiesel was necessary to remove the solvent by distillation.

## 2.4 Analytical procedure

The conversion of fatty acids to methyl esters can be calculated with the acid value according to the following equation:

$$x = \left(1 - \frac{AV_1}{AV_0}\right) \cdot 100 \quad (1)$$

where  $AV_0$  and  $AV_1$  are the acid values of feed and products, respectively. The acid value was determined as per the UNE-EN 14104:2003.

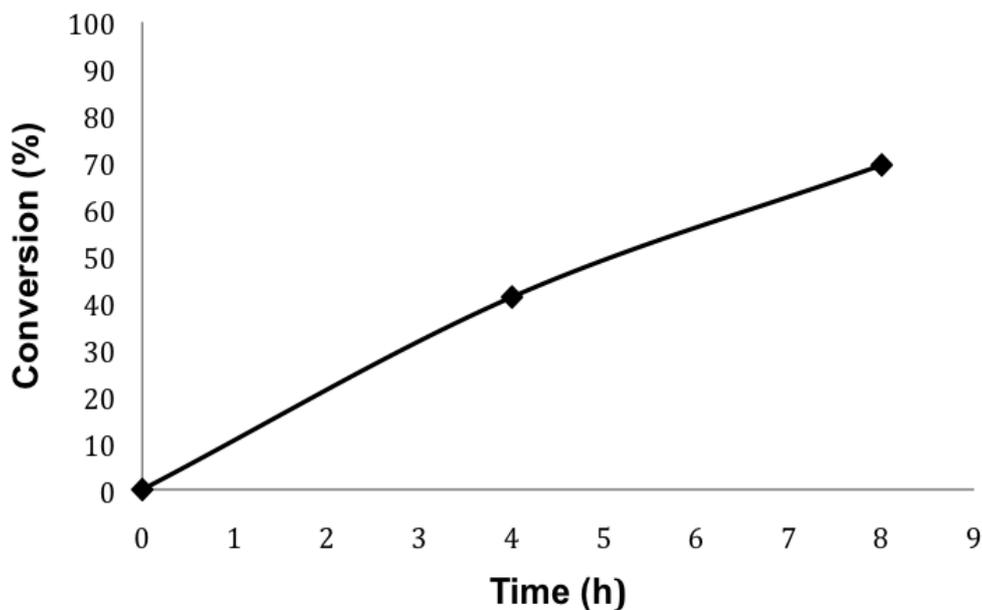


Figure 2. Variation of conversion with time

### 3. Results and discussion

The algae oil conversion with the reaction time for the transesterification is shown in Figure 2. It is obvious that the reaction rate increases significantly with the reaction time and it can be said that a higher conversion could be obtained with higher reaction times.

The reaction rate of basic transesterification of algae oil can be described:

$$-\frac{dC_A}{dt} = kC_A^a C_B^b - k' C_C^c C_D^d \quad (2)$$

where  $C_A$ ,  $C_B$ ,  $C_C$  and  $C_D$  denote the concentrations of fatty acids, methanol, methyl esters and water, respectively; a, b, c and d refer to their reaction orders and k and k' are the kinetic constants for the forward and reverse reactions, respectively. Considering that the methanol concentration is much higher than that of other components, the value of  $kC_B^b$  can be treated as a constant. On the other hand, k is far larger than k' (Tesser et al., 2005). For that reasons, the Equation (2) can be simplified to:

$$-\frac{dC_A}{dt} = k_1 C_A^n \quad (3)$$

The Equation (3) can be expressed as a function of the conversion (x) and the initial concentration of fatty acids ( $C_{Ao}$ ):

$$\frac{dx}{dt} = \frac{k_1}{C_{Ao}} (C_{Ao}(1-x))^n \quad (4)$$

When n=1, Equation (4) can be integrated to:

$$-\ln(1-x) = k_1 t \quad (5)$$

When n=2, equation (4) can be integrated to:

$$\frac{x}{1-x} = k_1 C_{Ao} t \quad (6)$$

Plotting the experimental results versus time, it can be determined the reaction order and the kinetic constant. As it can be observed in Figures 3 and 4, the transesterification reaction of algae oil fits reasonably well with the first order kinetic equation, while fits badly with the second order kinetic reaction. Then, the reaction order is 1 and the kinetic constant can be obtained from of the slope of the straight line, resulting in a value of  $0.145 \text{ h}^{-1}$ .

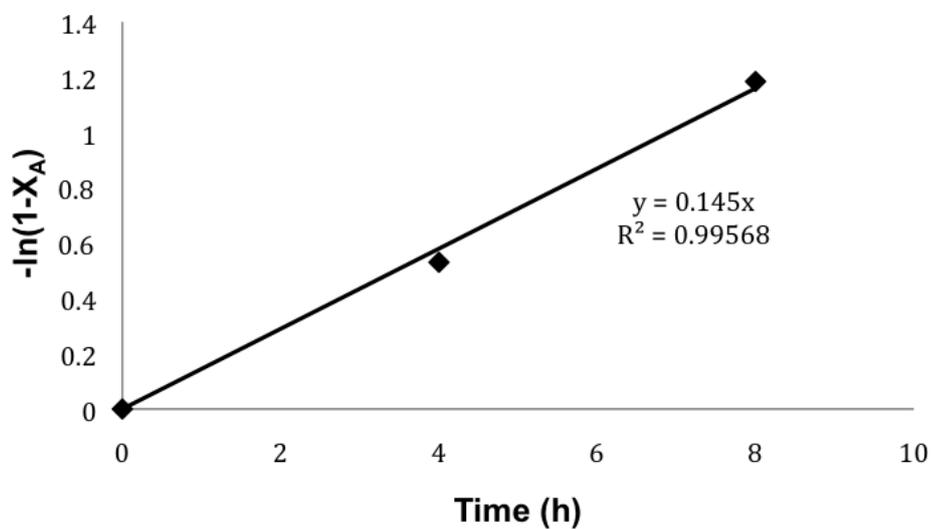


Figure 3: Plot of Equation 5 with the reaction results

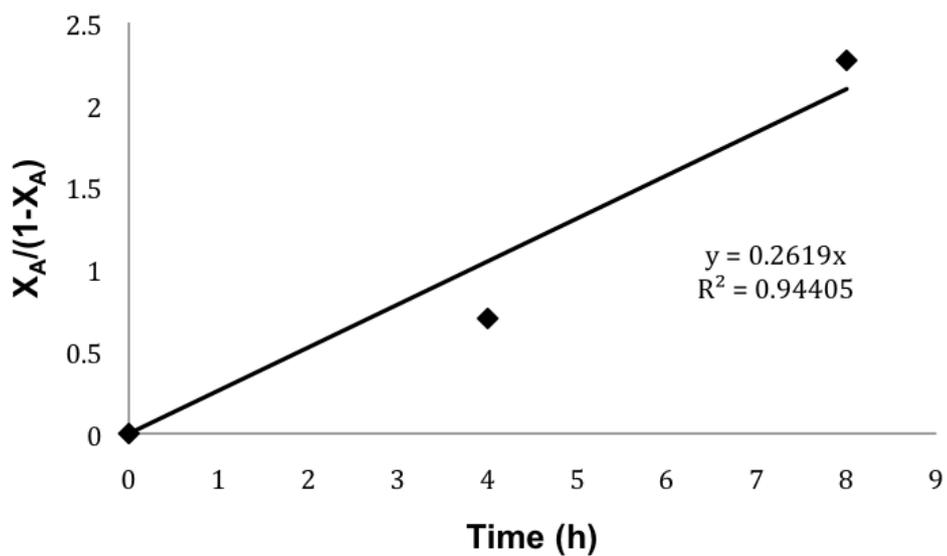


Figure 4: Plot of Equation 6 with the reaction results

#### 4. Conclusions

The transesterification of algae oil in methanol catalyzed by sodium hydroxide was investigated in this work. A kinetic model for the reaction was established. By fitting the kinetic model with the experimental results, the reaction order and kinetic constant were established resulting a first order kinetic.

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