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Pyrolysis of *Spirulina maxima*: Kinetic modeling and selectivity for aromatic hydrocarbons

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ABSTRACT

Microalgae, such as *Spirulina maxima* biomass is considered a potential raw material for fast pyrolysis process due to its low-lipid and high-protein contents. Aromatic hydrocarbons, which are widely used in industry, are the main derivatives of protein pyrolysis. In this study, thermogravimetric analyses were performed and activation energy values were identified using three methodologies: Friedman and Flynn-Wall-Ozawa isoconversional methods, Miura-Maki distributed activation energy model and the model of independent parallel reactions. The mean values of activation energy were 132.62, 143.77 and 136.89 kJ/mol, respectively, for the Flynn-Wall-Ozawa, Friedman and Miura-Maki models. The biomass pyrolysis was described by two different reactions using the independent parallel reactions model and the mean values of activation energy were between 48.58 and 51.52 kJ/mol for the mass fraction essentially composed by carbohydrate and between 143.61 and 288.55 kJ/mol for the mass fraction with protein as the main component. The micro-pyrolysis of the pure biomass was analyzed at different reaction temperatures (723, 823 and 923 K). At 923 K the highest yield of aromatic hydrocarbons and a decrease in oxygenated compounds were observed. Catalytic micro-pyrolysis was performed for *Spirulina maxima* using either zeolite HZSM-5 or niobic acid (HY-340) as catalysts. For HZSM-5, the biomass-to-catalyst ratio of 1:10 increased more than five times the production of hydrocarbons when compared to the pure biomass. The niobium-based catalyst (HY-340) did not present a significant effect on the production of these value-added compounds. Probably, for HY-340, the active sites are not predominantly Brønsted acid sites and/or the number of Brønsted acid sites was not sufficient to promote the production of aromatics. The present work is one of the first studies considering niobic acid as a catalyst for biomass pyrolysis and using the independent parallel reactions model for the determination of kinetic parameters for *Spirulina maxima*.

1. Introduction

Microalgae have been studied as an alternative source for the production of biofuels and chemical products due to their great biotechnological potential [1], by means of thermo-conversional processes such as pyrolysis. Fast pyrolysis presents high-yield conversion rates into gas, liquid and solid products at relatively moderate temperatures of 523 to 873 K [2,3]. The fast pyrolysis process involves the thermal decomposition of biomass in the total or partial absence of oxygen [3,4].

Thermogravimetry is an analytical technique that measures the variations in mass loss of a material as a function of time, temperature and heating rates. This technique allows for the estimation of kinetic parameters for solid decomposition, which are important in the mathematical modeling of pyrolysis. The thermogravimetric technique, which works at relatively low heating rates (up to 50 K/min) when compared to the rates required for fast pyrolysis (up to 20 K/ms), is useful for the evaluation of pyrolysis and volatilization of materials, since experimental techniques that require high heating rates cannot ensure accurate measurements of mass variation [5].

Studies have focused on the thermal decomposition of microalgae [6,7] and these data could help design and scale-up the thermochemical conversion systems. Extensive literature has been published on the pyrolysis kinetics of lignocellulosic biomass but very little information is available for microalgae [6].

Yuan et al. [8] demonstrated that the temperature corresponding to

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the main peak of the derivative mass loss curve for microalgae *Chlorella vulgaris* (569 K) was lower compared to lignocellulosic biomass. Ali and Bahadar [9] investigated the kinetic parameters of *Sargassum* spp. of Red Sea origin using thermogravimetric analysis; Friedman, Flynn-Wall-Ozawa, Kissinger-Akahira-Sunose and Starink methods were used to calculate the apparent activation energies using values of conversion from 10% to 90%; it was observed that the calculated energy activation values increased with higher conversion values. Yang et al. [10] estimated the activation energy values for the pyrolysis of *Chlorella sorokiniana 21* and *Monoraphidium 3s35* microalgae, using the distributed activation energy model at different heating rates and observed that the pyrolysis generated different bio-oils from distinct microalgal biomass and *C. sorokiniana 21* presented lower values of activation energy. Micro-pyrolysis is a reliable analytical technique that provides useful preliminary information about the complex pyrolysis process for biomass. According to Wang et al. [11] fast pyrolysis of *C. vulgaris* microalgae (after removal of most lipids) containing approximately 61% of protein, using a fluidized bed reactor, resulted in a bio-oil yield of 53%; containing aromatics, amines, carboxylic acids and phenolic compounds.

The cyanobacterium *Spirulina maxima* is a potential raw material for the production of bio-oil, since it contains small amounts of lipids and large amounts of proteins. Aromatic hydrocarbons are the main products of pyrolysis from the protein fraction, and these compounds are used in the production of dyes, explosives, repellents, etc. [12].

Considering the quality of bio-oil as a fuel, high oxygen contents are known to be undesirable because of oxidation reactions that render the fuel unstable [12]. Some studies have shown that bio-oil extracted from protein biomass is more stable than that extracted from lignocellulosic biomass, has lower oxygen content and higher calorific value. However, bio-oil from protein biomass usually has high nitrogen content. This can be offset by catalytic pyrolysis, a strategy to improve the quality of pyrolytic vapors that increases the amount of aromatic hydrocarbons and decreases the amount of nitrogen and oxygenated compounds [12,13]. Lorenzetti et al. [14] showed that HZSM-5 promoted a good denitrogenation effect for nitriles, amines and amides in the catalytic pyrolysis process of *Spirulina platensis*.

Anand et al. [15] studied the thermal stability and evaluated the conversion of *Spirulina platensis* to chemicals and intermediates via non-catalytic and catalytic fast pyrolysis using different zeolites. The HZSM-5 at 10:1 wt/wt loading to algae at 873 K was able to increase the production of some aromatics such as benzene, toluene and xylene.

Chagas et al. [12] studied the catalytic pyrolysis of *Spirulina* (*Arthrospira platensis and Arthrospira maxima.*) over several zeolite catalysts using pyrolysis/GC–MS. It was found that the high acidity HZSM-5 (SiO_2/Al_2O_3 ratio of 23) catalysts could maximize the conversion of *Spirulina* to aromatic hydrocarbons and the aromatic yields increased as the catalyst/biomass ratio increased from 1:1 to 10:1. Hydrated niobium pentoxide (HY-340) is an acidic catalyst that can be used in pyrolysis processes, but it is still poorly exploited. Carvalho [16] studied the catalytic pyrolysis of sorghum using HY-340 and observed that there was an increase in the production of furans and olefins and a decrease in the formation of oxygenates in pyrolysis products. In this context, the focus of this study was to investigate the thermal behavior of *Spirulina maxima* and estimate activation energy values based on thermogravimetric data, using two classical isoconversional models (Flynn-Wall-Ozawa and Friedman), the distributed activation energy model (Miura-Maki) and the model of independent parallel reactions. Different models were used, aiming to compare the determined values of activation energy, evaluating the effect of the methodology. Knowledge at the pyrolysis kinetics is helpful when dealing with the design of equipment in a thermochemical process, moreover, little information is available on the kinetics of microalgae pyrolysis.

The influence of temperature and the presence of HZSM-5 and HY-340 catalysts in the composition of the micro-pyrolysis products were also examined to determine the selectivity of these catalysts in the production of aromatic hydrocarbons. Currently, HZSM-5 has been studied in the pyrolysis process of algal biomass, but studies involving HY-340 have not been performed yet. Moreover, this is one of the first works using the independent parallel reactions model for the determination of kinetic parameters for *Spirulina maxima*.

2. Experimental section

2.1. Characterization of Spirulina maxima

The *Spirulina maxima* biomass was obtained from Empório Flor de Laranjeira (São Paulo, SP, Brazil), sold as dehydrated *Spirulina* (fine powder). The analyses were performed using the material as received. The microalgae were characterized by ultimate analysis. The analysis was performed using the same methods employed in previous studies [17,18] using method D3176 ASTM. Proximate and biochemical analyses was performed using the Official Methods of Analysis of AOAC International, including methods 923.03, 920.87, 925.10 and 960.39 for ash, crude protein (%N × 6.25), moisture and crude fat, respectively [19,20]. Carbohydrate percent was determined based on the difference from 100%. Table 1 describes the results of these analyses.

In Table 1, note that *Spirulina maxima* contains 80.41% of volatile matter, which is a large amount. Wang et al. [11] reported that the microalgae *Chlorella vulgaris* contains 66.56% volatiles; 15.67% lipids and 41.51% protein. As expected, the *Spirulina maxima* used in this study has high protein content, indicating that its biomass is suitable for the production of aromatic hydrocarbons. The ultimate analysis of this biomass revealed the high carbon content of this material, confirming its potential for the same.

The results for biomass characterization are presented as mean values ± standard deviation (S.D.), tests were performed in triplicate (except for biochemical analyses). The statistical calculations were carried out using Microsoft Excel® 2013 for Windows.

2.2. Thermal gravimetric analysis (TG)

The microalgae *Spirulina maxima* was subjected to thermogravimetric analysis in a Shimadzu DTG-60H thermal analyzer in a continuous atmosphere of inert nitrogen (99.999 purity) at a flow rate of 30 ml/min. To reduce the moisture content, the material was first heated to 373 K at a heating rate of 50 K/min (maximum heating rate of the equipment) and held at this temperature for 30 min. After this, the sample was heated to 1173 K to evaluate its thermal degradation. Five different heating rates were applied to minimize heat and mass transfer effects in the calculations of kinetic parameters: 5, 10, 15, 20 and 25 K/min. The first 30 min involved drying of the sample and as a result the data of this time interval were disregarded; therefore, mass changes due

Table 1
Proximate, biochemical and ultimate analyses for *Spirulina maxima*; results in wet basis. The data are presented as the mean ± S.D. (triplicate analyses), except for biochemical test.

Proximate analysis	(wt%)	Biochemical analysis	(wt%)
Moisture	5.23 ± 0.95	Protein	66.74 ± 0.17
Volatile matter	81.44 ± 0.72	Fiber	0.97 ± 0.03
Ash	7.43 ± 0.19	Ethereal extract	2.96 ± 0.07
Fixed carbon	5.9 ± 1.35	Carbohydrate	16.67[a]

Ultimate analysis (wt%)				
C	H	N	S	O
46.23	7.24	10.53	1.72	34.28

[a] Carbohydrate = 100(%) – moisture – ash – protein – fiber – ethereal extract.