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Design of a Multifunctional Reactor for Third Generation Biofuels Production

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Third generation biofuels also called oilgae are based in emerging technologies that ensures high fuel production per area unit and lower production costs. Microalgae oil appears as a promising biodiesel source due to their oil content is many times higher than oil content of other vegetal sources currently used.

This work shows the design of a multifunctional batch reactor used in pilot plant scale that works in three steps, cell wall hydrolysis, reducing sugars fermentation and in situ transesterification, the microalgae specie studied was *Chaetoceros Calcitrans*, this design is proposed in order to contribute to the process integration; the multifunctional reactor takes advantage of the reducing sugar yield for bioethanol production that is used as a transesterification alcohol.

Optimization of microalgal reducing sugars yield was performed using the software MatLab 7.0®, The best conditions for cell disruption gives a 15 % of reducing sugars yield after 100 min of reaction with a temperature of 121 °C, and acid concentration of 1%, transesterification temperature was fixed in 50 ºC with KOH stirring at 600 rpm and 50 min of reaction time, and product separation was made with a mixture water-hexane.

1. Introduction

Currently, there are two general problems related with fossil-derived liquid fuels; global warming linked with gas emissions produced after its combustion, and high prices of oil. For these reasons, research about biofuels production from renewable resources had been increasing. Third generation biofuels, also called advanced biofuels by the feedstocks and processes used for its production are produced from vegetable oils of microscopic organisms, mainly as microbes and microalgae.

Microalgae are potentially a promising biodiesel source, because oil content of some species of microalgae is between 30 and 100 times higher than conventional biodiesel sources (Chisti, 2007). These lipids can be produced by microalgae in short periods of time.

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An efficient lipid extraction from microalgae depends in a great way of the simplicity for break in and/or to destroy the cell wall of the microalgae, the composition of the cell wall vary with the specie of microalgae, for this reason, is necessary a step of cell disruption. Algal biomass contents hydrolysable cellulosic material. Acid hydrolysis is the typical process used for lignocellulosic material conversion in carbohydrates and sugars, for this reason, is proposed a first step of microalgal biomass hydrolysis for both reducing sugars production and helping oil extraction process through cell wall disruption, reducing sugars can be converted in bioethanol through fermentation process for third generation bioethanol production, multifunctional third generation biofuels batch reactor works in three steps, cell wall hydrolysis, reducing sugars fermentation and in situ transesterification (Figure 1).

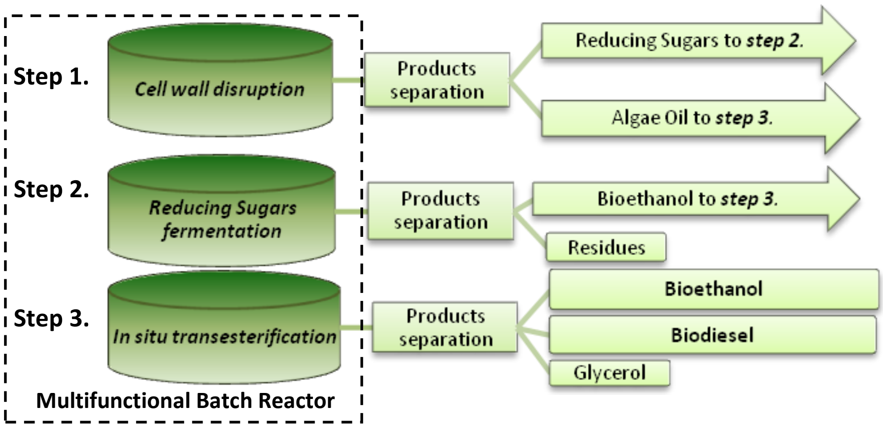

Figure 1 Third generation biofuels production scheme using multifunctional batch reactor.

2. Materials and Methods

Chaetoceros Calcitrans microalgae biomass was provided by Corporacion Instituto de Morrosquillo (Punta Bolivar, Colombia), algae was cultured in F/2 medium and harvested by flocculation, biomass was sun-dried and frozen until using. Cell disruption was carried out by preparing a mixture of sulfuric acid solution and biomass at a 10:1 ratio. The concentration of solution and time conditions were predicted by an experimental 2^2 central composite design and the reaction was taken place at 121 ºC in a 25 l batch reactor. Total reducing sugars were measured with the dinitrosalicylic acid (DNS) method described by Miller (1959), statistical analysis of main effects was made using STATISTICA 7.0

For kinetic modeling, experimental results were plot and reaction rates were established, kinetic parameters were found using MatLab®. Reducing sugars yield from microalgal biomass was modeled for different temperatures and acid concentrations. Following the model, optimal conditions for the first stage was found, and operation conditions for transesterification and fermentation stages were adjusted according with the model developed, experimental data and literature.

3. Results

3.1 Experimental

According to reducing sugars yields obtained in preliminary experiments, an experimental 2^2 central composite design was proposed, the levels are shown in table 1, the response variable is the yield of reducing sugars and the independent variables are both acid concentration and reaction time.

Table 1 Experimental 2^2 central composite design.

	levels				
Factors	-1.41	-1	0	1	1.41
H2SO4 concentration (M)	0.066	0.08	0.115	0.15	0.164
Time (min)	22.721	60	150	240	277.279

The execution of this design shows the values of reducing sugars yield that were used as a basis for kinetic parameters calculation, with the experimental results, a response surface was built (Figure 2), the yield of total reducing sugars increases with reaction time and acid concentration.

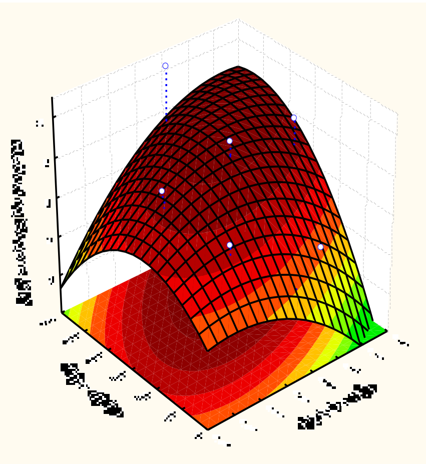

Figure 2 Reducing sugar yield for Chaetoceros Calcitrans microalgae specie as a function of acid concentration and process time (reaction temperature: 121 °C).

3.2 Kinetic Model for Cell Disruption

According with the successfully developed (Tellez-Luis et al. 2002, Gamez. 2006), a consecutive first order reaction, with two irreversible reaction steps is shown as a first approach for microalgae cellulosic material behavior in equation (1), where MCM is the microalgal cellulosic material, RS are the reducing sugars produced and DP are the degradation products.

$$MCM \xrightarrow{k_1} RS \xrightarrow{k_2} DP \qquad (1)$$

Based in these two reactions, the differential equations that describe the changes of microalgal cellulosic material and products are as follows:

$$\frac{dC}{dt} = -k_1[C] \tag{2}$$

$$\frac{dR}{dt} = k_1[C] - k_2[R] \tag{3}$$

Equation (2) express the monomerization of cellulosic material reaction rate and Equation (3) describes the total reducing sugars formation rate, where C is the cellulosic material concentration and R is total reducing sugar concentration. MatLab® was used to find reaction rates k_1 and k_2 whose behavior are described for Equation (4), kinetic parameters found are shown in Table 2.

$$k_i = C_{acid}^{n} A_i e^{-E_i/RT} \tag{4}$$

Table 2 Kinetic model results for Chaetoceros Calcitrans biomass hydrolysis

Sulphuric acid T=121 °C				
	n	*A*, min^{-1}	*E*, kJ/mol	*k*, min^{-1}
Reducing sugars	0.61	0.89	12.98	4.7E-03
Degradation products	0.35	0.22	13.13	1.9E-03

Based on model results for different temperatures (Figure 3), is shown that an increase on reaction temperature has not a big effect on reducing sugars production; however, the effect on degradation products formation is advantaged, is also shown that with a reaction time near 225 min, there is a maximum sugar yield for all temperatures, based on these results, is chosen for the cell disruption a temperature of 121 °C, decreasing in this way the energy requirements for reactor operation.

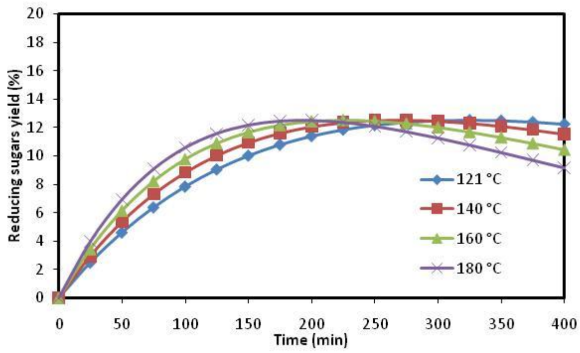

Figure 3 Model based effect of temperature on total reducing sugars yield into a multifunctional reactor (acid concentration = 0.12 %).

Figure 4 shows the reducing sugars yield from microalgae biomass at different acid concentrations, while the amount of sulfuric acid is increased, the time for the maximum reducing sugars production decreases, the addition of acid increases also the quantity of total reducing sugars that can be obtained, an acid concentration of 1 % gives the best results for the operation of the multifunctional reactor. Based on those results, a reaction time of 100 min is chosen.

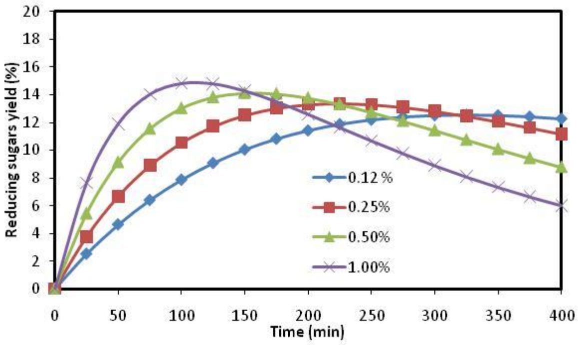

Figure 4 Model based effect of acid concentration on total reducing sugars yield into a multifunctional reactor (temperature = 121 °C).

3.3 Reducing Sugars Fermentation

Reducing sugars are used as a substrate for bioethanol production by activity of Saccharomyces cerevisiae, the hydrolysis product must be concentrated by evaporation. Sharma et al (2002), studied different operation conditions for this microorganism focusing on bioethanol production from reducing sugars, based on that information, optimum parameters were adjusted for local conditions and raw material (Table 3).

Table 3 Operating conditions for microalgae reducing sugars fermentation

Temperature	pH	Bioethanol yield	Fermentation efficiency	Reaction time	Impeller speed
28 °C	5.0	0.44 (g/g)	85%	1080 min.	150 rpm.

3.4 Transesterification of Microalgae Oil

Chaetoceros Calcitrans lipid content is reported in values between 10 % and 30 % (Brown et al. 1989, 1997). KOH is used for catalyze transesterification of algae oil for biodiesel production, alcohol used for this transesterification is bioethanol produced in the step 2 of the process, based on experiental results, operating conditions of the multifunctional reactor for transesterification process are shown in Table 4; additional conditions are also shown based on reported summaries (Helwani et al. 2009).

Table 4 Operating conditions for microalgae oil transesterification step

Temperature	Pressure	Catalyst	Molar ratio alcohol/oil	Reaction time	Impeller speed
50 °C	1 atm.	KOH	6:1	50 min.	600 rpm.

4. Conclusion

Multifunctional batch reactor designed in this work gives the possibility to combine important steps of third generation biofuels production chain producing third generation biofuels, and allows to study the kinetic reaction parameters for *Chaetoceros Calcitrans* biomass acid hydrolysis, conditions for all steps were found, maximum reducing sugars yield (15 %) is reached after 100 min of reaction with a temperature of 121 °C, and acid concentration of 1 %, for transesterification, temperature decreases until 50 °C, with KOH stirring at 600 rpm and 50 min of reaction time, bioethanol can be produced from algal reducing sugars, but, this reaction takes more time than hydrolysis and transesterification reactions.

Acknowledgements

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