CHEMICAL ENGINEERING TRANSACTIONS

VOL. 27, 2012

Guest Editors: Enrico Bardone, Alberto Brucato, Tajalli Keshavarz
Copyright © 2012, AIDIC Servizi S.r.l.,
ISBN 978-88-95608-18-1; **ISSN** 1974-9791

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at: www.aidic.it/cet

DOI: 10.3303/CET1227063

Simulation of a Hydrogen Production Process from Algae

Daniela Galatro[a], Elisa Verruschi[a,*]

[a]Universidad Nacional Experimental Politecnica (UNEXPO), Centro de Investigaciones de Procesos. Avenida Corpahuaico, Barquisimeto, Venezuela
galatrod@gmail.com

Sustainable sources of renewable energies are highly valuable in a world where the global energy demand is considerably increasing. The conceptualization of an efficient alternative fuel process production is based on the synergy of the reaction engineering, thermal integration, separation optimization, etc. Process simulation software are powerful tools that allows process designers to integrate these modules to get an optimized design: sustainable, environmentally friendly and cost efficient. A simulation model of the hydrogen production from micro-algae biomass was developed in Pro II. Algae are a rich source of carbohydrates. Sugars can be obtained by hydrolysis and then fermented to produce bioethanol which is consequently converted to hydrogen by catalytic reforming. The simulation was structured in three (3) main reaction units and corresponding side sub-units / equipment as separation trains, heat exchangers, etc. The first reaction unit is the enzymatic hydrolysis of micro-algae, based on the enzymatic hydrolysis of Chloroccum sp by using cellulase. The kinetics is fitted with Michaelis-Mente's model of rapid equilibrium, as described by Harun et. al (2010). The second reaction section is the bioethanol fermentation which is conducted in a converter reactor with a complementary FORTRAN subroutine. Downstream separation processes to refine the alcohols produced are also modelled. Finally the third reaction module includes the ethanol reforming over Ni Al_2O_3 catalyst as described by Akande et. al (2006). The simulation model allows users to analyse and optimise the process by using various process conditions, design configurations, energy integration options, etc.

1. Introduction

The production of biofuels and hydrogen is increasing significantly due to the increased price of oil and the need for energy security. Commercial simulation software vendors have been closely working with the biofuel producers to ensure that the models can represent the production process conditions and therefore, allowing for the efficient and optimal process design and operational evaluation. Recent enhancements to tools like Pro II include a Bioethanol component database, custom unit operation modules and others. Proprietary correlations of the process can be fed in Pro II using the spreadsheet unit linked with Microsoft Excel. Existing utilities as the FORTRAN calculator can be also useful for modelling and simulation.

A simulation model of the hydrogen production from micro-algae biomass was developed in Pro II. The process is divided in three (3) main modules: cellulose hydrolysis, glucose fermentation and ethanol reforming.

Please cite this article as: Galatro D. and Verruschi E., 2012, Simulation of a hydrogen production process from algae, Chemical Engineering Transactions, 27, 373-378 DOI: 10.3303/CET1227063

1.1 Bioethanol from Algae

Algae are a relatively new biomass source for the production of renewable energy. They can have a high biomass yield per area, do not require agricultural land and fresh water is not essential (nutrients can be supplied by wastewater).

Bioethanol is an alcohol produced by fermenting sugars typically from plant like sugar cane or corn. Recent advances in cellulosic biomass are enabling the production of bioethanol from algae.

1.2 Ethanol reforming

Hydrogen has a significant future potential as an alternative fuel that can solve the problems of CO_2 emissions. One of the techniques to produce hydrogen is by steam reforming of bioethanol. All the oxygenated hydrocarbons in ethanol can be reformed completely to hydrogen and carbon dioxide. CO_2 can be later separated from hydrogen by membrane technology. The reforming of crude ethanol to produce hydrogen using different catalysts like Co/ZnO, $Cu/Mn/Al_2O_3$ and Ni/Al_2O_3 has been widely investigated. It was demonstrated that catalysts based on Ni loading on alumina support was the optimum catalyst and gave a maximum conversion of crude ethanol, according to Akande et. al (2006).

2. Hydrolysis unit

Two main hydrolysis methods are widely used to produce monomeric sugars required for fermentation. These are the acid hydrolysis and enzymatic hydrolysis. In the acid hydrolysis, the acid dissolves the hemicellulosic components of the biomass and converts the cellulose into fermentable sugars. Dilute sulphuric acid is the most used acid, giving high hydrolysis yields. On the other hand, in the enzymatic hydrolysis, enzymes are used to release the fermentable sugars from the biomass. The process cost of this hydrolysis method is considerably lower than acid hydrolysis as it minimizes acid corrosion under mild temperatures and pH.

The enzymatic hydrolysis of Chloroccum sp. by using cellulose obtained from Trichoderma ressei is simulated in the first module called Hydrolysis unit. The kinetics of hydrolysis was fitted with Michaelis-Menten's model of rapid equilibrium by Harun et. al (2011). Hydrolysis was conducted under different temperatures, pH and substrate concentration, with constant enzyme dosage. The highest glucose yield was 64.2% (w/w) at a temperature of 40 °C, pH 4.8 and a substrate concentration of 10 g/l of microalgal biomass. Arrhenius parameters were also calculated in this study.

Water and cellulose at ambient conditions are mixed and then preheated to 40 °C. The expected glucose yield is calculated based on a set of correlations obtained by correlating the experimental results obtained by Harun et. al (2011) as function of the pH and temperature of the mixture. These correlations are included in the calculator utility PH-T.

pH < 5.45, at 40 °C:

$$YIELD = 0.7619pH^3 - 12.182pH^2 + 66.653pH - 58.697 \quad (1)$$

pH ≤ 5.45, at 40 °C:

$$YIELD = 6.1038\, pH^2 - 89.776pH + 373.98 \quad (2)$$

The real yield is estimated by the calculator utility YIELD.

A conversion reactor is used to simulate the hydrolysis of the cellulose; the set of reactions is described as follows:

Cellulose + Water → nGlucose

$$C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6 \quad (3)$$

Cellulose + (n/2) water → (n/2) Cellobiose

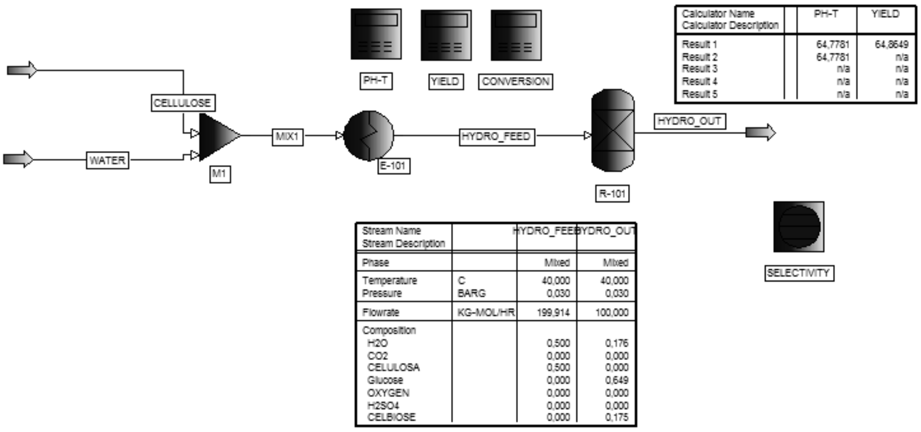
$$C_6H_{10}O_5 + 0.5H_2O \rightarrow 0.5C_{12}H_{22}O_{11} \quad (4)$$

The Arrhenius parameters are included in the conversion reactor and the conversion ratio of the first and second reaction is calculated with the controller utility SELECTIVITY, by varying both conversions until the ratio between the real and expected yield is equal to 1.

Table 1: Arrhenius parameters relating to temperature effect on hydrolysis

Stage	A (s^{-1})	E_a (kJ/mole)
Cellobiose production	6.98×10^{11}	66.38
Glucose production	1.82×10^{11}	21.56

NRTL was chosen as thermodynamic method for the vapour-liquid equilibrium (aqueous organic system).
The Pro II flow diagram of this unit is shown in figure 1.



Calculator Name Calculator Description		PH-T	YIELD
Result 1		64,7781	64,8649
Result 2		64,7781	n/a
Result 3		n/a	n/a
Result 4		n/a	n/a
Result 5		n/a	n/a

Stream Name Stream Description		HYDRO_FEE	YDRO_OUT
Phase		Mixed	Mixed
Temperature	C	40,000	40,000
Pressure	BARG	0,030	0,030
Flowrate	KG-MOL/HR	199,914	100,000
Composition			
H2O		0,500	0,176
CO2		0,000	0,000
CELULOSA		0,500	0,000
Glucose		0,000	0,649
OXYGEN		0,000	0,000
H2SO4		0,000	0,000
CELBIOSE		0,000	0,175

Figure 1: Hydrolysis unit flow diagram

The relative error of the calculated yield by the model is less than 1% respect to the experimental study. The model is accurate to evaluate the effect of the pH and temperature on the enzymatic hydrolysis. The result of this sensitivity analysis for pH variation is shown in figure 2.

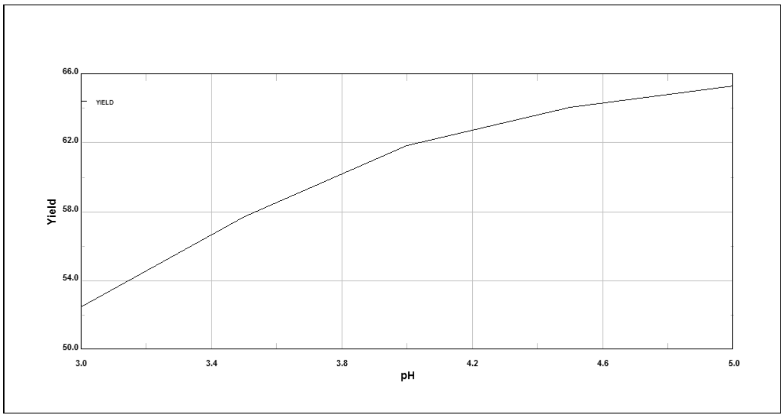


Figure 2: Glucose Yield versus pH at 40 °C

3. Fermentation unit

The organisms of interest to industrial operations in fermentation of ethanol are *Saccharomyces cerevisiae, S. uvarum, Schizosaccharomyces pombe,* and *Kluyueromyces sp*. yeast, under anaerobic conditions, metabolize glucose to ethanol. The yield in practical fermentation usually doesn't exceed 90 – 95%. The use of bacteria for fermentation like Z. mobile has disadvantages, such as: inability to convert complex carbohydrate polymers, a considerable amount of byproducts and formation of extracellular levan polymer.

The kinetic parameters of glucose fermentation by Saccharomyces uvarum yeast are fully documented by Najafpour et. al (2002). Multiple correlations can be obtained with these data; a simple correlation between the glucose and ethanol concentration is shown as follows:

Ethanol concentration (g/l) = -0.8871*Glucose concentration (g/l) + 5.7656 (5)

The simplified reaction set is described as follows:

Glucose → 2 Ethanol + 2 Carbon dioxide
$C_6H_{12}O_6 \rightarrow 2C_2H_6O + 2CO_2$ (6)

Glucose + 2 Water → 2 Carbon dioxide + 4 Methanol
$C_6H_{12}O_6 + 2H_2O \rightarrow 2CO_2 + 4CH_4O$ (7)

Glucose → 2 Carbon dioxide + Methanol + Propanol
$C_6H_{12}O_6 \rightarrow 2CO_2 + CH_4O + C_3H_8O$ (8)

A conversion reactor was simulated in Pro II, supported by a FORTRAN subroutine where the glucose concentration, ethanol concentration and ethanol yield data and corresponding correlations are included.

The relative error of the calculated yield by the model is less than 1.3% respect to the experimental study. The model is accurate to estimate the ethanol yield in glucose fermentation by Saccharomyces uvarum.

3.1 Separation unit

Ethanol and other alcohols are separated from the water in a 50 trays distillation column. The specifications of the column include: maximum recovery of alcohols in overhead and process water recovery from the bottom. Initial estimates of net vapour and liquid rate per tray were included as input of the simulation, thus a simplified temperature profile to accelerate the convergence. The algorithm used in this sub-section for the vapour-liquid-liquid calculated phases is Chemdist.

The Pro II flow diagram of the fermentation unit is shown in figure 3.

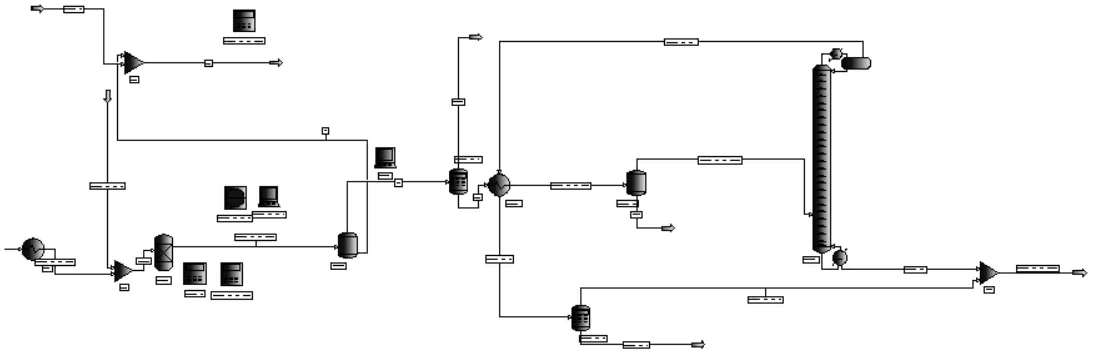


Figure 3: Fermentation unit flow diagram

4. Hydrogen unit

Akande et. al (2006) performed a kinetic modelling of the production of hydrogen by the catalytic reforming of ethanol over a 15%-Ni/Al_2O_3 catalyst prepared by the co-precipitation technique. The model is of the form $-r_A = (2.08 \times 10^3 e^{-4430/RT} N_A)/[1 + 3.83 \times 10^7 N_A]^2$.
Ethanol reforming reaction can be represented by:

Ethanol + 3 Water $\rightarrow$ 2 Carbon dioxide + 6 Hydrogen
$C_2H_6O + 3H_2O \rightarrow 2CO_2 + 6H_2$ (9)

Some of the secondary reactions of the ethanol reforming are the ethanol decomposition to methane, ethanol dehydration, etc.
Main reactions and a kinetic procedure based on the model of Akande et. al (2006) were included in a conversion reactor in Pro II. A yield of 65.9 % was obtained by simulation. The relative error of the calculated yield by the model is less than 0.5% respect to the experimental study. The model is accurate to estimate the hydrogen yield by ethanol reforming.
The Pro II flow diagram of the ethanol reforming unit is shown in figure 4.

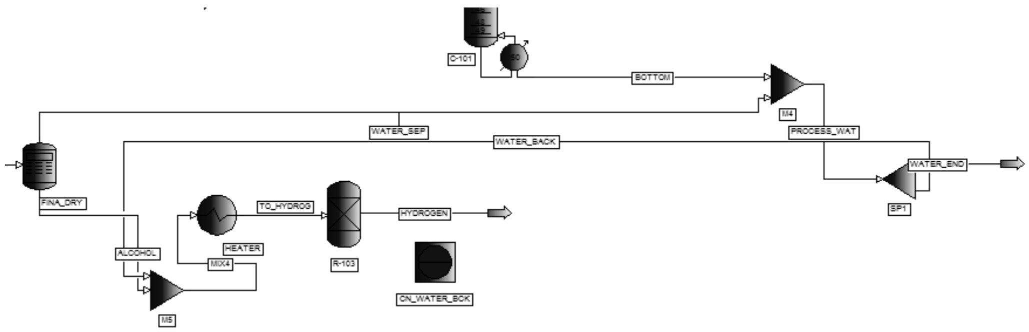


Figure 4: Ethanol reforming unit

A controller is simulated to control the water process stream back to the inlet reactor to ensure the required conversion.
Grayson - Streed was chosen as thermodynamic method for this section.

5. Integrated process

An integrated model to obtain hydrogen from Algae is shown in the figure 5.

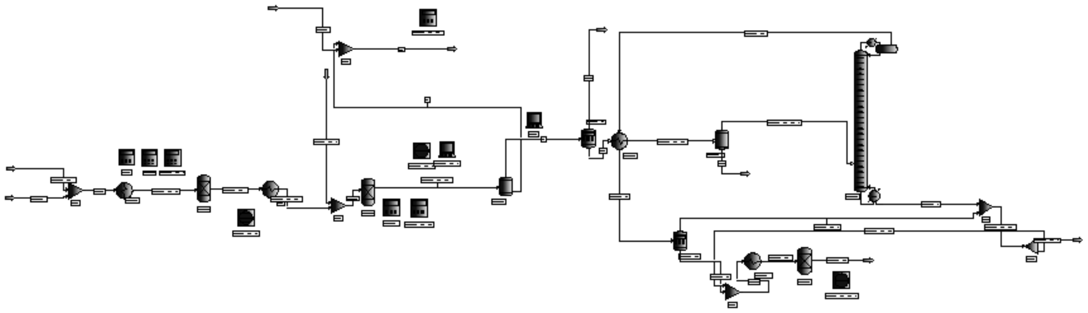


Figure 5: Simulation model of a Hydrogen production process from Algae

A summary of the results are shown in table 2.

Table 2: Simulation results

Stream	**Alcohol**
Temperature, °C	40 / >200
Pressure, barg	0.02
pH	4.8
Molar composition, fraction	
Ethanol	0.86
Methanol	0.01
Propanol	0.04
Molar ratios	
Cellulose / Ethanol	0.3
Water / Hydrogen	21.7
Water / Ethanol	17.0

Recycling options are shown for heat integration in the separation unit and water feed for the hydrolysis unit. An optimizer utility is included to maximize the ethanol yield in the fermentation reactor by obtaining the optimal water / glucose ratio.

Sensitivity studies and process conditions evaluation can be performed by using this model in order to minimize the energy consumption of utilities, maximizing yields by improving or updating kinetic models, etc.

6. Conclusions and recommendations

A simulation model of a hydrogen production process from algae was developed with Pro II. This model allows users to analyze the design and optimize the process using case studies to evaluate heat integration, different operating conditions and schemes, different compositions, etc. Integration with FORTRAN – use models, calculator utilities, controllers and optimizer unit automates these case studies. Overall operating and capital costs can be potentially minimized with this model.

More detailed and updated kinetics model and parameters must be included in this model to improve the reaction sections. Other potential areas to be optimized are the separation unit, recycling and splitting streams (ratios), etc.

References

Akande A., Aboudheir A., Idem R., Dalai A., 2006, Kinetic Modeling of Hydrogen Production by the Catalytic Reforming of Crude Ethanol over a Co-precipitated Ni-Al_2O_3 Catalyst in a Packed Bed Tubular Reactor, International Journal of Hydrogen Energy, 31, 1707 – 1715, DOI: 10.1016/j.ijhydene.2006.01.001

Harun R., Danquah M., 2011, Enzymatic Hydrolysis of Microalgal Biomass for Bioethanol Production, Chemical Engineering Journal, 168, 1079 – 1084, DOI: 10.1016/j.cej.2011.01.088

Krishnan, M., Ho, N. Tsao, G., 1999, Fermentation Kinetics of Ethanol Production from Glucose and Xylose by Recombinant Saccharomyces, Applied Biochemistry and Biotechnology, 77-79.

Najafpour G., Kam L., 2002, Evaluation and Isolation of Ethanol Producer, 16th SOMChe, Malaysia.

Suma P., Srinivas K., Nazmul M., 2007, Modeling Intrinsic Kinetics of Enzymatic Cellulose Hydrolysis, Biotechnol. Prog., 23, 626 – 637, DOI: 10.1021/bp060322s