



INTERNATIONAL CONFERENCE ON

Chemical and Biochemical Engineering

20-22 July 2015
PARIS-FRANCE

ABSTRACTSBOOK

Kinetic-Based Model of Base-Catalyzed Biodiesel Production Process

L. M. S. Silva¹, N. S. Caetano^{1,2}

¹ Centro de Inovação em Engenharia e Tecnologia Industrial (CIETI), Instituto Superior de Engenharia do Porto (ISEP)
Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto – Portugal

² Laboratory for Process Engineering, Environment, Biotechnology and Energy (LEPABE), Faculty of Engineering of the
University of Porto (FEUP) – Portugal

Tlf: +351 228340500; email: lms@isep.ipp.pt

Introduction – Third generation biodiesel may prove to be a sustainable energy alternative to fossil fuels. Microalgae have a lot of potential as a biodiesel feedstock because of its high yield in lipids (up to 30, 50 or 70 wt% of dry biomass) [1]. Nevertheless, technical, economical and environmental problems have still to be solved before diesel from oil-producing microalgae becomes commercial.

The transesterification reaction of triglycerides (TG) is based on a three-reversible reaction mechanism where a fatty-acid group attached to the glycerol structure is reacted with methanol (MeOH) to form a fatty-acid methyl ester (FAME). The procedure involves the TG conversion to diglycerides, which are then converted to monoglycerides, finally yielding glycerin associated to the production of one molecule of FAME in each step [2]. In this work free fatty acid content of oil and TG saponification (a side reaction) rate were considered negligible and the reaction rate is chemically controlled with a second order law for all forward and reverse steps. Because it has been proved that the fatty acid composition of vegetable oils and their biodiesel fuels is identical [3], it may be concluded that different fatty acid chains of TG have an identical reactivity towards methanol. So, a pure triolein feed oil was used in the simulation where the kinetic parameters were taken from Nouredini and Zhu. [4].

Model description - The ASPEN Plus chemical process simulator was used to model the biodiesel process. In Figure 1 a flow diagram of the process is presented. Due to immiscible liquid phases formed in the reaction step, the NRTL-RK property prediction method was chosen. Concerning the water wash unit (EXTRACT), UNIFAC-LLE model was used following a recommendation of Kuramochi et al. [5]. The transesterification reaction was conducted in a stirred tank reactor (CSTREACT) with a residence time of an hour at 4 bar and 60 °C and the excess methanol was recycled back to the MIXER block. For this purpose a design specification computes the MeOH fresh flowrate necessary to fulfill a MeOH/TG molar ratio on the reactor feed stream of 6. A methanol mass recovery of 99% on the top of the methanol separation column (COLUMN1) is imposed with 6 equilibrium stages and a reflux ratio of 2 by manipulating the distillate flowrate (TOPUMP3).

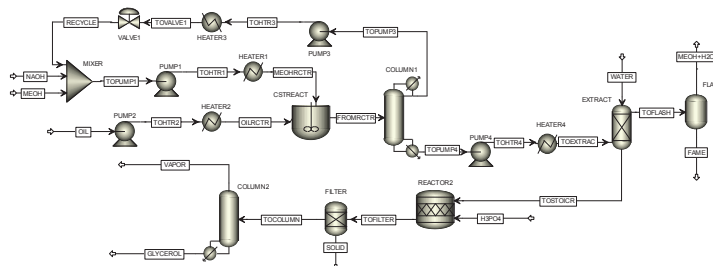


Figure 1 – Aspen Plus flowsheet of the biodiesel from microalgae production process

Results and Discussion – For a 1.6 m³ reactor volume, simulation shows that FAME yield is 77%. A heat duty of about -67 kW is released from the reactor for a 1000 kg/hr of processed oil. A 10 equilibrium stages liquid-liquid column simulates the water wash unit in which 100% of glycerol is recovered in the extract phase (TOSTOICR) with a water feed of 50 kg/h while almost the entire FAME and glycerides present in the feed stream (TOEXTRACT) are recovered in the raffinate phase (TOFLASH).

Conclusions – Kinetic model used in this work reveals a FAME yield slightly less than experimental data. The activity coefficient models NRTL and UNIFAC-LL predict well the phase equilibria on the separation and purification units. This flowsheet is a valuable framework to test different operational conditions and implement sensitivity analysis, in order to devise which steps should be the object of further research.

References

- [1] Mata, T.M.; Martins, A.A.; Caetano, N.S. Microalgae for biodiesel production and other applications: a review. *Renewable Sustainable Energy Rev.* **2010**, *14*, 217–232.
- [2] Freedman, B.; Butterfield, R. O.; Pryde, E. H. Transesterification kinetics of soybean oil. *J. Am. Oil Chem. Soc.* **1986**, *63*, 1375–1380.
- [3] Wu, M.; Wu, G.; Han, Y.; Zhang, P. Fatty acid composition of six edible vegetable oils and their biodiesel fuels. *China Oils and Fats* **2003**, *28*(12), 65–67.
- [4] Nouredini, H.; Zhu, D. Kinetics of transesterification of soybean oil. *J. Am. Oil Chem. Soc.* **1997**, *74*, 1457–1463.
- [5] Kuramochi, H.; Maeda, K.; Kato, S.; Osako, M.; Nakamura, K.; Sakai, S. Application of UNIFAC models for prediction of vapor-liquid equilibria and liquid-liquid equilibria relevant to separation and purification processes of crude biodiesel fuel. *Fuel* **2009**, *88*, 1472–1477.