WEENTECH Proceedings in Energy

ICEEE 2016

16th -18th August 2016
Heriot-Watt University, Edinburgh
United Kingdom

Volume 3: International Conference on Energy, Environment and Economics, September 2016

ISSN: 2059-2353
ISBN: 978-9932795-2-2

www.weentech.co.uk

Edited by:
Dr. Renu Singh, IARI, New Delhi, India
Dr. Anil Kumar, PSU, Thailand
Published by World Energy and Environment Technology Ltd.

CFD modelling and simulation of biodiesel production in an ultrasonic reactor

João Paulo S. Andrade, Leandro S. Oliveira, Adriana S. Franca*

Department of Mechanical Engineering, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brazil

Corresponding author's mail: adriana@demec.ufmg.br

Abstract

Biodiesel production at industrial level is usually based on the transesterification of vegetable oils with an alcohol and homogeneous catalysts in mechanically stirred batch reactors. Among the most recent advances in transesterification processes, the use of ultrasound stands out, given the effective improvements to the process, both in terms of degrees of conversions and of reducing reaction time and energy consumption. Thus, in the present study, a CFD simulation of transesterification in an ultrasound-assisted reaction was performed. Reaction rates were evaluated by solving a set of differential equations describing the reaction kinetics, with coefficients being based on non-linear regression of second-order models based on experimental data. The effect of cavitation was incorporated by a pressure model. The obtained simulation results were in agreement with the experimental data, and the effects of increase in ester yield and decrease in reaction time observed in previously developed experimental studies were confirmed, with a consequent reduction in energy savings.

Keywords: computational fluid dynamics; biodiesel; ultrasound.

1. Introduction

Vegetable oils are usually converted to biodiesel by a transesterification reaction, in which a short chain alcohol, e.g., methanol or ethanol, reacts with the triglycerides molecules in the oil, producing glycerin and biodiesel (alkyl esters of fatty acids) [1]. Methanol is the most commonly employed alcohol for worldwide biodiesel production, however, given that ethanol is obtained from plant sugars while methanol is commonly produced from natural gas or petroleum, ethanolysis provides a more sustainable pathway for this biofuel production in comparison to methanolysis [1].

Ultrasound irradiation has been known to intensify chemical reactions due to cavitational effects, either by generating free radicals or intensifying local turbulence [2]. In the case of biodiesel production, studies have demonstrated that enhancements in reaction rate can be associated to physical effects, in which cavitational microbubbles are formed, grow up to a critical size while being advected in the bulk flow and violently collapse, generating intense local microturbulence and creating an intimate mixing of the immiscible reactants [2,3]. Recent studies have demonstrated the potential of sonochemical or ultrasound-based reactors for biodiesel synthesis. General conclusions were that lower frequencies promoted shorter reaction times whereas higher frequencies led to higher ester yields, and that power input needed to be optimized according to frequency [3-6].

In a recent study, we developed and tested a biodiesel production unit with ultrasound-irradiated circulation flow reactor for vegetable oils transesterification [2]. This reactor allowed for increases in ester yield, decreases in reaction times, reduction in reagent consumption and consequent energy savings in regard to the conditions for a conventional batch stirred reactor. Nonetheless, further investigations on how this specific reactor works are necessary for improving design and operation parameters. In that regard, numerical methods (computational fluid dynamics, CFD) can be quite helpful. Thus, in the present study, a CFD simulation of transesterification in an ultrasound-assisted reaction was performed. Simulation results were compared to experimental data as well as to simulation results obtained for a conventional transesterification reaction in stirred tank reactor

2. Methodology

Several studies have dealt with the description of transesterification reaction kinetics for biodiesel production and conclusions on order of reaction and estimates of reaction rate constants vary widely [7-9]. The study by Komers et al. [3] provided a detailed reaction kinetics model based on careful examination of chemical mechanisms and competing saponification reactions. Although it is based on the methanolysis of rapeseed oil using potassium hydroxide as catalyst, it is deemed able to describe transesterification reactions of any vegetable oil with any alkyl alcohol and any base catalyst [1,9] and thus was selected for use in this study. Kinetic coefficients were based on model proposed by Ahiekpor & Kuwornoo [10], and evaluated by non-linear

regression of experimental data according to the following equations [1]:

$$q_E = \frac{k_E q_{E,t}^2}{1 + k_E q_{E,t} t} \quad (1)$$

$$q_{TG} = \frac{1}{q_{TG,0}^{-1} + k_{TG} t} \quad (2)$$

$$q_{ROH} = \frac{1}{q_{ROH,0}^{-1} + k_{ROH} t} \quad (3)$$

where ROH represents the alcohol,TG the triglyceride, and E the ester mixture (biodiesel), t is the time and q is concentration. Once the coefficients were estimated, the set of 7 non-linear ordinary differential equations comprising the Komers model [3] was solved and results were then updated to the CFD model.

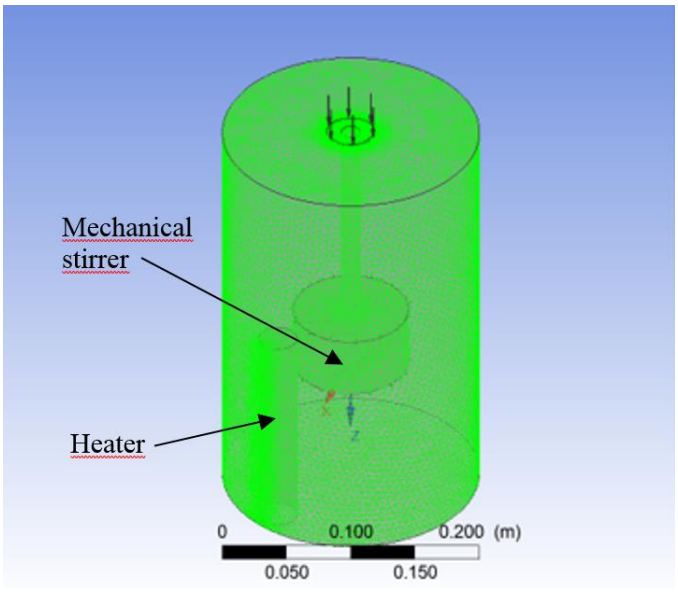
The CFD simulations employed the CFX 12.1 code (ANSYS, Inc., USA), and both the stirred tank and ultrasonic reactors were evalutated. The corresponding discretization domains are shown in Fig 1. The k-Epsilon turbulence model was employed, since it is deemed suitable for a wide range of simulations, with relative low computational demand.

In order to take into account the effect of cavitation in the case of the the ultrasonic reactor, the pressure field was calculated according to the Helmholtz equation (4), with the effect of cavitation bubbles evaluated as described in equation (5) [11]:

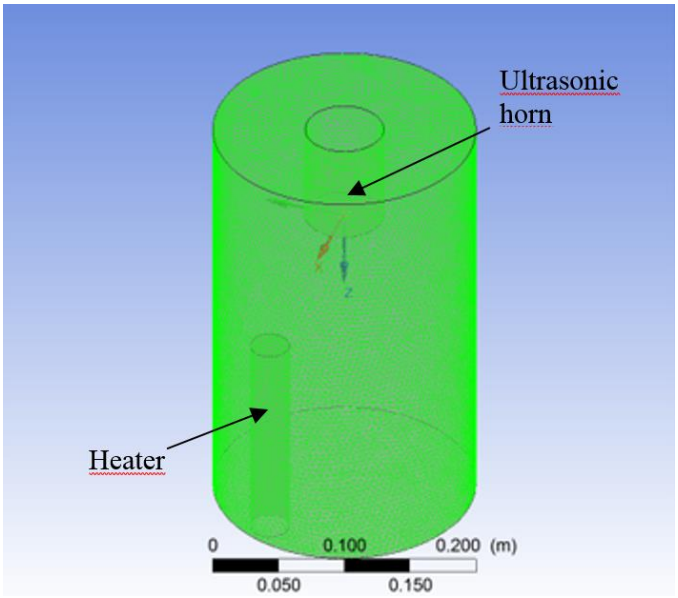
$$\nabla^2 P + k_c^2 \cdot P = 0 \quad (4)$$

$$k_c^2 = \frac{\omega^2}{c^2}\left(1 + \left(4\frac{\pi c^2 n_b R_0}{\omega_0^2 - \omega^2 + 2ib}\right)\right) \quad (5)$$

where $\omega = 2\pi f$ is the angular velocity, c is the sound velocity, n_b represents the number of bubbles per unit volume, R_0 is the average bubble radius, b is a damping effect parameter, and ω_o is the ressonance frequency. These equations were solved employing the software *COMSOL Multiphysics 5.2* and the obtained pressure field was then interpolated and incorporated to the CFD model. Simulation parameters were the following: impeller rotational speed = 120 rpm; inlet flow rate = 0.5 kg/s); alcohol-to-oil molar ratio = 6:1, catalyst-to-oil mass ratio = 1.5%.



(a)



(b)

Fig. 1 Representation of the discretization domains: (a) stirred tank; (b) ultrasonic reactor (ANSYS, Inc.).

3. Results and discussion

The calculated average concentration profiles obtained for the stirred tank reactor are shown in Fig. 2. Ethanol and oil concentrations decrease due to the transesterification reactions. Diglycerides and monoglycerides presented an initial peak of concentrations, due to their formation from triglycerides, and a subsequent decrease, as they were consumed to form glycerol. There was good agreement

between simulation and experimental results. Results are consistent with published literature data [1].

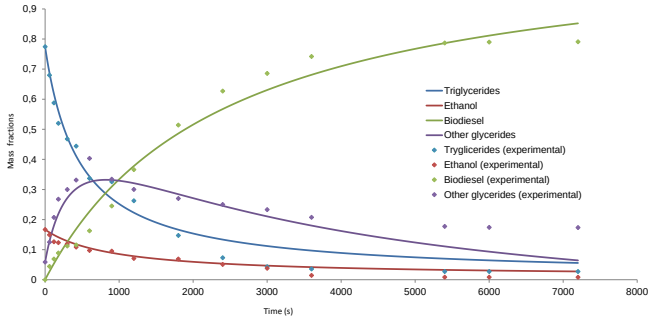


Fig. 2. Average mass fractions versus time (in seconds): experimental vs. simulated results for the stirred tank reactor.

Results obtained for the effect of ultrasound on the pressure field are presented in Fig. 3. High and low presure regions, characteristic of the ultrasound waves can be readily perceived. A high pressure field is observed just below the horn emitting surface. High ultrasonic power induces cavitation bubbles and thus the ultrasonic pressure is attenuated rapidly in a short distance from the horn emitting surface. Ultrasonic waves are diffracted and also strongly absorbed by the bubbles. Close to the reactor bottom surface, a high pressure field is formed due to superposition of the ultrasound propagation wave and the reflective wave.

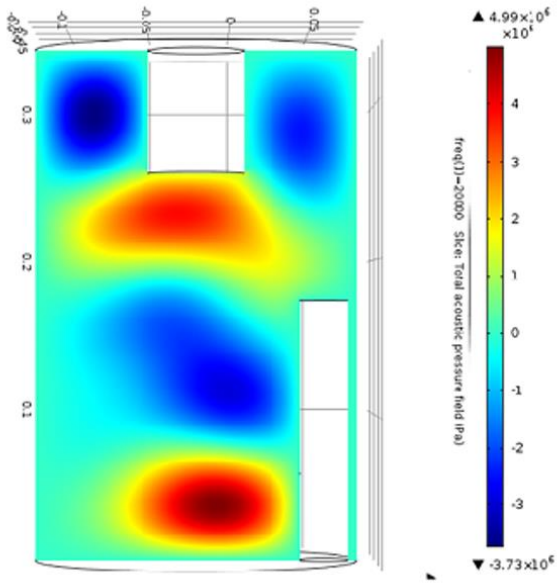


Fig. 3. Simulated pressure distribution in the ultrasound reactor.

During ultrasound irradiation, cavitation bubbles are formed and expand under the influence of the ultrasound wave, with evaporation of the low boiling reactant at the gas-liquid interface (bubble wall), and, during the subsequent compression phase, condensation of the reactant vapor occurs at the bubble interface. Prior to condensation, the reactant vapor molecules need to diffuse toward the gas-liquid interface. At the final moments of bubble collapse, the dynamics of the bubble motion is far more rapid than the diffusion of vapor. Thus, not all of the reactant vapor that enters the bubble during expansion escapes during compression. The entrapped vapor molecules are subjected to extremely high temperatures and pressure reached during bubble collapse and dissociate into reactive species With fragmentation of the bubble during compression, these species are released into the bulk medium where they induce/accelerate chemical reactions [3], promoting a significant decrease in reaction time and increase in biodiesel formation, as can be observed in Fig. 4, in which the experimental and numerical results are compared for both ultrasound-assisted and conventional transesterification reactions. With ultrasound, biodiesel conversion was increased up to approximately 87% in 3 min and 94% in 60 min. There is also very good agreement between experimental and simulation results, confirming the applicability of the developed model.

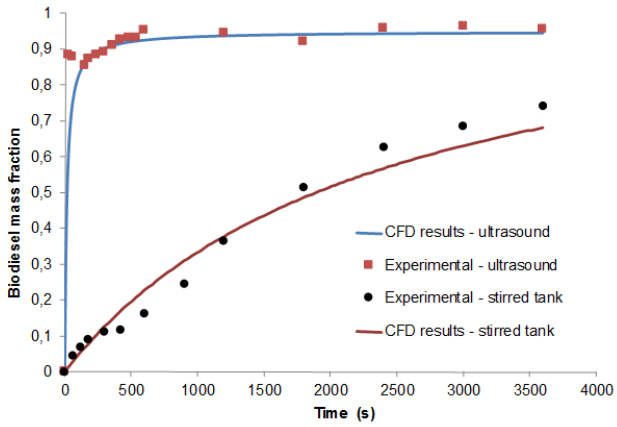


Fig. 4. Biodiesel conversion: comparison of simulation and experimental results obtained for the ultrasound and stirred tank reactors.

4. Conclusions

Homogeneous catalysis for the transesterification reaction of soybean oil with ethanol in an ultrasound-irradiated reactor was investigated by numerical simulation with CFD. The pressure field was calculated separately, using Helmholtz equation, and incorporated into the CFD calculations, together with reaction kinetics constants generated from experimental data involving ultrasound irradiation. It was demonstrated that ultrasound irradiation greatly enhances the reaction rates when

compared to mechanical stirring in conventional processes in stirred tank reactors. Simulation results agreed well with experimental data.

References

[1] Poley, I., Oliveira, L.S. (2013) CFD Modeling and Simulation of Transesterification Reactions of Vegetable Oils with an Alcohol in Baffled Stirred Tank Reactors. Applied Mechanics and Materials, 390, 86-90.

[2] Brasil, Alex N., Oliveira, L.S., Franca, A.S. (2015) Circulation flow reactor with ultrasound irradiation for the transesterification of vegetable oils. Renewable Energy, 83, 1059-1065.

[3] Kalva, A., Sivasankar, T., Moholka,V. S. (2009) Physical mechanism of ultrasound-assisted synthesis of biodiesel. Ind. Eng. Chem. Res., 48, 534–544.

[4] Mahamuni, N.N., Adewuyi, Y.G. (2009) Optimization of the synthesis of biodiesel via ultrasound-enhanced base-catalyzed transesterification of soybean oil using a multifrequency ultrasonic reactor. Energ. Fuel, 23, 2757–2766.

[5] Cintas, P., Mantegna, S., Gaudino, E.C., Cravotto, G. (2010) A new pilot flow reactor for high-intensity ultrasound irradiation. Application to the synthesis of biodiesel. Ultrasonics Sonochemistry, 17, 985-989.

[6] Borges, M.E., Díaz, L. (2012) Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: a review. Renew. Sustain. Energy Rev., 16, 2839-2849

[7] Freedman, B., Pryde, E.H., Mounts, T.L. (1984) Variables affecting the yields of fatty esters from transesterified vegetable oils. J. Am. Oil Chem. Soc., 10, 1638-1643.

[8] Bikou, E., Louloudi, A., Papayannakos, N. (1999) The effect of water on the transesterification kinetics of cotton seed oil with ethanol, Chemical Engineering Technology, 22, 70-75.

[9] Komers, K., Skopal, F., Stloukal, R., Machek, J. (2002) Kinetics and mechanism of the KOH - catalyzed methanolysis of rapeseed oil for biodiesel production, European Journal of Lipid Science and Technology, 11, 728-737.

[10] Ahiekpor, J. C., Kuwornoo, D. K. (2010) Kinetics of palm kernel oil and ethanol transesterification. International Journal of Energy and Environment, 1, 1097-1108.

[11] Hussain, M. N., Samad, T., Daqaq, M., Janajreh, I. (2016) Numerical modelling of sonicated, continuous transesterification and evaluation of reaction kinetics for optimizing biodiesel reactor design. International Journal of Thermal & Environmental Engineering, 11, 79-86.

Acknowledgement

Authors acknowledge financial support from CAPES, CNPq and FAPEMIG.

Commonwealth Energy and Sustainable Development Network (CESD-Net)

CESD-Net is a major global initiative in energy and sustainable development. The objective of network is to promote energy and sustainable development in commonwealth countries.
Focussing on Multidisciplinary Research, Promoting Future Low Carbon Innovations, Transferring Knowledge and Stimulating Networking among Stakeholders to Ensure the UK Achieves World Leading Status in Energy and Sustainable Development. https://www.weentech.co.uk/cesd-net/

The 1st International Conference on Energy, Environment and Economics (ICEEE 2016) was held at Heriot-Watt University, Edinburgh, EH14 4AS, UK, 16-18 August 2016. ICEEE2016 focused on energy, environment and economics of energy systems and their applications. More than fifty eight delegates from 31 countries with diverse expertise ranging from energy economics, solar thermal, water engineering, automotive, energy, economics and policy, sustainable development, bio fuels, Nano technologies, climate change, life cycle analysis etc. made conference true to its name and completely international. During conference total 51 oral presentations and six posters were shared between delegates. The presentations showed the depth and breadth of research across different research areas ranging from diverse background. ICEEE2016 aimed:

- To identify and share experiences, challenges and technical expertise on how to tackle growing energy use and greenhouse gas emissions and how to promote sustainability and economical, cost effective energy efficiency measures.

In total 11 technical sessions and two invited talks both from academia and industry provided insight into the recent development on the proposed theme of the conference. Preparation, organisation and delivery of the conference started from July 2015 and further co-ordinated by vibrant team of Conference Centre, Heriot Watt University. Conference organisers would like to acknowledge support from the sponsors particularly World Scientific Publication ltd and its team members for the delivery of the conference. Organisers are also thankful to all reviewers who contributed during peer review process and their contributions are well appreciated. At the end and during vote of thanks following awards have been announced and we would like to congratulate all well deserving delegates.

- Best Paper –Academia: Amela Ajanovic, EEG, TU Vienna, Austria
- Best Paper – Student : Christian Jenne,University of Duisburg-Essen, Germany
- Best Poster – Student: Yoann Guinard, University of New South Wales, Sydney, Australia
- Best Poster – Academia: E. Salleh, Universiti Kebangsaan Malaysia, Malaysia
- Active Participation Award - Yoann Guinard, University of New South Wales, Sydney, Australia

At the end we would like to extend our gratitude to all of you for your participation and hopefully welcome you again during ICEEE2017.

Editors:
Dr. Singh is Senior Scientist at Indian Agricultural Research Institute, New Delhi, India. Her area of expertise are bio energy and bio fuels, environmental engineering, carbon accounting and renewable energy integration for rural development.
Dr. Kumar is visiting faculty at Prince of Songkla University, Thailand. He have 16 years of research and teaching experience in the field of solar energy, drying and energy efficiency.

WEENTECH Proceedings in Energy- International Conference on Energy, Environment and Economics, September 2016
Edited by:
Dr. Renu Singh, IARI, New Delhi, India
Dr. Anil Kumar, PSU, Thailand
Publisher: World Energy and Environment Technology Ltd., Coventry, United Kingdom
Publication date: 12 September 2016
ISSN: 2059-2353
ISBN: 978-9932795-2-2
To purchase e-book online visit www.weentech.co.uk or email conference@weentech.co.uk