Control Strategies for a Biodiesel Process by Reactive Absorption

Costin Sorin Bildea[1], Anton Alexandru Kiss*[2]

[1]University POLITEHNICA of Bucharest, Dpt. of Chemical Engineering, Romania
[2]AkzoNobel – Research, Development and Innovation
Velperweg 76, 6824 BM, Arnhem, Netherlands
tony.kiss@akzonobel.com

Integrated biodiesel processes based on reactive separations powered by solid acid/base catalysts are available nowadays, offering significant advantages such as minimal capital investment and operating costs, as well as no catalyst-related waste streams and no soap formation. However, the controllability of the process is just as important as the capital and operating savings. In such processes the small number of degrees of freedom is a drawback which makes it difficult to set the reactants feed ratio correctly and consequently to avoid impurities in the products. This work considers the process control of biodiesel production by reactive absorption, the main result being an efficient control structure that ensures the excess of methanol that is necessary for the total conversion of the fatty acids and for prevention of the difficult separations is fulfilled, while maintaining high purity of the water by-product. Rigorous simulations were performed – using Aspen Plus and Aspen Dynamics as efficient computer aided process engineering tools – for a plant producing 10 ktpy biodiesel from waste vegetable oil with high free fatty acids content, using solid acids as green catalysts.

1. Introduction

Biodiesel is an alternative fuel produced from green sources such as waste vegetable oils, animal fat or even frying-oils from the food industry (Kulkarni et al., 2006). Such waste raw materials can contain a substantial amount of free fatty acids (FFA), up to 100%. At present, employing waste and non-edible raw materials is mandatory to comply with the ecological and ethical requirements for biofuels. Nowadays, modern plants replaced the homogeneous catalysts with solid bases or acids, thus eliminating the salt waste streams and simplifying the downstream processing steps. Moreover, integrated processes based on reactive distillation (Kiss et al., 2006a; 2006b; 2008; Kiss, 2009; Dimian et al., 2009) or reactive absorption (Kiss, 2009) are now available, offering significant advantages such as minimal capital investment and operating costs, as well as no catalyst-related waste streams and no soap formation.

This work considers the process control of biodiesel production by reactive absorption. The results are given for a plant producing 10 ktpy biodiesel from waste vegetable oil with high free fatty acids content (up to 100 %), using solid acids as green catalysts.

Compared to reactive distillation, the absence of a reboiler and a condenser makes reactive absorption a simpler process. However, the drawback is the small number of degrees of freedom that makes it difficult to set the reactants feed ratio correctly and consequently to avoid impurities in the products. In this work, Aspen Plus and Aspen Dynamics were used to perform rigorous simulations for testing various control structures. An efficient control structure is presented, that ensures the ratio of reactants which guarantees the total conversion of the fatty acids therefore preventing difficult separations, and keeping high the purity of water by-product.
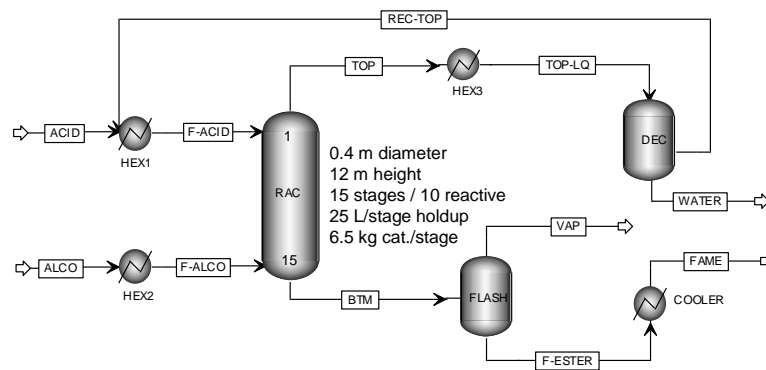

Figure 1: Flowsheet of a biodiesel production process by reactive absorption.

2. Process Description

Figure 1 presents the flowsheet of a biodiesel production process based on a reactive absorption column. The production rate is 10 ktpy fatty acid methyl esters (FAME) manufactured from 100 % fatty acids and methanol. The fatty components were lumped into one fatty acid and its fatty ester. Lauric acid/ester was selected as lumped component due to the availability of experimental results, kinetics and VLLE parameters for this system (Kiss, 2009). The column has a diameter of 0.4 m. There are 15 theoretical stages with a liquid holdup of 18 L. Stages 3 to 12 are reactive, the catalyst loading being 6.5 kg. The fatty acid is pre-heated then fed as hot liquid in the top of the reactive column while a stoichiometric amount of alcohol is injected as vapor into the bottom of the column, thus creating a counter-current flow regime over the reactive zone.

Table 1. Summary of the main process streams

	ACID	ALCO	F-ACID	F-ALCO	WATER	FAME
Mole flowrate, kmol/h	5.824	5.876	5.824	5.876	5.827	5.873
Mass flow rate, kg/h	1166.73	188.30	1166.73	188.30	105.05	1249.98
Temperature, ºC	20	20	160	65.44	51.77	30
Purity, %wt	100	100	100	100	99.9	99.9

Water by-product is removed as top vapor, then condensed and separated in a decanter from which the fatty acids are recycled back to the column while water by-product is

recovered at high purity. The fatty esters are delivered as high purity bottom product of the RA column. The hot product is flashed first to remove the remaining methanol, and then it is cooled down and stored. Table 1 presents the mass balance.

3. Problem Statement

Reactive absorption offers indeed significant advantages such as minimal capital investment and operating costs, as well as no catalyst-related waste streams and no soap formation. However, the controllability of the process is just as important as the capital and operating savings. In processes based on reactive distillation or absorption, feeding the reactants according to their stoichiometric ratio is essential to achieve high products purity. Thus, the fatty acid is completely converted to fatty esters when there is an excess of methanol, but the excess of methanol becomes an impurity in the top stream and thereafter in the water by-product. On the contrary, when there is an excess of fatty acids, the purity of water by-product remains high, but the conversion of fatty acids is incomplete hence it cannot be removed from the final product by simple flashing. Since the separation of fatty acids from fatty esters is more difficult than the separation of fatty acids from water, this situation should be avoided. This constraint must be fulfilled not only during the normal operation, but also during the transitory regimes arising due to planned production rate changes or unplanned disturbances.

4. Results and Discussion

Figure 2 (left) shows the first control structure tested (CS-1a). The flow rate of fresh acid is fixed and determines the production rate. The flow rate controller on alcohol stream receives its setpoint as the measured column-inlet acid flow multiplied by the desired alcohol / acid ratio.
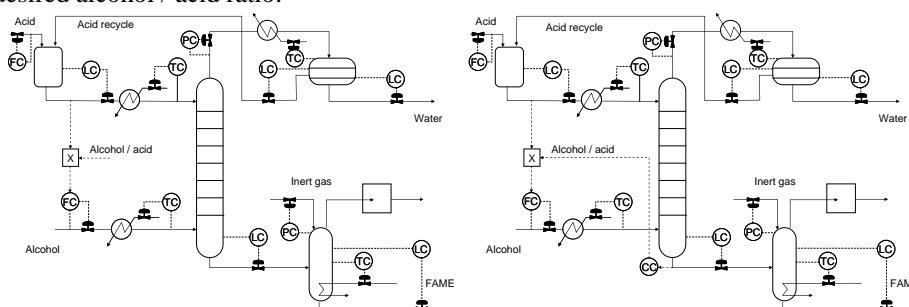

Figure 2: Control structure CS-1a (left) and CS-1b (right)

The sensitivity analysis (Figure 3) shows that the purity depends on the ratio alcohol / acid and that there is an optimum value for which both purities are high (Figure 3, left). The optimal ratio versus temperature is shown in Figure 3, right. Remarkably, this optimal value appears to be independent of the reaction rate. Nevertheless, the challenge remains to find the variables to be measured (and controlled) such that the alcohol/acid and temperature are set at the best values. Figure 4 proves that modifying the fresh acid flow rate is a direct way for changing the production rate. The dynamics of the acid recycle is slow. However, the purity of FAME decreases and the main impurity is the

fatty acid, which is unacceptable. It should be stressed that in control structure CS-1a any inaccuracy of measuring the acid flow rate will be reflected by deviation of the alcohol / acid ratio from the required value and therefore by impure products.
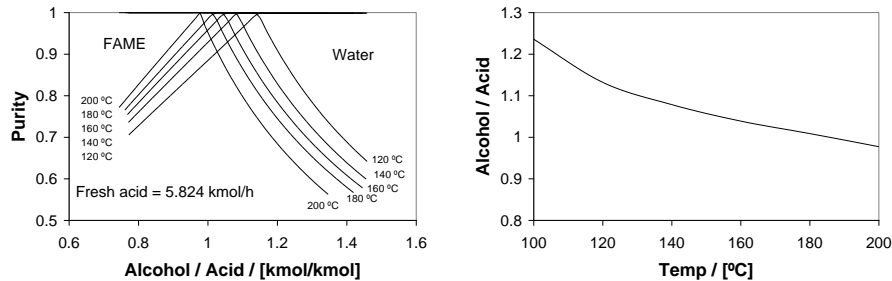

Figure 3: CS-1a – purity vs reactants ratio at various temperatures of the column-inlet acid feed (left); Optimum ratio vs temperature of the column-inlet acid feed (right)
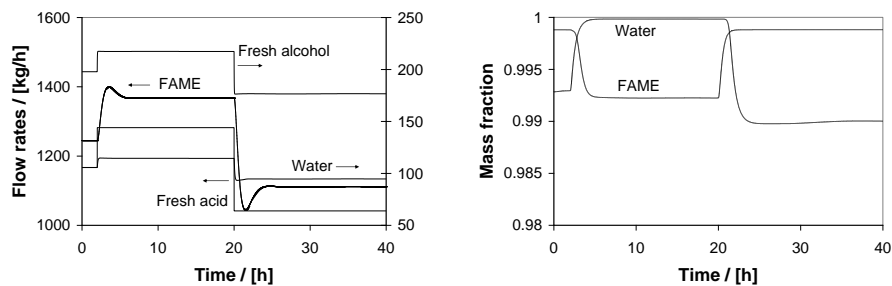

Figure 4: Dynamic simulation results for CS-1a (at t=2 h, fresh acid rate is increased by 10 %, from 5.824 to 6.4 kmol/h, while at t =20 h, it is decreased by 10 %)

For this reason and considering FAME as the main product, the control structure CS-1b (Figure 2, right) adds a concentration controller that measures the concentration of acid in the bottom and adjust the ratio alcohol / acid. Figure 5 presents the dynamic simulation results for control structure CS-1b. At t = 2h, the fresh acid rate is increased to 110% of the nominal value (from 5.824 kmol/h to 6.4 kmol/h). At t=20 h, is decreased to 90% of the nominal value (from 6.4 kmol/h to 5.2 kmol/h). The production rate changes properly, but the water purity is too low during large production times.
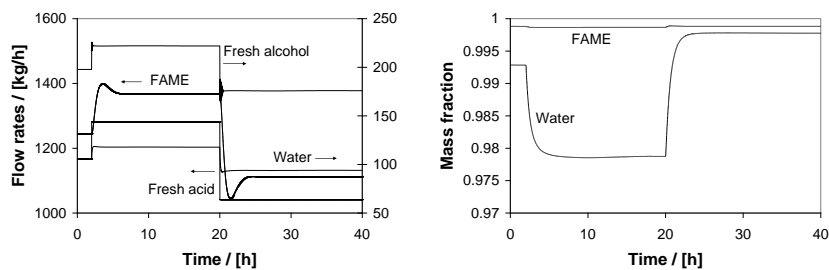

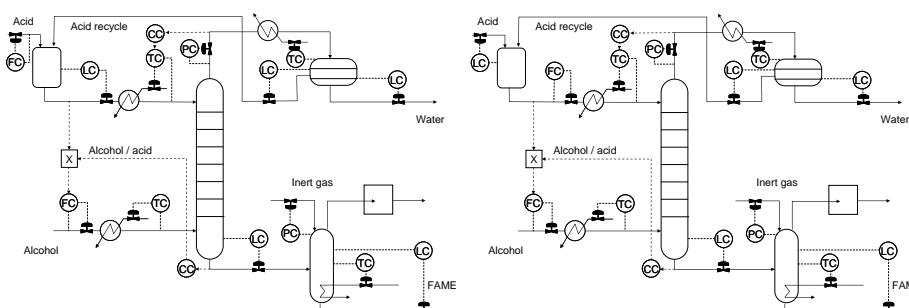*Figure 5: Dynamic simulation results for control structure CS-1b*

Figure 6: Control structure CS-1c (left) and CS-2 (right)

The control structure CS-1c (Figure 6, left) adds another concentration controller. The setpoint of the column-inlet acid temperature is manipulated, in a cascade fashion, by a concentration controller which prevents that an excessive amount of methanol arrives in the top of the column by increasing the temperature and thus the reaction rate in the upper part of the column. Figure 7 shows the dynamic simulation results for the control structure CS-1c. The same scenario was tested as for CS-1b. The production rates are also properly changed and the purity is significantly better.

Kiss et al. (2007) discuss another option for controlling the inventory of reactants in the process, namely fixing the flow rate of the reactant at the inlet of the reactive section (stream F-ACID in Figure 1) and bringing the reactant into the process by means of a level controller. This control structure, denoted by CS-2, is illustrated in Figure 6, right.

When the level and control loops around the buffer tank were switched, dynamic simulation showed that the gain of both controllers in the concentration - temperature cascade at the top of the column had to be reduced in order to attain stable operation. Figures 7 and 8 show the results of dynamic simulation. The production rate can be easily manipulated (although in an indirect manner) by changing the setpoint of the acid-flow controller. The purity of the product streams remains high, although a slight degradation of the performance is observed.
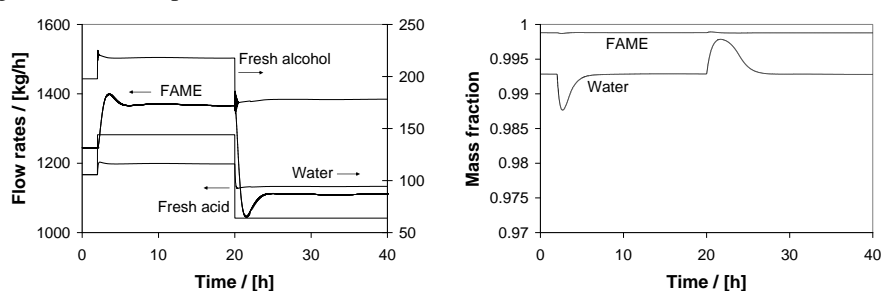

Figure 7: Dynamic simulation results for control structure CS-1c. Production rate changes are easily achieved and the products purity is maintained at high values
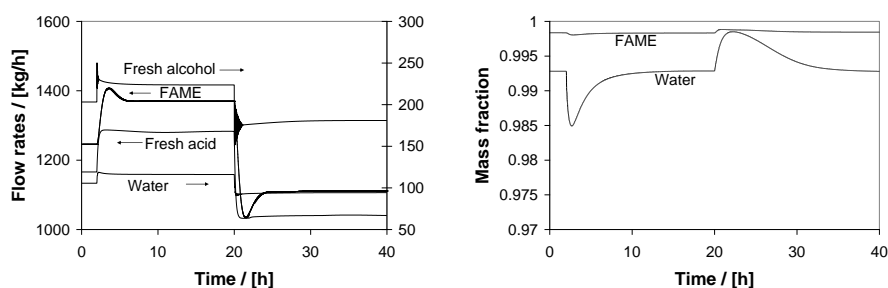
Figure 8: Dynamic simulation results for control structure CS-2. Production rate changes are easily achieved and the products purity is maintained at high values.

5. Conclusions

Integrated biodiesel processes based on reactive absorption have fewer degrees of freedom compared to reactive distillation. This makes it difficult to set the reactants feed ratio correctly and consequently avoiding impurities in the products. Aspen Plus and Aspen Dynamics can be successfully used as efficient computer aided process engineering tools to perform rigorous simulations for testing various control structures. The main result of this study is an efficient control structure that can ensure the stoichiometric ratio of reactants and fulfills the excess of methanol operating constraint that is sufficient for the total conversion of the fatty acids and for prevention of the difficult separations (e.g. fatty acid – fatty ester).

References

Dimian A. C., Bildea C. S., Omota F., and Kiss A. A., 2009, Innovative process for fatty acid esters by dual reactive distillation. Comput. Chem. Eng. 33, 743-750.

Kiss A. A., Dimian A. C., and Rothenberg G., 2006a, Solid acid catalysts for biodiesel production - Towards sustainable energy, Adv. Synt. Catal. 348, 75-81.

Kiss A. A., Rothenberg G., Dimian A. C. and Omota F., 2006b, The heterogeneous advantage: Biodiesel by catalytic reactive distillation, Top. Catal. 40, 141-150.

Kiss A. A., Bildea C. S., and Dimian A. C., 2007, Design and control of recycle systems by non-linear analysis, Comput. Chem. Eng. 31, 601-611.

Kiss A. A., Dimian A. C., and Rothenberg G., 2008, Biodiesel by reactive distillation powered by metal oxides, Eng. Fuels 22, 598-604.

Kiss A. A., 2009, Novel process for biodiesel by reactive absorption, Sep. Pur. Tech., 69 280-287.

Kulkarni M. G., and Dalai A. K., 2006, Waste Cooking Oil - An Economical Source for Biodiesel: A Review. Ind. Eng. Chem. Res. 45, 2901-2913.