

Cost minimization in noncatalytic biodiesel production plants

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Abstract

In the present study, we propose an optimization model for the minimization of capital and operating costs in a supercritical methanol biodiesel plant, considering alternative process schemes together with the convenience or not to use a cosolvent in the chemical reaction. A rigorous process simulation model, based on a group contribution equation of state is integrated with a successive quadratic programming algorithm to solve the nonlinear problem. Optimization results show that noncatalytic biodiesel production with supercritical methanol can be economically competitive with conventional catalyzed production.

Keywords: biodiesel, supercritical, transesterification, optimization.

1. Introduction

Biodiesel is comprised of esters of short chain alcohols made from renewable biological sources, such as vegetable oils, and it can be used as an alternative diesel fuel. Biodiesel can considerably reduce emissions, it is biodegradable and nontoxic. However, raw material and production costs are the main concern for commercialization of this product. Most of the conventional methods for biodiesel production use a basic or acid catalyst (Freedman et al., 1984, Fukuda et al., 2001, Lotero et al., 2005) and more recently, enzymes (Watanabe et al., 2000; Varma and Madras, 2007). While conventional catalytic transesterification of oils gives several byproducts, the single phase supercritical transesterification takes place at high pressures and temperature, not requiring the use of a catalyst. This feature makes the process not sensitive to water and free fatty acid content in the feed, avoiding the need for a pre-treatment step (Kusdiana and Saka, 2004; Cao et al., 2005) and additional separation steps downstream the reactor. Furthermore, free fatty acids in the feed oil are esterified simultaneously. Reaction time takes seconds to minutes in supercritical processes while catalyzed transesterification takes minutes to hours. The absence of pretreatment, soap removal and catalyst removal can significantly reduce the capital cost of a biodiesel plant. However, the need for high pressures and temperatures can be associated to high operating costs for the supercritical process. Therefore, development of reliable simulation and optimization models is required for the design of economically feasible supercritical biodiesel production processes.

In this work, we develop an optimization model for the minimization of capital and operating costs in a supercritical methanol biodiesel plant, based on rigorous process models, nonlinear programming techniques and thermodynamic predictions with a Group Contribution Equation of State with Association (Gross., 1996; Ferreira et al., 2004). Thermodynamic predictions have in turn been checked with available

experimental equilibrium data from the literature and data obtained in our group laboratory (Hegel et al., 2007). We have formulated a nonlinear programming (NLP) problem for an 80,000 ton/y biodiesel plant, using soybean oil and methanol as raw materials. The model allows exploring different plant capacities and alternative productions schemes by solving different NLPs, together with the convenience of including or not a co-solvent in the chemical reaction. Numerical results confirm that non-catalytic biodiesel production with supercritical methanol is economically competitive with conventional catalyzed production.

2. Thermodynamic modeling of supercritical soybean oil transesterification

Thermodynamic modeling of phase equilibrium of the reactants and reaction products in the two phase region and the determination of the homogeneous region are required for a reliable reactor design. Furthermore, the design of the downstream separation train requires the accurate prediction of the distribution of components between phases in the heterogeneous region (Espinosa et al., 2007, Diaz et al., 2008).

Binary and ternary systems including reactants and reaction products and water have been studied at different operating conditions. Binary interaction parameters have been taken from the literature (Espinosa et al. 2000; Ferreira et al., 2004; Andreatta et al., 2008). Figure 1 shows a good agreement between the Group Contribution Equation of State (GCA-EoS) estimations when compared to experimental data on LLE of the ternary methanol + methyl oleate + glycerol by Negi et al. (2006) at 333 K and atmospheric pressure. Reliable phase equilibria predictions of this mixture are especially important to identify operating conditions in the first separator that assure high recovery and purity of methanol in the vapor phase. Our study concludes that three phases in equilibrium (two liquid phases and one vapor phase) are necessary in order to obtain methanol rich vapor phase while glycerol and methyl esters remain in the liquid phases. The existence of two liquid phases in the first separator has been imposed as a restriction in the mathematical model.

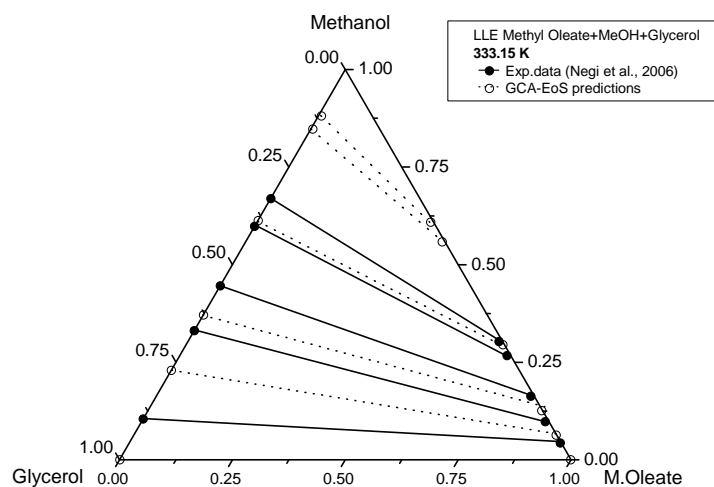


Figure 1. Ternary phase equilibria for the reaction products (methyl oleate and glycerol) and excess methanol at 333.15 K and one bar. Experimental data (Negi et al., 2006) and GCA-EoS predictions

3. Optimization Model

The optimization model for the noncatalytic transesterification of soybean oil with methanol at high pressure includes reliable thermodynamic predictions with the GCA-EoS equation of state and alternative schemes indicated as discontinuous lines in Fig. 2.

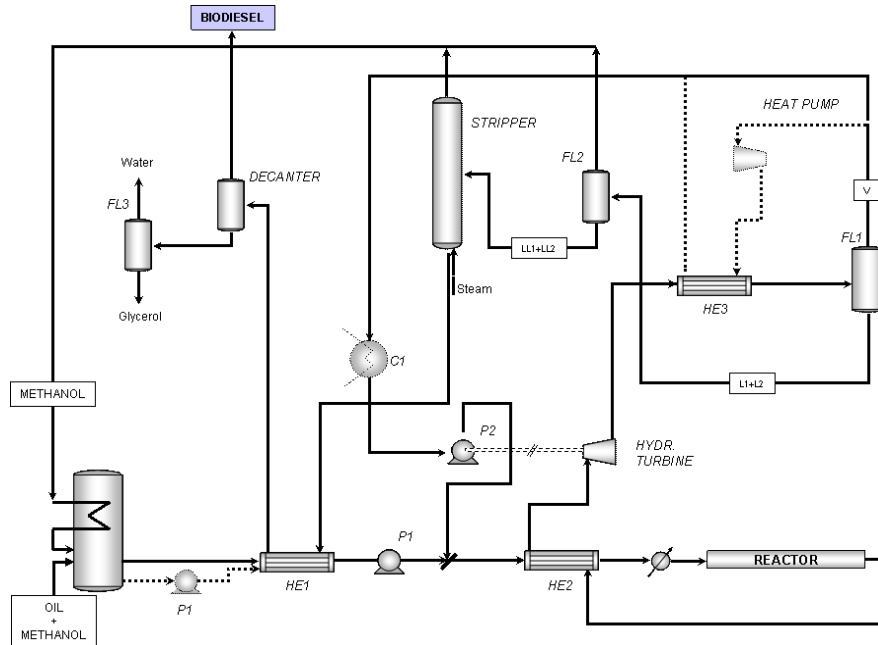


Figure 2. Superstructure of supercritical biodiesel production plant

We have formulated a nonlinear programming (NLP) problem for each analyzed process scheme, for an 80,000 ton/y biodiesel plant. The objective is the minimization of capital and operating costs for a supercritical methanol plant considering a project life of ten years. Capital cost correlations have been implemented from Ulrich (1984), Peters and Timmerhaus (1991) and Institut Français du Pétrole (1981).

Operating costs correspond to steam and cooling water requirement in heat exchangers, and electrical consumption for pumps and compressors. Optimization variables are the operating pressure in the supercritical reactor and in the first methanol recovery unit (FL1), pressure change in the heat pump, inlet steam flowrate in the stripper and distillate to feed ratio in this unit. The process model includes mass and energy balances in equipment, design equations, thermodynamic equilibrium equations (GCA-EoS) and recycle convergence equations as nonlinear equalities. Inequality constraints impose the existence of two liquid phases in the 1st separator, aqueous and organic phases, to provide high methanol recovery in the recycle stream with low glycerol content. A minimum methanol recovery of 90% and maximum glycerol mass concentration of 1% in this stream are required. Additionally, constraints on maximum water content in the recycled methanol from the top of the stripper, products purity specification of 99 wt% for methyl oleate (biodiesel) and product purity specification above 95wt% for glycerol are imposed. Product specifications, as required by European norms (EN 14214), have been also included as additional constraints in the optimization model. The resulting

nonlinear programming problem has been solved with a Successive Quadratic Programming (SQP) algorithm (Biegler et al., 1985).

4. Discussion of Results

Based on experimental results (Hegel et al., 2007) operating pressure in the reactor has been taken from 98 to 110 bar to ensure around 100% oil conversion to biodiesel, at 570 K. Following Kusdiana and Saka (2001) experimental results, the reaction has been modeled as first order and rate equations have been included in the optimization model. The supercritical transesterification reaction is carried out in a tubular reactor with 24 to 1 methanol/oil molar ratio. The possibility to use propane as a co-solvent (also to obtain 100% conversion at lower pressures), as suggested by Cao et al. (2005) has been considered, taking a molar propane/methanol ratio of 0.05 in the reactor. As compared to these authors' results, we have obtained a slightly higher residence time in the reactor (13.59 against 10 min) and slightly lower residence time with the process without co-solvent (13.59 against 15.37). Process variables, equipment energy consumption and biodiesel composition in the final product are shown in Table 1 for supercritical processes with and without co-solvent.

Table 1. Main variables of the supercritical biodiesel process

Variable	C3/Meth=0.00	C3/Meth=0.05
Separator Pressure, FL1 (bar)	6	6.5
Pres. change Heat Pump (bar)	3	9.5
Methanol recovery in recycle (%)	93	95
Glycerol in recycle (wt%)	0.3	0.6
Biodiesel in recycle (wt%)	0.2	0.3
Biodiesel purity (wt%)	99.9	99.8
Methanol in Biodiesel (wt%)	0.07	0.1
Glycerol in Biodiesel (ppm)	76	97
Water in Biodiesel (ppm)	473	395
Tubular Reactor Volume (m ³)	25	31
Reactor Tubes Length (m)	28	30
Feed Pump Power, P1 (kW)	99.81	99.87
Compressor Power, HP* (kW)	116.63	337
Heat in Heat Pump (kW)	2362.33	2956.55
Hidraulic Turbine Power (kW)	69.90	75.15
Recycle Pump Power, HP ^a (kW)	61.70	69.81

^a HP: Heat Pump

It can be noted that optimal operating pressure for the first separator is 6 bar, which ensures LLV equilibrium at the conditions determined in the heat pump (150°C to 160°C) and a pressure change of 3 bar has been determined in the heat pump. However, when propane is used as a co-solvent, this pressure change is not enough to completely condense the propane + methanol mixture. Therefore, one alternative is the addition of

external cooling, as this mixture has its bubble point around 363 K, which is too low to heat the feed to the first separator. Another alternative is to increase the upper bound on pressure change in the heat pump, which reduces the latent heat of vaporization of the condensing methanol + propane mixture, avoiding the requirement of additional cooling. The propane/methanol mixture must be subcooled to avoid cavitations in the pump. Biodiesel purity is above 99%wt in both cases, as required. The feed pump and the compressor have the main energy consumption. The integration between the hydraulic turbine and the recycle pump has been possible in the analyzed cases.

Table 2 shows optimal cost values with and without propane used as co-solvent in a 0.05 molar ratio to methanol. In cost calculations, investment cost has been annualized considering a project life of ten years and soybean oil price as 60 US\$/t. When operating with a co-solvent both operating and capital costs are higher due to the need for compression at higher pressure in the heat pump compressor of the methanol-propane recycle. However, as mentioned earlier, the reaction kinetics is increased when propane is used as cosolvent, reducing the residence time in the reactor. The last column in Table 2 shows results for a process scheme with no heat pump. As compared to the one with heat pump, it can be seen that operating costs have increased in 470 % due to higher steam requirement for heating the feed to the first separator. Capital costs are a slightly lower because there is no need for a compressor and the biodiesel production cost has increased in almost 4 %.

Table 2. Cost comparison for the plant with and without the use of a co-solvent

Costs	24-to-1, HPump C3/Meth=0.	24-to-1, HPump C3/Meth=0.05	40-to-1, HPump C3/Meth=0.	40-to-1, no HPump C3/Meth=0.
Operating (US\$/h)	34.32	55.81	50.08	284.89
Operating (US\$/t biodiesel)	3.41	5.56	4.98	28.23
Capital (US\$/t biodiesel)	4.66	5.88	5.15	4.47
Plant (US\$)	2,287,826	2,876,631	2,526,000	2,195,050
Production Cost (US\$/t biodiesel)	598.98	608.55	626.32	650.72

5. Conclusions

Different alternatives to supercritical biodiesel production have been studied in the present work by formulating nonlinear programming problems based on rigorous process models and thermodynamic predictions for each process scheme. Numerical results indicate that the use of propane as co-solvent slightly reduces the residence time in the reactor but increases both production and capital costs. Operating costs are significantly reduced considering the use of a heat pump scheme, making the supercritical biodiesel production economically competitive with conventional catalytic production and providing additional advantages that include no need for feed treatment, catalyst and soap removal.

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