

Model-Based Cost Minimization in Noncatalytic Biodiesel Production Plants

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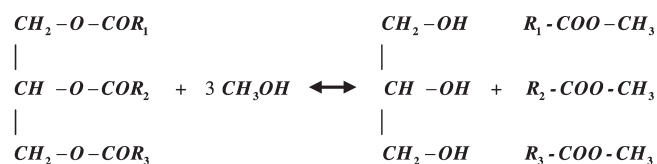
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In this work, we have formulated a series of nonlinear programming models based on first principles and rigorous thermodynamic predictions, to perform economic evaluation for different scheme alternatives in supercritical methanol transesterification for biodiesel production. The model includes thermodynamic predictions with a group contribution equation of state that have been favorably compared, in this work, to the available experimental data for the different mixtures at different operating conditions. The resulting nonlinear programming problem for cost minimization has been solved with a successive quadratic programming algorithm. Numerical results indicate that the use of a heat pump within the noncatalytic biodiesel production scheme significantly reduces operating costs, making this technology economically competitive as compared to conventional ones.

Introduction

Energy demand estimations for 2030 give more than a 70% increase in the world energy demand. Furthermore, taking into account increasing CO₂ emissions to the atmosphere by fossil fuels combustion, the reliance on fossil fuels is not sustainable. Biofuels are the fourth-ranked source of primary energy consumed in the world after oil, coal, and gas, and they constitute the leading renewable energy today. Biodiesel or vegetable oil methyl esters are used to replace or complement diesel fuel, while bioethanol is used to replace or complement gasoline. Alternatively, biodiesel can be produced from waste cooking oils.

Biodiesel is industrially produced by the transesterification of vegetable fatty oils with methanol. Most commonly used vegetable oils are rapeseed (Europe), soybean (America), sunflower, palm oil (Asia), and even waste cooking oil. Fatty oils are essentially mixtures of saturated and unsaturated mixed triglycerides of long fatty acid chains that chemically react with alcohol to produce a mixture of fatty acid alkyl esters. A typical triglyceride transesterification reaction with methanol follows this scheme, with equal or different radicals R₁, R₂, and R₃:



Triglyceride Methanol Glycerol Methyl esters

This is a reversible reaction and requires an excess of methanol to shift the reaction to the right side and obtain high yields of methyl esters (i.e., biodiesel). Most of the

conventional methods for biodiesel production use a basic or acidic catalyst^{1–4} and, more recently, enzymes.^{5,6} When the reaction between the oil and methanol is carried out with a basic or acidic catalyst at moderate temperatures, the immiscibility between oil and methanol cannot be avoided and it has a negative effect on the rate of the reaction. The reaction is initially slow because of the two-phase nature of the oil/methanol system and slows even further because of polarity problems. Alkali-catalyzed transesterification is much faster than the acid one. The preferred alkali catalyst is sodium hydroxide. However, if the oil has a higher content of free fatty acids and water, an acid catalyst may be a better choice.⁷

The alkali-catalyzed process, which takes place at atmospheric pressure and moderate temperatures (50–80 °C), is sensitive to both water and free fatty acids content in the feed. Free fatty acids can react with the catalyst to produce soaps and water. To maximize methyl esters production, it has been suggested that vegetable oils with less than 0.5% of free fatty acids should be used.¹ Even a low water content in the feed may cause ester saponification, consume the catalyst, and reduce its efficiency. Consequently, conventional catalytic processes require a pretreatment step to reduce free fatty acid and water concentration in the feed.⁷

On the other hand, the single-phase supercritical transesterification process takes place at high pressures (10–20 MPa) and temperatures (560–600 K) and it does not require 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

(1) Freedman, B.; Pryde, E. H.; Mounts, T. L. *J. Am. Oil Chem. Soc.* **1984**, *61*, 1638–1643.

(2) Ma, F.; Hanna, M. A. *Bioresour. Technol.* **1999**, *70*, 1–15.

(3) Fukuda, H.; Kondo, A.; Noda, H. *J. Biosci. Bioeng.* **2001**, *92*, 405–416.

(4) Lotero, E.; Liu, Y.; Lopez, D. E.; Suwannakarn, K.; Bruce, D. A.; Goodwin, J. G., Jr. *Ind. Eng. Chem. Res.* **2005**, *44*, 5353–5363.

(5) Watanabe, Y.; Shimada, Y.; Sugihara, A.; Noda, H.; Fukuda, H.; Tominga, Y. *J. Am. Oil Chem. Soc.* **2000**, *77*, 355–360.

(6) Varma, M. N.; Madras, G. *Ind. Eng. Chem. Res.* **2007**, *46*, 1–6.

(7) Van Gerpen, J. *Fuel Process. Technol.* **2005**, *86*, 1097–1107.

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for a pretreatment step.^{8–10} Additionally, free fatty acids in the feed oil are esterified simultaneously. The reaction time takes seconds to minutes in supercritical processes, while catalyzed transesterification takes minutes to hours.^{8,11}

Different operating conditions have been proposed for noncatalytic transesterification. Saka and Kusdiana¹¹ used a small 5 cc batch reactor, charged with rapeseed oil and methanol, to study the reaction at around 620 K and 45 MPa. Under these extreme conditions, oil conversion was completed in less than 6 min. Kusdiana and Saka⁹ studied the reaction kinetics, and they reported a drastic change in the reaction rate, between 540 and 570 K. Cao et al.¹⁰ proposed the use of propane as a co-solvent to obtain a single supercritical phase at lower pressure and temperature. Their results show that operation at milder conditions is possible while keeping a high reaction rate. Recently, He et al.¹² carried out experiments in a continuous reactor at 35 MPa and 583 K, with a high methanol/oil ratio, and they obtained high conversions with a residence time of 25 min. Varma and Madras⁶ proposed operation at 573 K and 20 MPa. Hegel et al.¹³ have shown that it is possible to obtain high conversion at moderate pressures 10–15 MPa and temperatures close to 600 K if the reactor global density is carefully controlled. However, the optimum methanol/oil molar ratio is close to 40.

The absence of pretreatment, soap removal, and catalyst removal steps can significantly reduce the capital cost of a biodiesel plant. However, the need for high pressures and temperatures can be associated with high capital and operating costs for the supercritical process. Therefore, the design of economically feasible supercritical biodiesel production processes requires the development of reliable simulation and optimization models. Nevertheless, there are only a few papers on computational modeling of conventional biodiesel plants^{14–17} and supercritical biodiesel ones.^{18,19} Zhang et al.^{14,15} have modeled and simulated four catalyzed biodiesel plant schemes using HYSYS (Hypertech Systems). They explored the technological and economic implementation of homogeneous transesterification by means of alkaline and acid catalysts, concluding that the simple acid-catalyzed process is the best option for biodiesel production. In a later work, Haas et al.¹⁶ developed an ASPEN-based computer model (Aspen Tech, Cambridge, MA) including capital and operating costs to produce biodiesel by alkali-catalyzed transesterification from crude soybean oil. Van Kasteren and Nisworo¹⁸ also used ASPEN to model biodiesel plants by supercritical technology. They report design variables and sensitive key factors for the economic feasibility of plants with three different capacities (8000, 80 000, and 125 000

tons/year), producing biodiesel from waste cooking oils. The use of methanol or bioethanol was also analyzed by the authors to estimate the effect of this alternative on the final biodiesel price. They conclude that the supercritical process can compete with catalyzed processes and that the production costs can be significantly reduced using waste cooking oil and selling the glycerol obtained as a side product.

More recently, West et al.¹⁹ have designed and simulated four continuous biodiesel plant schemes using HYSYS. The comparison of three traditional catalyzed processes with one supercritical process is reported, considering a plant capacity of 8000 tons/year of biodiesel, obtained by transesterification of waste cooking oil. For this reduced plant capacity, the authors conclude that the heterogeneous acid catalyst process is the most economically attractive method to produce biodiesel. However, taking into account that the operational scale and design have a significant effect on both capital and production costs,^{18,20} this conclusion could not be the same for different plant capacities and process designs.

In the above examples, simulation models are applied to thermodynamic tools available in the computational software and there is no report about phase equilibria of the complex mixtures involved in the process. Only sensitivity factors are described to identify the best options to reduce the final price of biodiesel fuel. However, to our knowledge, there are no rigorous optimization models of supercritical biodiesel plants in the literature coupled with reliable thermodynamic predictions of the complex phase equilibrium.

The objective of this work is to develop an optimization model for the minimization of capital and operating costs in a supercritical methanol biodiesel plant based on first-principle-based process models, nonlinear programming (NLP) techniques,^{21,22} and thermodynamic predictions with a group contribution equation of state with association.^{23,24} The model allows us to explore different plant capacities and alternative production schemes by solving different NLPs, together with the convenience of using virgin oil or waste cooking oil as raw material and/or including a co-solvent in the chemical reaction. Thermodynamic predictions have in turn been checked with available experimental equilibrium data from the literature and data obtained in our group laboratory.¹³ Numerical results confirm that noncatalytic biodiesel production with supercritical methanol is economically competitive with conventional catalyzed production.

Biodiesel Plant Scheme

In this work, we propose alternative design schemes for supercritical biodiesel production, which are embedded within the superstructure shown in Figure 1. There is a feed tank (V1), where part of excess methanol is mixed with fresh methanol and vegetable oil. The feed stream is pumped to the reactor pressure (10–12 MPa) and preheated in two heat exchangers (HE1 and HE2) and a heater (HE3) to the desired reaction temperature (570–580 K). The stream leaving the reactor is cooled in the second heat exchanger (HE2) with the

(8) Demirbaş, A. *Energy Convers. Manage.* **2002**, *43*, 2349–2356.

(9) Kusdiana, D.; Saka, S. *Bioresour. Technol.* **2004**, *91*, 289–295.

(10) Cao, W.; Han, H.; Zhang, J. *Fuel* **2005**, *84*, 347–351.

(11) Saka, S.; Kusdiana, D. *Fuel* **2001**, *80*, 225–231.

(12) He, H.; Wang, T.; Zhu, S. *Fuel* **2007**, *86*, 442–447.

(13) Hegel, P.; Mabe, G.; Pereda, S.; Brignole, E. A. *Ind. Eng. Chem. Res.* **2007**, *46*, 6360–6365.

(14) Zhang, Y.; Dube, M. A.; McLean, D. D.; Kates, M. *Bioresour. Technol.* **2003**, *89*, 1–16.

(15) Zhang, Y.; Dube, M. A.; McLean, D. D.; Kates, M. *Bioresour. Technol.* **2003**, *90*, 229–240.

(16) Haas, M. J.; McAloon, A. J.; Yee, W. C.; Foglia, T. A. *Bioresour. Technol.* **2006**, *97*, 671–678.

(17) West, A. H.; Posarac, D.; Ellis, N. *Int. J. Chem. React. Eng.* **2007**, *5*, A37.

(18) van Kasteren, J. M. N.; Nisworo, A. P. *Resour. Conserv. Recycl.* **2007**, *50*, 442–458.

(19) West, A. H.; Posarac, D.; Ellis, N. *Bioresour. Technol.* **2008**, *99*, 6587–6601.

(20) Bender, M. *Bioresour. Technol.* **1999**, *70*, 81–87.

(21) Diaz, M. S.; Gros, H.; Brignole, E. A. *Comput. Chem. Eng.* **2000**, *24*, 2069–2080.

(22) Espinosa, S.; Diaz, S.; Brignole, E. *Ind. Eng. Chem. Res.* **2002**, *41*, 1516–1527.

(23) Gros, H. P.; Bottini, S. B.; Brignole, E. A. *Fluid Phase Equilib.* **1996**, *116*, 537–544.

(24) Ferreira, O.; Brignole, E. A.; Macedo, E. A. *J. Chem. Thermodyn.* **2004**, *36*, 1105–1117.

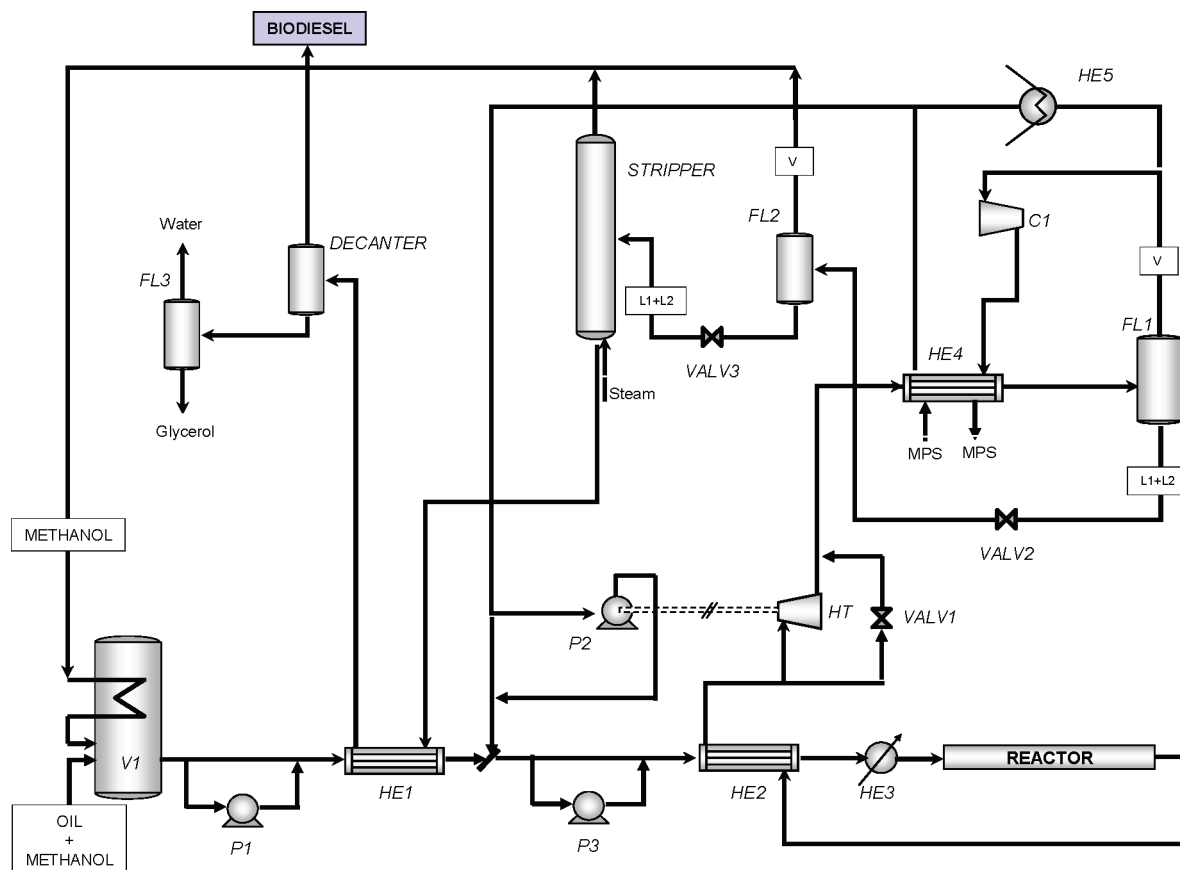


Figure 1. Superstructure of the noncatalytic biodiesel production plant. Discontinuous lines stand for alternative connections and equipment.

incoming feed, and its pressure is reduced to 0.6–1 MPa. This stream is heated in HE4 and sent to a first separator (FL1). A large fraction (90%) of methanol is recovered in this separator as the vapor stream. The supercritical process requires an important excess of methanol (above 10 times the stoichiometric ratio); therefore, there is a large amount of methanol that has to be recovered from the reaction products and recycled to the reactor. The energy content of the methanol recycle cannot be properly integrated with the cold streams. We propose a heat pump scheme as an efficient way of evaporating methanol from the reaction products, as one design alternative. In the heat pump scheme, the vapor stream leaving the first separator (FL1), mainly methanol, is compressed (C1), condensed in the first separator reboiler (HE4), and mixed with the incoming feed, before entering the second heat exchanger (HE2). If there is no heat pump, methanol is condensed in an additional cooler (HE5) and medium pressure steam is the utility in HE4. We have considered two pumping alternatives for the reactor feed: (a) one pump (P1) corresponding to the fresh feed and methanol recycle from the second separator and stripper and an additional pump (P2) for the main methanol recycle from the first separator [integrated to the hydraulic turbine (HT)] and (b) one sole pump (P3) that performs the entire reactor feed pumping. In this last scheme, there is a valve (VALV1) and no integration is performed with this stream.

The pressure of the liquid stream mainly composed of biodiesel, glycerol, and methanol, leaving the first separator (FL1) is further reduced to about 0.15 MPa and flashed to a second separator (FL2). The liquid phase leaving FL2 is sent to a steam stripper to completely remove the methanol from

the biodiesel + glycerol + water heterogeneous mixture. The methanol vapor stream from the second separation tank (FL2) is mixed with the methanol stream from the stripper partial condenser and recycled to the feed tank to preheat the contents of the feed tank. The bottom stream from the stripper (biodiesel + glycerol + water) is cooled by heat exchange with the feed (HE1) and sent to an adiabatic decanter tank from which the biodiesel product stream is recovered. A third flash (FL3) allows the separation of glycerol and water.

On the basis of the biodiesel process scheme, the properties and phase equilibria of the following mixtures are of interest: (a) methanol + fatty oil, (b) methanol + fatty oil + propane (alternatively used as a co-solvent), (c) methanol + glycerol + fatty ester under LL, LV, and LLV equilibria, and (d) methanol + glycerol + fatty ester + water under LL, LV, and LLV equilibria. In the following section, thermodynamic group contribution with association equation of state (GCA-EoS) predictions for these mixtures are compared to experimental data from the literature to ensure reliable thermodynamic estimations for the posterior process design.

Thermodynamic Modeling of the Biodiesel Process

Oil transesterification with supercritical methanol for biodiesel production has been extensively studied in the literature to determine the best operating conditions to ensure high conversion to biodiesel.^{8,10–13} The molar alcohol/oil ratio as well as pressure and temperature determine whether there is a single homogeneous phase or a multi-phase system in the reactor. The main reason for operating at high temperature and pressure is to obtain complete miscibility between methanol and the vegetable oil and, consequently, high conversion in shorter time. However, process

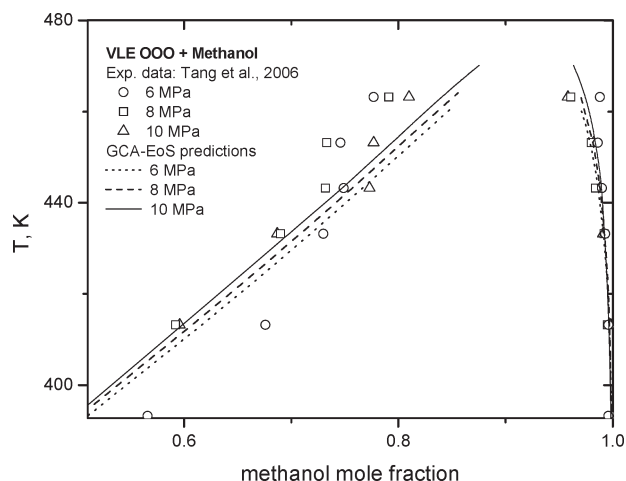


Figure 2. Phase equilibria for the methanol + triolein mixture. Experimental data were from ref 25 and GCA-EoS predictions at three different pressures.

thermodynamics still requires further investigation. Recent experimental studies^{13,25} indicate that complete oil + methanol miscibility can be achieved at temperatures between 470 and 480 K, below the critical temperature of methanol (512.15 K). Moreover, regarding the effect of heterogeneous phase conditions on biodiesel production, Hegel et al.¹³ have observed high conversion in most cases, even when operating in the two-phase region, with a methanol/oil molar ratio between 40 and 50 and temperature and pressure conditions in the range of 560–580 K and 9–12 MPa, respectively. The reaction rate at temperatures below 500 K is very low, but above 570 K, it is considerably increased.^{9,13} Therefore, it is possible to model phase equilibria of the reactants (only vegetable oil and alcohol) from ambient conditions to 500 K at zero conversion and, thereafter, in the whole range of temperatures and pressures of interest for the reaction products (glycerol, monoesters, methanol, and co-solvents), at 100% conversion. To determine the phase state at each point of the process, the phase equilibrium is modeled in a wide range of process conditions. In this work, we have modeled process phase equilibrium with a GCA-EoS.²⁴ The triglyceride has been modeled as composed of triolein ($C_{57}H_{104}O_6$), which is the main component in soybean oil. Methyl oleate ($C_{19}H_{36}O_2$) has been chosen to represent the fatty acid methyl ester product (biodiesel). Triolein is composed of paraffinic groups (CH_3 and CH_2), olefinic groups ($CH=CH$), and the main group, characteristic of triglycerides, called the TG group, $[(CH_2COO)_2(CHCOO)]$. Methyl oleate is composed of paraffinic groups (CH_3 and CH_2), olefinic groups ($CH=CH$), and the characteristic group of methyl esters, CH_2COO . The remaining group components (methanol, glycerol, and water) have been modeled as pure groups.

As a first step, binary interaction parameters for methanol and paraffinic groups have been tuned on the basis of the experimental data for triolein and methanol,²⁵ as shown in Figure 2, at three different pressures. Table 1 shows binary and non-randomness parameters determined for this system considering cross-association,²⁴ and Table 2 shows the associated standard deviations.

The remaining binary interaction parameters have been taken from the literature, as shown in Table 3. Satisfactory GCA-EoS predictions for liquid–liquid equilibrium for the system

(25) Tang, Z.; Du, Z.; Min, E.; Gao, L.; Jiang, T.; Han, B. *Fluid Phase Equilib.* **2006**, *239*, 8–11.

(26) Espinosa, S.; Foco, G.; Bermúdez, A.; Fornari, T. *Fluid Phase Equilib.* **2000**, *172*, 129–143.

(27) Andreatta, A. E.; Casas, L. M.; Hegel, P.; Bottini, S. B.; Brignole, E. A. *Ind. Eng. Chem. Res.* **2008**, *47*, 5157–5164.

Table 1. GCA-EoS Binary Interaction Parameters for Phase Equilibria Predictions in Vegetable Oil + Methanol and Vegetable Oil + Methanol + Propane Mixtures

<i>I</i>	<i>j</i>	<i>kij</i>	<i>k'ij</i>	<i>Aij</i>	<i>Aji</i>	references
TG ^a	CH ₃ /CH ₂	0.860	0	0	0	26
	CH=CH	0.883	0	0	0	26
CH ₃ OH	TG	1.000	0	0	0	this work
	CH ₃ /CH ₂	0.970	0.2	-1	5	this work

^aTG group = $[(CH_2COO)_2(CHCOO)]$.

Table 2. Standard Deviations for the Binary System Methanol + Triolein^a

<i>P</i> (MPa)	STD <i>x</i> (%)	STD <i>y</i> (%)
6	7.93	0.92
8	5.81	0.42
10	2.71	0.90

^aExperimental data were from ref 25 and the GCA-EoS model.

Table 3. GCA-EoS Binary Interaction Parameters for Phase Equilibria Predictions in Fatty Acid Methyl Esters + Methanol + Glycerol + Water and Fatty Acid Methyl Esters + Methanol + Glycerol + Water + Propane Mixtures

<i>I</i>	<i>J</i>	<i>kij</i>	<i>k'ij</i>	<i>aij</i>	<i>aji</i>	references
H ₂ O	CH ₃	0.65	0	0.5	15	23
	CH ₂	0.62	0	0.7	16.5	23
CH ₂ COO	CH ₃ /CH ₂	0.869	0	0	0	26
	H ₂ O	1.	0	0	0	24
glycerol	CH ₃ /CH ₂	1.0174	0	0	0	27
	CH ₂ COO	1.09	-0.02	0	0	27
	CH ₃ OH	1.04	0	0	0	27

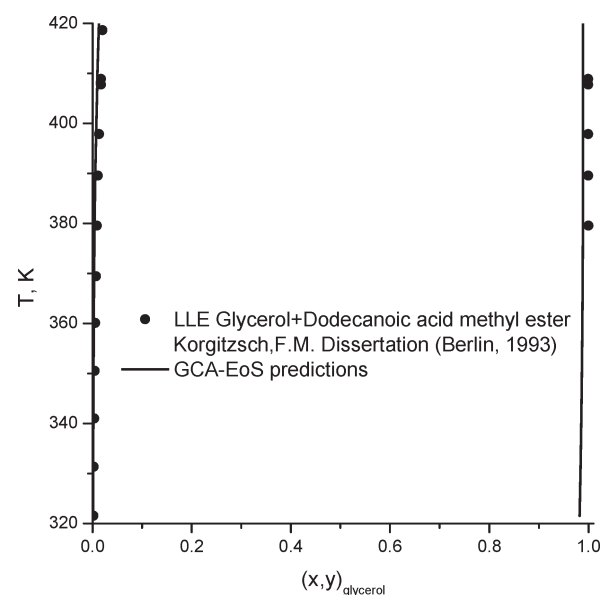


Figure 3. Liquid–liquid phase equilibria for the binary system glycerol + methyl dodecanoate. Experimental data³⁵ and GCA-EoS predictions were at atmospheric pressure.

methyl ester + methanol are shown in Figure 3, as compared to the experimental data.³⁵ Figure 4 shows a comparison between the experimental data³⁵ and liquid–liquid predictions for the system methyl ester + water, in an amplified scale.

To model processes downstream of the supercritical reactor, the ternary system methyl ester + methanol + glycerol has been studied at different operating conditions. Figures 5 and 6 show a good agreement between the group contribution equation of state predictions and experimental data on liquid–liquid extraction

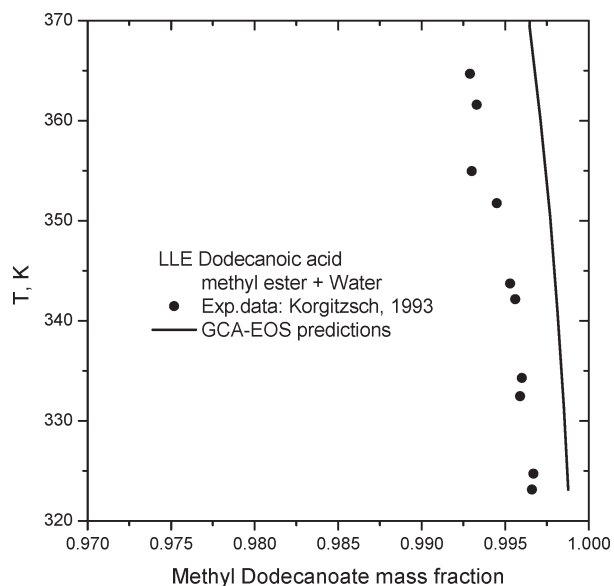


Figure 4. Liquid–liquid phase equilibria for the binary system water + methyl dodecanoate. Experimental data³⁵ and GCA-EoS predictions were at atmospheric pressure for the organic phase.

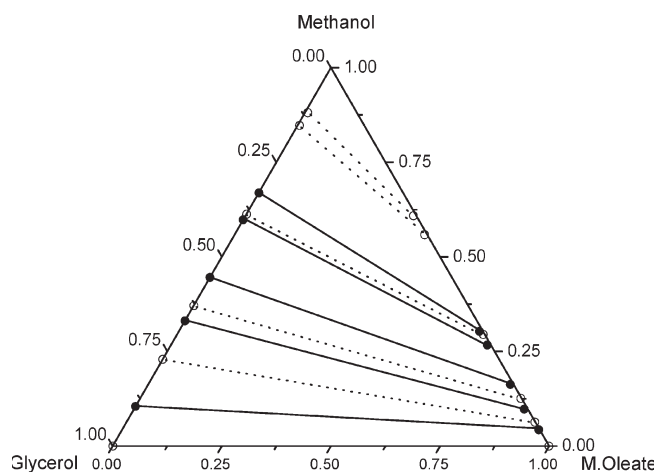


Figure 5. Ternary phase equilibria for the system methanol + methyl oleate + glycerol, at 333.15 K. (● and ▽) Experimental data²⁸ and (○ and ···) GCA-EoS model predictions.

(LLE) of the ternaries methanol + methyl esters + glycerol^{28,35} and at 333 K and atmospheric pressure, as seen comparing the experimental and predicted two-phase region and the slope of the lines.

To find conditions for producing a methanol-rich vapor product in the first separator (FL1 in Figure 1), thermodynamic phase equilibria of the methanol + methyl oleate + glycerol mixture is explored in a wide range of pressures, temperatures, and compositions. When two phases are present in the separator, glycerol and methanol distribute between both phases, reducing recovery and purity of methanol in the vapor phase. On the other hand, if the separator operating conditions are modified to find three phases in equilibrium (two liquid phases and one vapor phase), methanol with high purity is obtained in the vapor phase, while glycerol and methyl esters remain in the liquid phases. We have imposed the existence of two liquid phases as a nonlinear constraint in the optimization model.

Finally, thermodynamic behavior of the methanol + methyl oleate + glycerol mixture has been studied, focusing attention on the operation of the heat pump described in the previous section. Figure 7 shows the bubble point lines at different pressures, on a

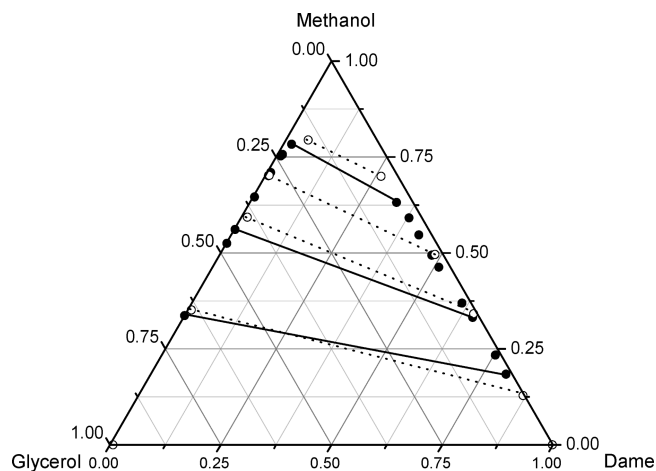


Figure 6. Ternary phase equilibria for the system methanol + methyl dodecanoate + glycerol, at 333.15 K. (● and ▽) Experimental data²⁸ and (○ and ···) GCA-EoS model predictions.

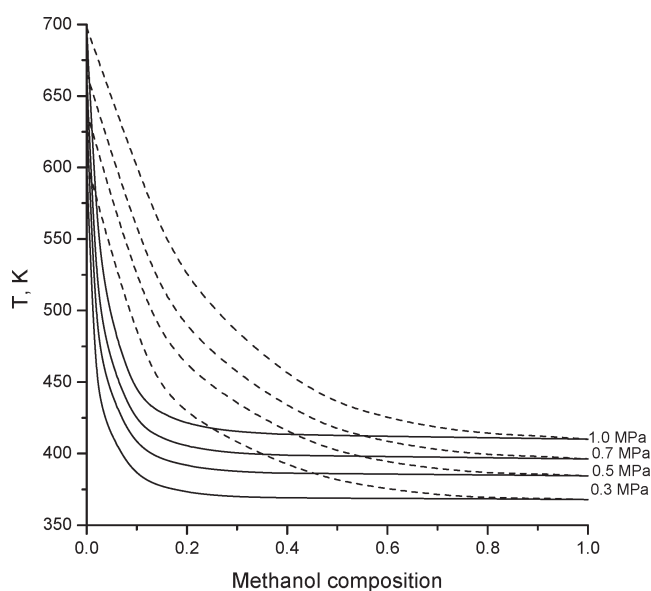


Figure 7. Bubble point lines for the ternary mixture methanol + (3:1 methyl oleate + glycerol) on a mass (—) and molar (· · ·) basis.

molar and mass basis. The pressure difference across the heat pump has been considered as an optimization variable to make possible the reboiler/condenser heat exchange. Numerical results have shown that a pressure difference of 0.3–0.4 MPa in the heat pump is required when no co-solvent is used. When propane is added as the co-solvent, higher pressure changes are required.

Reactor Model

Three different reactive mixtures have been studied in the present work: two mixtures with 24:1 and 40:1 methanol/oil molar ratios and a third one with propane as the co-solvent (24:1 as the methanol/oil molar ratio and 0.05:1 as the propane/methanol molar ratio). On the basis of the yield and kinetics of supercritical experimental results reported by Kusdiana and Saka,²⁹ the transesterification reaction was

(28) Negi, D. S.; Sobotka, F.; Kimmel, T.; Wozny, G.; Schomäcker, R. *Ind. Eng. Chem. Res.* **2006**, *45*, 3693–3696.

(29) Kusdiana, D.; Saka, S. *Fuel* **2001**, *80*, 693–698.

carried out in an isothermal multi-tube reactor designed to achieve high conversion (above 98%), considering first-order kinetics.²⁹ The differential algebraic equation system has been solved with a fourth-order backward differentiation formula. The reaction has been modeled in the vapor phase and considered as one of first-order with an activation energy of 45 350 kJ/kmol as estimated from experimental data by Kusdiana and Saka.²⁹ Cao et al.¹³ reported a substantial increase of the reaction rate when propane is used as the co-solvent. Therefore, we have estimated a 100% increase in the reaction rate constant when using a co-solvent based on experimental data showing a 20% increase in methyl ester yield when adding propane as the co-solvent.¹⁰

The pressure drop in the reactor has been limited to 5 kPa, and it has been estimated using the following definition of the Moody friction factor:

$$f = \frac{-2D \left(\frac{dp}{dx} \right)}{\rho u_m^2}$$

where f is the dimensionless friction factor, D is the tube diameter, ρ is the fluid density, and u_m is the mean velocity of the flow calculated from the continuity equation as a function of the rate mass flow through the tube, fluid density, and the cross-sectional area of the tube. The friction factor has been calculated with correlations given by Incropera et al.³⁰ as a function of the Reynolds number. Residence time, pressure drop, and dimensions of the reactor calculated for the different analyzed schemes are presented in the Discussion of the Results.

Process Optimization

Having tuned and validated the thermodynamic model for the systems involved in a biodiesel production process, we have developed a rigorous optimization model for the non-catalytic transesterification of soybean oil with methanol at high pressure. Alternative schemes include the existence or non-existence of a heat pump and the pumping of the feed prior to or after the first heat exchanger. We have formulated a NLP problem for each analyzed process scheme based on rigorous models for process units and thermodynamic predictions performed with the GCA-EoS. The objective is the minimization of capital and operating costs for a supercritical methanol plant as follows:

$$\text{Obj} = \sum_i \text{CapCost}_i + \sum_j \text{OpCost}_j + \sum_k F_k C_k$$

$i = \text{P1, P2, P3, HE1, HE2, HE3, HE4, HE5, reactor, FL1,}$

$\text{FL2, FL3, stripper, dec, C1, HT}$

$j = \text{P1, P3, HE3, HE4, HE5, stripper, C1}$

$k = \text{oil, methanol}$

taking into account that, if P1 and P2 are used, P3 is not required and vice versa; if a heat pump is included, C1 is used and HE5 is not required. Capital cost correlations are given in the Appendix, and they have been implemented from

(30) Incropera, F. P.; De Witt, D. P. *Fundamentals of Heat and Mass Transfer*, 4th ed.; John Wiley and Sons: New York, 1999.

(31) Ulrich, G. D. *A Guide to Chemical Engineering Process Design and Economics*; John Wiley and Sons: New York, 1984.

(32) Peters, M. S.; Timmerhaus, K. D. *Plant Design and Economics for Chemical Engineers*; McGraw-Hill: New York, 1991.

Table 4. Lower and Upper Bounds for Design Variables

design variables	lower bound	upper bound
reactor pressure (MPa)	10.	14
separator pressure, FL1 (MPa)	0.5	1.2
pressure change in the heat pump (MPa)	0.2	1.0
steam flow rate (kg/h)	150	350
distillate/feed (kg/kg)	0.001	0.3

Table 5. Nonlinear Inequality Constraints in the Optimization Model

equipment	limitation	bound
first separator	L1 and L2 (kmol/h)	≥ 1 .
first separator (FL1)	methanol recovery (%)	≥ 90
first separator (FL1)	glycerol in recycle (wt %)	≤ 1
methanol stripper	water content in methanol (wt %)	≤ 1
decanter	biodiesel purity (wt %)	≥ 99
third separator (FL3)	glycerol purity (wt %)	≥ 95
heat exchangers	temperature difference (°C)	≥ 8
biodiesel specifications	(EN 14214)	
decanter	methanol in biodiesel (wt %)	≤ 0.2
decanter	triglyceride in biodiesel (wt %)	≤ 0.2
decanter	glycerol in biodiesel (ppm)	≤ 200
decanter	water in biodiesel (ppm)	≤ 500

Ulrich,³¹ Peters and Timmerhaus,³² and correlations reported by the Institut Français du Pétrole,³³ considering a project life of 10 years. Operating costs correspond to medium-pressure steam (MPS) consumption in the bottom feed to the stripper and, if there is no heat pump, HE4, high-pressure steam in HE3, and cooling water (CW) in HE5, if there is no heat pump, as well as electrical motor consumption as drivers for pumps (P1 and P3) and compressors (C1).

Design variables have been selected on the basis of a previous local sensitivity analysis of the proposed process and thermodynamic behavior of the different systems, as well as knowledge of the biodiesel process. We have selected five design variables that correspond to the operating pressure in the supercritical reactor and in the first methanol recovery unit (FL1), pressure change in the heat pump, inlet steam flow rate in the stripper, and distillate/feed ratio in this unit. Lower and upper bounds on these variables are shown in Table 4. The methanol/oil ratio is an important variable affecting the methyl ester yield. An excess of methanol is required to shift the equilibrium toward biodiesel production. However, high molar ratios increase capital and operating costs. For the sake of model robustness, we have not included the methanol/oil ratio as a design variable but we have performed process optimization at two methanol/oil ratios corresponding to recommended optimal values based on experimental research from the literature^{9–12} and experiments carried out at our laboratory.¹³

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 first separator, aqueous and organic phases, to provide high methanol recovery in the recycle stream with low glycerol content (the organic phase, if present, is mainly glycerol). A minimum methanol recovery of 90% and maximum glycerol mass concentration of 1% in this stream are allowed. Additionally, constraints on maximum water content in the recycled methanol from the top of the stripper, product purity specification of 99 wt % for methyl oleate (biodiesel), and product purity specification above 95 wt % for glycerol are imposed. Table 5 shows a detail of

(33) Institut Français du Pétrole. *Manual of Economic Analysis of Chemical Processes*; McGraw-Hill: New York, 1981.

these constraints, as well as product specifications, as required by European norms (EN 14214), which have also been included as nonlinear constraints in the optimization model. The resulting NLP model has been implemented in Fortran 90 and solved with a successive quadratic programming (SQP) algorithm,³⁴ within a sequential approach.

Discussion of the Results

We have formulated several NLP problems for the different process schemes shown in Figure 1, with different methanol/oil ratios. The possibility to use propane as a co-solvent (also to obtain almost 100% conversion at lower pressures), as suggested by Cao et al.,¹⁰ has also been considered. In the first case (NLP1), we have considered a scheme with pumps P1 and P2 (integrated to the hydraulic turbine) and the heat pump (compressor C1), for a methanol/oil ratio equal to 40:1. A second process scheme (NLP2), with the same methanol/oil ratio, does not include a heat pump; i.e., there is no compressor (C1) in the flowsheet, the heating utility in HE4 is MPS, and methanol recycle is condensed in HE5 with cooling water. In the third process scheme (NLP3), the heat pump is included but only pump P3 stands for feed pumping, with no hydraulic turbine (P1 and P2 are not in this scheme). Finally, the last case (NLP4) is the same process scheme as NLP1, considering the use of propane as the co-solvent (propane/methanol ratio = 0.05) and the methanol/oil ratio equal to 24:1.

In all cases, 80 000 tons/year of vegetable oil are processed, taking into account bound variables and inequality constraints shown in Tables 4 and 5. The stripper operating pressure is 0.152 MPa. On the basis of the experimental results,¹³ the reactor operating pressure has been bound between 10 and 14 MPa to ensure oil conversion to biodiesel above 99%, at 570 K, which is the reactor operating temperature in all analyzed cases. Optimal design variable values are shown in Table 6. It can be noted that the minimum cost is obtained by operating the reactor at 10 MPa, the lower bound,

Table 6. Optimal Design Variable Values in the Studied Process Schemes

optimization variables	NLP1	NLP2	NLP3	NLP4
reactor pressure (MPa)	10	10	10	10
separator pressure, FL1 (MPa)	0.99	1.02	1.00	0.65
pressure change in the heat pump (MPa)	0.4		0.4	0.95
steam flow rate (kg/h)	330	328	330	232
distillate/feed (kg/kg)	0.019	0.018	0.019	0.003

to ensure phase homogeneous conditions at 570 K while fulfilling process specifications. With regard to pressure change in the heat pump, it can be mentioned that the scheme with the co-solvent (NLP4) requires a larger pressure change because, at lower pressures, the propane + methanol mixture has its bubble point around 363 K, which is too low to heat the feed to the first separator. Therefore, it is necessary to increase the 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. It must be noted that the optimal operating pressure for the first separator is between 0.65 and 1.02 MPa in all cases, which ensures liquid–liquid vapor equilibrium at the temperature determined in the heat pump (424–438 K).

Process variables, equipment energy consumption, and biodiesel composition in the final product are shown in Table 7. Biodiesel purity is above 99.8 wt % in all cases, as well as biodiesel quality specifications by the European norms (EN 14214). This fact highlights the supercritical technology goodness for biodiesel production. It can be noted that HE4 has the main energy consumption (around 3000 kW in all cases), which does not require heating utility in the heat pump schemes (NLP1, NLP3, and NLP4). It is clear that the use of a heat pump can reduce energy consumption, which has been confirmed with the numerical results shown in Table 8. The feed pump and the compressor have the main energy consumption in the heat pump schemes. The integration between the hydraulic turbine HT and the recycle pump P2 has been possible in NLP1, NLP2, and NLP4, as reported in the last two rows of Table 7. From this table, the coefficient of performance (COP) for the heat pump can be calculated. It must be pointed out that the schemes with a heat pump (NLP1 and NLP3) provide the largest value (21.4 and 21.3, respectively). Even though the addition of a co-solvent (NLP4) provides a lower heat pump COP (8.4), the use of a heat pump is still recommended.

A detail of cost information is shown in Table 8 for the four analyzed schemes. A typical methanol/oil ratio in the reactor of 40:1 with a heat pump (NLP1) has associated operating costs of 4.98 U.S. \$/ton of biodiesel and capital costs of 5.64 U.S. \$/ton of biodiesel, considering a project life of 10 years with a 10% interest rate, with a plant cost of 2 770 972 U.S. \$. The production cost, with soybean oil as the raw material (560 U.S. \$/ton) and methanol (300 U.S. \$/ton) is 626.82 U.S. \$/ton of biodiesel. If a less expensive oil is used as the raw

Table 7. Optimal Process Variable Values in the Studied Process Schemes

variable	NLP1	NLP2	NLP3	NLP4
HE1 outlet feed temperature (K)	372.05	373.75	343.25	385.25
HE2 outlet feed temperature (K)	536.95	539.35	535.45	556.15
FL1 temperature (K)	424.34	426.15	426.42	437.32
C1 outlet temperature (K)	452.15		454.28	508.95
stripper bottom temperature (K)	391.25	393.55	394.76	396.75
residence time (min)	15.66	18.53	15.26	7.81
methanol recovery in FL1 vapor (%)	90.16	90.0	91.26	95.41
glycerol in FL1 vapor stream (wt %)	0.1	0.1	0.1	0.3
biodiesel in FL1 vapor stream (wt %)	0.1	0.1	0.1	0.6
biodiesel stream purity (wt %)	99.81	99.90	99.91	99.80
methanol in biodiesel stream (wt %)	0.1	0.09	0.07	0.1
glycerol in biodiesel stream (ppm)	72	74	75	97
water in biodiesel stream (ppm)	475	473	473	395
feed pump power, P1 (kW)	110.59	110.59		99.87
compressor C1 power (kW)	153.81		158.62	336.97
heat in HE4 (kW)	3288.10	3360.03	3372.08	2956.45
hydraulic turbine power (kW)	106.26	97.54		75.14
pump P2 power (kW)	102.68	95.56		69.82

Table 8. Optimal Capital, Operating Costs and Production Costs for the Four Analyzed Alternatives, Processing 80 000 Tons/Year Vegetable Oil

process units	NLP1	NLP2	NLP3	NLP4
feed pump, P1 (U.S. \$)	359146	359146		344356
recycle pump, P2 (US \$)	348310	338155		297337
feed pump, P3 (U.S. \$)			473292	
heat exchanger, HE1 (U.S. \$)	296126	299653	301137	368395
heat exchanger, HE2 (U.S. \$)	450794	518524	456275	807661
heat exchanger, HE3 (U.S. \$)	205877	120116	203480	60131
heat exchanger, HE4 (U.S. \$)	320342	321221	326340	219114
heat exchanger, HE5 (U.S. \$)		155039		
reactor (U.S. \$)	185211	188092	184805	150970
hydraulic turbine, HT (U.S. \$)	81871	74654		59544
compressor, C1 (U.S. \$)	217254		221796	367099
separator tank, FL1 (U.S. \$)	108839	104982	109829	118801
separator tank, FL2 (U.S. \$)	65005	63738	62922	33602
separator tank, FL3 (U.S. \$)	39094	38231	39092	120377
stripper (U.S. \$)	53478	53660	53787	59340
decanter (U.S. \$)	39626	39405	39263	39097
total capital cost (U.S. \$)	2770972	2674616	2472018	3045823
capital (U.S. \$/ton of biodiesel) amortization = 10 year	5.64	5.45	5.04	6.22
operating cost (U.S. \$/ton of biodiesel)	4.98	28.22	6.07	5.71
production cost (U.S. \$/ton of biodiesel) (soybean oil = 560 U.S. \$/ton)	626.82	651.70	630.31	609.43
production cost (U.S. \$/ton of biodiesel) (waste cooking oil = 210 U.S. \$/ton)	278.77	303.71	282.17	260.78

material, such as waste cooking oil (210 U.S. \$/ton), the production cost is 278.77 U.S. \$/ton. It is important to note that only the biodiesel production cost is reported in this table; i.e., we have not included the revenues from glycerol sale.

Numerical results in Table 8 confirm that the use of a heat pump is recommended. Costs can be reduced if the use of a co-solvent is considered (NLP4), which requires a lower methanol/oil ratio (24:1) and renders a lower total cost, even though capital costs are higher. Both operating and capital costs are higher because of the need for compression at higher pressure in the heat pump compressor of the methanol–propane recycle. As mentioned earlier, the reaction kinetics is increased when propane is used as the co-solvent, reducing the residence time in the reactor (see Table 7).

Conclusions

We have formulated first-principle-based models for supercritical methanol transesterification for biodiesel production. The model includes thermodynamic predictions with a group contribution equation of state that have been compared to the available experimental data for the different complex mixtures in the process. Rigorous process models are used for each process unit. Different alternatives to supercritical biodiesel production have been studied in the present work by formulating NLP problems for each process scheme. Numerical results indicate that the use of a heat pump significantly reduces operating costs. This alternative can be further improved using propane as the co-solvent, which reduces the residence time in the reactor and requires a lower methanol/oil ratio in the reacting mixture. Even though both production and capital costs are increased in this scheme, production costs are lower because of the requirement of supercritical methanol. The economical analysis has shown that the non-catalytic supercritical biodiesel production is economically competitive as compared to the conventional catalyzed production, with additional advantages that include no need for feed treatment, catalyst, and soap removal.

(34) Biegler, L. T.; Cuthrell, J. E. *Comput. Chem. Eng.* **1985**, *9*, 257–265.

(35) Korgitzsch, F. M. Study of phase equilibria as a fundament for the refinement of vegetable and animal fats and oils. Ph.D. Dissertation, Technical University of Berlin, Berlin, Germany, 1993.

Appendix

Cost Correlations. Investment cost correlations are in U.S. \$/h. Estimations are based on 8000 h/year operation.

Equipment units have been considered as made of stainless steel. Cost indexes are I_{CE} , for correlations from Ulrich,³¹ and $I_{Marshall}$, for correlations from Peters and Timmerhaus.³² We have estimated a project life of 10 years ($n = 10$). The annualization has been calculated, considering a 10% interest rate, as follows:

$$a = \frac{i(i+1)^n}{(i+1)^n - 1}$$

The range of applicability of the correlations can be found in the corresponding references. Capital basic costs from correlations have been affected by a 1.8 factor to account for contingencies and charge and a 1.3 factor for new plants.³¹

Compressor Cost. The installed cost of alternative and centrifugal compressors + electrical motor is as follows:³²

$$C_{\text{compressor}} = I_{\text{Marshall}}/256(1228.9 + 1853.44Ws^{0.65655})$$

where Ws (kW) stands for shaft work.

Pumps Costs. The installed cost for the pump is as follows:³¹

$$C_{\text{pump}} = I_{CE}/315(1567.93 + 3531.97Ws^{0.43646} \\ (-3.9927 + 5.4028p^{0.20515}))$$

where Ws is shaft work (kW) and p stands for pressure (atm).

Hydraulic Turbine Cost. The installed cost for the hydraulic turbine is as follows:³⁶

$$C_{\text{HT}} = 800Ws$$

where Ws is shaft work (kW).

Heat Exchangers Cost. The installed cost for fixed tube sheet and U-tube heat exchangers is as follows:³¹

$$C_{\text{HE}} = I_{CE}/400(3653.64 + 377.04\text{area}^{0.79534} \\ (5.7455 + 0.0213p^{0.84909}))$$

(36) Manuals from the Department of Hydraulics, Universidad Nacional del Comahue, Neuquén, Argentina, 2007.

where area is the exchanger surface area (m^2) and p stands for pressure (atm).

Vessels Cost. Vertical vessels have been selected for the decanter, stripper, and separators³³

$$C_{\text{vessels}} = 1.15(I_{\text{CE}}/182.1(C_{\text{shell + heads}}f_{\text{m}}f_{\text{c}} + C_{\text{access}} + C_{\text{packing}})f_{\text{p}})$$

$$\text{with } C_{\text{shell + heads}} = \text{weight}(2 - \log D)$$

where $C_{\text{shell+heads}}$ is the shell and heads cost, C_{access} is the accessories cost, C_{packing} is the packing cost, f_{m} is the correction factor for material, f_{c} is the correction factor for thickness, f_{p} is the pressure correction factor, and 1.15 stands for installation costs.

The cost of shell + heads and cost of accessories are both a function of the vessel diameter, which has been calculated from the continuity equation, at 80% of flooding point

$$D = \frac{4V_{\text{max}}M_{\text{g}}}{\pi\rho_{\text{g}}0.8u_{\text{s,g}}}$$

where V_{max} is the maximum vapor flow and M_{g} is the gas molecular weight.

Flooding velocity has been calculated through Souders–Brown correlation

$$u_{\text{s,g}} = K_{\text{SB}} \left(\frac{\rho_{\text{l}} - \rho_{\text{g}}}{\rho_{\text{g}}} \right)^{0.5}$$

where K_{SB} is the Souders–Brown constant and ρ_{l} and ρ_{g} are the top liquid and vapor densities.

Vessels height has been estimated as recommended by Ulrich for separators and decanters: $H = 5D$.

Reactor Cost³¹.

$$C_{\text{reactor}} = I_{\text{CE}}/400(C_{\text{vessel}} + C_{\text{coil}})$$

$$C_{\text{vessel}} = f_{\text{mv}}10^{(3.6 + 0.17 \log V + 0.083 \log^2 V)}$$

$$C_{\text{coil}} = f_{\text{mc}}10^{(3.2 + 0.31 \log A_{\text{coil}} + 0.053 \log^2 A_{\text{coil}})}$$

where C_{vessel} is the vessel cost, as a function of the reactor volume V , and C_{coil} is the coil cost, as a function of the total coil surface area A_{coil} . f_{mv} and f_{mc} are the bare module factors as a function of materials and operating pressure. The reactor volume is estimated from the reactor design equations, and the coil surface area is calculated as a function of the number of tubes and the length of tubes in the reactor.