Energy consumption minimization in bioethanol dehydration with supercritical fluids

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Abstract

In this work, we propose a rigorous model for bioethanol dehydration process with supercritical propane to minimize energy consumption. Thermodynamic predictions are performed with an upgraded Group Contribution with Association Equation of State, GCA-EOS. As compared to the basic scheme for dehydration with supercritical fluids, vapor recompression, as well as feed preconcentration could be highly energy efficient. We further consider alternative integration schemes between process streams, associated to different nonlinear programming problems. Special attention has been devoted to a new scheme that integrates the vapor recompression scheme to the preconcentration step, which provides additional reduction in total energy consumption. We demonstrate that bioethanol dehydration can be a sustainable alternative that is energetically competitive with molecular sieves in the production of this biofuel.

Keywords: Bioethanol, dehyextraction, near critical fluid, NLP.

1. Introduction

Alternatives to fossil fuels are being investigated to reduce the world's dependence on non-renewable resources. Biofuels are currently considered as relevant sustainable technologies due to energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. The reduction of greenhouse gases pollution is the main advantage of utilizing biomass energy. The most common renewable fuel is ethanol derived from corn grain (starch) and sugar cane (sucrose). Wood, straw and even household wastes may also be economically converted to bioethanol. However, there is need for decreasing energy consumption in the entire bioethanol supply chain to make it economically competitive with fossil fuels. Much research is being pursued on the use of lignocellulosic biomass as an attractive feedstock for future supplies of ethanol. On the other hand, downstream processes of bioethanol separation and dehydration are being studied. Karuppiah et al. (2008) have proposed different design alternatives for the transformation of corn kernels to fuel ethanol, using distillation together with molecular sieves and adsorption units with corn grits to achieve fuel-grade bioethanol. The use of pervaporation membranes has been also analyzed as an alternative to extractive distillation and molecular sieves (Hoch & Espinosa, 2008). The use of light hydrocarbons as supercritical solvents for bioethanol dehydration has been proposed as a low energy consumption technology (Brignole et al., 1987, Horizoe et al., 1993). The basic process consists of two steps, the extraction of bioethanol from the aqueous solution with a near critical solvent, and a final separation of ethanol from the solvent in a distillation train. The light hydrocarbon solvent has good selectivity for ethanol and water-solvent relative volatility becomes greater than

one at the solvent recovery column (water entrainment effect). The inclusion of different alternatives to the basic scheme has been formulated as a mixed integer nonlinear programming (MINLP) problem whose solution has provided improved energy consumption options (Gros et al., 1998, Diaz et al., 2000).

In this work, we further consider alternative integration schemes between process streams within different nonlinear programming (NLP) problems. In particular, we analyze a new scheme that integrates the vapor recompression scheme to the pre-concentration step, which can provide additional reduction in total energy consumption. Thermodynamic predictions are performed with an upgraded Group Contribution with Association Equation of State, GCA-EOS (Jorgensen, 1988; Gros et al., 1996, Ferreira et al, 2004). Numerical results show that process economics are comparable to the use molecular sieves.

2. Process Description

2.1. Basic dehydration with supercritical fluids

In a basic bioethanol dehydration process with supercritical light hydrocarbons (Diaz et al., 2000), the main units are the high pressure extractor and solvent recovery columns, as shown in Fig. 1. The supercritical fluid solvent stream enters the extraction column at the bottom, while the ethanol-water mixture is fed to the top of the column. The column is operated at conditions near the critical temperature of the solvent and at pressure above the critical. The extract (mainly ethanol and solvent) contains a small amount of water. The raffinate mainly consists of water and a very small amount of bioethanol and almost no solvent. The extract is reduced in pressure through a valve and fed to a distillation column to recover the solvent. In this column, the solvent is recovered and the complete dehydration of bioethanol is obtained, through entrainment of water by the near critical solvent. The distillate is returned as the supercritical solvent to the extractor and almost absolute bioethanol is obtained as bottoms product in the distillation unit. In this process, numerical results strongly depend on the accuracy of the thermodynamic model predictions of key phase equilibrium properties.
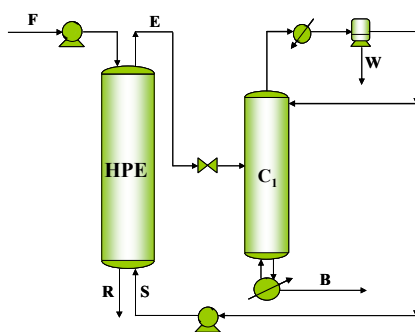

Figure 1. Basic extraction-dehydration scheme. HPE: high-pressure extractor, C_1: dehydration column, F: aqueous feed, R: raffinate, B: dehydrated bioethanol, S: solvent.

2.2. Alternative process schemes

Figure 2 shows the extraction-dehydration process superstructure that embeds process schemes analyzed in this work. The recovery of ethanol from dilute aqueous solutions can be achieved with low energy consumption by ordinary distillation, if the separation goal is the complete alcohol removal from the solution (and not dehydrated ethanol). In

this case, the high alcohol-water relative volatility for dilute aqueous mixtures, allows the increase of ethanol concentration using a simple stripping column. Therefore, *preconcentration* (PC) of the process feed reduces the flowrate of the aqueous solution to the extractor and, consequently, supercritical solvent requirements. The use of a two solvent recovery columns scheme (C1+C2) makes possible energy integration between the feed preconcentration and first solvent recovery column, such as matching the top vapor from the preconcentrator (C) to the reboiler of the first solvent recovery column (HE1). However, the stream matches depend on the preconcentrator operating pressure. There is an alternative vapor *recompression* scheme (RC), in which energy consumption is mainly determined by the compression work provided to the overhead vapor of the first distillation column (C1). The required energy in the column reboiler/condenser (HE3) is supplied by the condensation of the recompressed vapor (V_{C1}). An alternative scheme analyzed in this work is to use a turbine (TC) as driver for the compressor (RC) and integrate the exhaust steam stream to the preconcentrator reboiler (HE1). The turbine operates with middle pressure steam. No external heating services are thus required. The use of vapor recompression is justified from the low temperature difference between top and bottom at this column, achieved when a rather high concentration of solvent is kept in the bottom product. This gives low energy consumption for vapor recompression at the expense of some additional energy consumption by conventional heating in the second separating column.
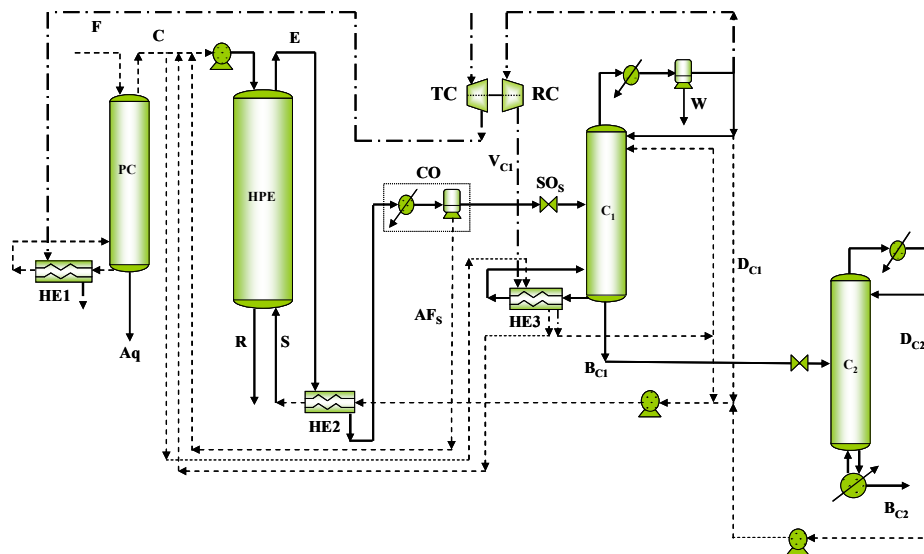
Figure 2. Superstructure for extraction-dehydration process. HPE: high-pressure extractor, C1: dehydration column, C2: second solvent recovery column, F: aqueous feed, R: raffinate, B: dehydrated bioethanol, S: solvent, CO: cooling unit, SOs: solvent organic stream, AFs: aqueous feedback stream, PC: preconcentrator, RC: recompressor, HE1: preconcentrator reboiler; HE2: solvent heater, HE3: column C1 reboiler. Full line: basic flowsheet; dashed line: alternative schemes; dashed point line: optimal scheme.

3. Mathematical model for extraction-dehydration with supercritical fluids

Different process alternatives have been formulated as a series of NLP problems. Main design variables are extraction temperature (TE) and pressure (PE), solvent flow rate (S) and reflux ratio at dehydration first column (RC1). Their bounds are shown in Table 1.

Table 1. Design variable bounds

Variable	Lower bound	Upper bound
Extractor Temperature, T_E (K)	325.00	420.00
Extractor Pressure, P_E (bar)	40.00	100.00
Reflux ratio, R_{C1}	0.30	2.50
Solvent, S (kmol/h)	45.00	1500.00

The process mathematical model (Diaz et al., 2000) includes first principles rigorous models for high-pressure multistage extractors (Kehat & Ghitis, 1981), low and high-pressure distillation columns (Naphtali & Sandholm, 1971) and a multiphase flash (Michelsen, 1982). The key thermodynamic properties of the extraction-dehydration process are based on the Group Contribution Equation of State with Association, GCA-EOS model (Skjold-Jorgensen, 1988, Gros et al, 1996) that provides reliable phase equilibrium predictions at high pressure in mixtures with association. Operating bounds and process specifications have been included as inequality constraints, as shown in Table 2.

Table 2. Inequality constraints

Unit	Constraint	Description	Bound
Extractor	r1	Ethanol recovery (%)	≥ 98.50
Solvent recovery column C_1	r2	Water composition in top vapor phase of C_1	$\leq Y_{H2O(sat)}$
Solvent recovery column C_1	r3	Ethanol recovery (%)	≥ 98.00
Solvent recovery column C_1	r4	Ethanol (solvent free basic) in bottom of C_1	≥ 99.00
Preconcentrator	r5	Ethanol recovery (% molar)	≥ 99.50
Preconcentrator	r6	Energy available from preconcentrator vapor	$\geq QreboilerC_1$
Preconcentrator	r7	Preconcentrator vapor-reboiler C_1 temperature difference	≥ 15.00

The goal of this work is to minimize the dehydration process energy consumption to provide an economically attractive clean technology. The objective function is composed of several terms corresponding to pumping energy for liquids (solvent and aqueous feed) and heating requirement in distillation columns (PC, C1, C2), as well as

their integration in the different proposed flowsheet schemes. Mechanical energy (kJ/kg) has been affected by a factor of 3.0 (Streich & Bolkart, 1982) to convert it to an amount of thermal energy of equivalent cost, so as evaluate the different alternatives on a similar cost basic. Nonlinear programming problems have been solved with a Successive Quadratic Programming algorithm (Biegler and Cuthrell, 1985).

4. Discussion of results

In this work, we consider the dehydration process downstream the fermentation step in a bioethanol plant. A typical feed to this sector is 10,000 kg/h of an aqueous solution with 10 wt% ethanol concentration. Propane is the near critical solvent (Tc=369,8, Pc=41,9 bar). Units specifications are: *extractor,* 10 stages; *first solvent recovery column*, 35 stages, pressure: 25 bar; *second solvent recovery column*: pressure: 12 bar; reflux ratio, 0,70. We have formulated four nonlinear programming (NLP) problems corresponding to the most attractive process schemes determined in previous work (Diaz et al., 2000) and a new integration scheme between turbo-compressor and preconcentrator reboiler.

Table 3 shows optimal conditions and minimum energy consumption for each scheme. As compared to the basic supercritical extraction-dehydration scheme, vapor recompression or feed preconcentration can be highly energy efficient (columns 2 and 3 in Table 3). The last column in Table 3 shows that the proposed scheme integrating the exhaust steam stream from the turbine to the preconcentrator reboiler gives the optimal structure for the high pressure bioethanol dehydration process. This option improves the integrated energy consumption in about: 29% respect to the preconcentration option, 65% respect to the recompression option and 88% respect to the basic scheme. The optimal scheme also shows lower operating temperature and pressure in the extractor, and an important reduction in solvent requirement, as compared to the remaining schemes.

Table 3 Optimal operating conditions and energy consumptions for each alternative process.

	Basic	Vapor Recompression	Preconcentration	Preconcentration + Recompression
T_E (K)	397	393.06	362.81	361.28
S (kmol h^{-1})	760	820.71	194.50	200.00
R_{C1}	1.50	1.50	0.98	0.90
P_E (bar)	100	78.93	55.00	55.00
Ethanol purity (%)	99.00	99.99	99.00	99.00
Ethanol recovery in C_2	98.00	98.00	98.87	98.65
Preconcentrator (kJ kg^{-1})	-	-	3184.98	3188.84
Column C_1 (kJ kg^{-1})	22200.00	22284.46	3735.46	3697.64
Column C_2 (kJ kg^{-1})	500.00	261.33	254.28	255.45
Pumping (kJ kg^{-1})	3500.00	2511.72	291.67	299.18
Recompression (kJ kg^{-1})	-	5.995.32	-	325.73
Integrated energy consumption (kJ kg^{-1})	26200.00	8768.36	4346.79	3082.93

5. Conclusions

We have formulated nonlinear programming problems based on first principles rigorous models with reliable thermodynamic predictions by a Group Contribution Equation of State with association (GCA-EOS), to analyze different designs for bioethanol dehydration plants, using propane as the supercritical or near critical solvent. The GCA-EOS model gives reliable properties predictions of highly nonideal azeotropic mixtures at low and high pressure conditions. Four process schemes have been optimized (basic supercritical extraction-dehydration, vapor recompression, feed preconcentration and preconcentration + vapor recompression). Numerical results show that the *preconcentrator+recompression* scheme provides a significant reduction in energy consumption, making the high pressure process comparable to the use of the well-known dehydration technology with molecular sieves. We are currently including both capital and operating costs in our analysis to perform a detailed cost comparison. Nevertheless, optimization results indicate that the supercritical extraction-dehydration of bioethanol can be energy efficient, helping to make bioethanol a sustainable and economically competitive alternative to non-renewable fossil fuels.

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