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Bioenergy II: Modeling and Multi-Objective Optimization of Different Biodiesel Production Processes

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Abstract

One of the most promising renewable fuels proposed as an alternative to fossil fuels is biodiesel. The competitive potential of biodiesel is limited by the price of vegetable oils, which strongly influences the final price of biofuels. An appropriate planning and design of the whole production process, from the seed to the biodiesel end product, is essential in order to contain the fallout of energy inefficiencies in the high price of the end product. This study focuses on the characteristics of the production process currently used to produce biodiesel.

Refined vegetable oil can be converted into biodiesel by means of a great variety of techniques and technologies, many of which are still not suitable for application on an industrial scale. The solution of greatest interest is homogeneous alkaline transesterification with KOH and methanol. Even when dealing with this type of conversion, it is impossible to establish a universal pattern to describe the conversion or purification stages because there are various possible solutions that make each system different from another. When we look more closely at the state of the art in industrial biodiesel production plants, we also encounter the potential problems introduced by the type and characteristics of the raw materials.

Comparing some of the reference solutions that have inspired numerous installations, an optimization analysis was conducted using ASPENPLUS 2006, for the modeling of the process, and modeFRONTIER 4.1 for the optimization procedure. The optimization analysis was carried out using a multi-objective genetic algorithm optimization in order to define the configuration of the main parameters that guarantee the best trade-off between the maximization of the purity of some

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important compounds and the minimization of energy requirements in the process. The results of this analysis were Pareto frontiers that identify a family of configurations which define the best trade-off between the objectives. Using the Pareto frontiers we then selected the configuration that requires the minimum energy consumption. Among these optimal configurations there is one which guarantees the lowest specific energy consumption while all the optimal configurations obtained respected the requirements of EN 14214, in terms of biodiesel quality.

KEYWORDS: biodiesel, sunflower oil, process simulation, mode frontier, genetic algorithm

INTRODUCTION

Biodiesel is a mixture of fatty acid esters derived from the triglycerides contained in vegetable oils or animal fats (Meher et al., 2006). There are various methods for converting vegetable oils into biodiesel, but the most commonly used is a transesterification reaction between an alcohol and the vegetable oils, induced by a catalyst to form fatty acid esters and glycerol (Ma and Hanna, 1999). The nature of the transesterification reaction depends on the type of catalyst used, which may be alkaline, acid or enzymatic. Transesterification is a three-step reaction in which triglycerides are converted consecutively into diglycerides, monoglycerides and glycerol. Fatty acid esters are produced at each stage of the reaction (Freedman et al, 1986).

$$\text{Triglycerides (TG)} + R'OH \leftrightarrow \text{Diglycerides (DG)} + R'COOR_1 \quad (1)$$

$$\text{Diglycerides (DG)} + R'OH \leftrightarrow \text{Monoglycerides (MG)} + R'COOR_2 \quad (2)$$

$$\text{Monoglycerides (MG)} + R'OH \leftrightarrow \text{Glycerol (GL)} + R'COOR_3 \quad (3)$$

The most common alcohol used is methanol, due to its low price and availability (Khnote et al, 2005). The relative esters obtained are called Fatty Acid Methyl Esters (FAME).

Alkaline transesterification is more efficient and takes place faster than its acid counterpart, but the oil being treated should be anhydrous and have an acid value below 1 (Wright et al., 1944; Feuge and Grose, 1949; Freedman et al., 1984). Any water in the reacting mixture will use up the catalyst, reducing the yield of the reaction.

Designing the industrial biodiesel production process involves considering all the stages of conversion and biodiesel purification, and the equipment required. We consider two possible industrial processes, based on the alkaline transesterification of refined vegetable oil and methanol-like alcohol. The processes were modeled with ASPENPLUS 2006 (20.0.3595, Aspen Technology Inc.), for a transesterification reaction with KOH and methanol at a temperature of 60°C. Subsequently we also studied the problem of optimization, considering the specific energy consumption in order to produce biodiesel with the standards required by EN 14214. The optimization problem was solved with modeFRONTIER 4.1.1 (Esteco, 2008), using a multiobjective genetic algorithm (MOGA-II).

PROCESS DESIGN

To optimize the process and identify the configuration with the lowest specific energy consumption, complete process simulations were performed with the ASPENPLUS software. This software includes a full database of compounds to choose from. The compounds needed are methanol, KOH, glycerol, potassium phosphate, phosphoric acid, water, triolein and methyl oleate. The software requires the determination of the proper thermodynamic model in order to predict the phase equilibria of the systems. The phase equilibria to be predicted are the vapor-liquid equilibria (VLE) and the liquid-liquid equilibria (LLE) of biodiesel mixtures. The most suitable theoretical models for the prediction of phase equilibria are those based on group contributions, which are able to predict phase equilibria when the compounds involved show great differences in shape and molecular structure. Among these models UNIFAC is the most commonly used (Negi et al., 2006). Recent publications on the subject of phase equilibria for mixtures containing biodiesel report that the most suitable models for the prediction of phase equilibria are UNIFAC-DORTMUND, GCA-EOS and A-UNIFAC (Andreatta et al., 2007; West et al.,2008; Hidetoshi et al., 2009]. These three models are all able to predict VLE but only UNIFAC-DORTMUND is also able to predict LLE and for this reason the UNIFAC-DORTMUND model was chosen for our study.

For the simulation we also needed to identify the layout of the process, defining all the equipment required and its relative position. The two processes considered are illustrated in Figs 1-2. The processes analyzed here treated about 2000 kg/h of vegetable oil, using an oil to methanol ratio of 1:6 and a KOH ratio of 1% by mass of vegetable oil (Freedman et al, 1984).

PROCESS OPTIMIZATION

The optimization of an entire process is a difficult task. The problem requires the identification of all the variables, objectives and constraints to be met. Multiobjective optimization identifies a set of optimal trade-offs that can satisfy all the constraints and objectives defined (Abraham et al., 2005). The result of the optimization procedure is a Pareto-optimality, from which the solution of the optimization problem is chosen. Optimization was carried out with modeFRONTIER software, which is a tool that facilitates the analysis of optimization problems. This software requires the definition of the variables, constraints and objectives, and the optimization algorithm to be used. Two different objective functions were defined, one representing the quality of the compounds produced and another regarding energy consumption. These two functions are as follows:

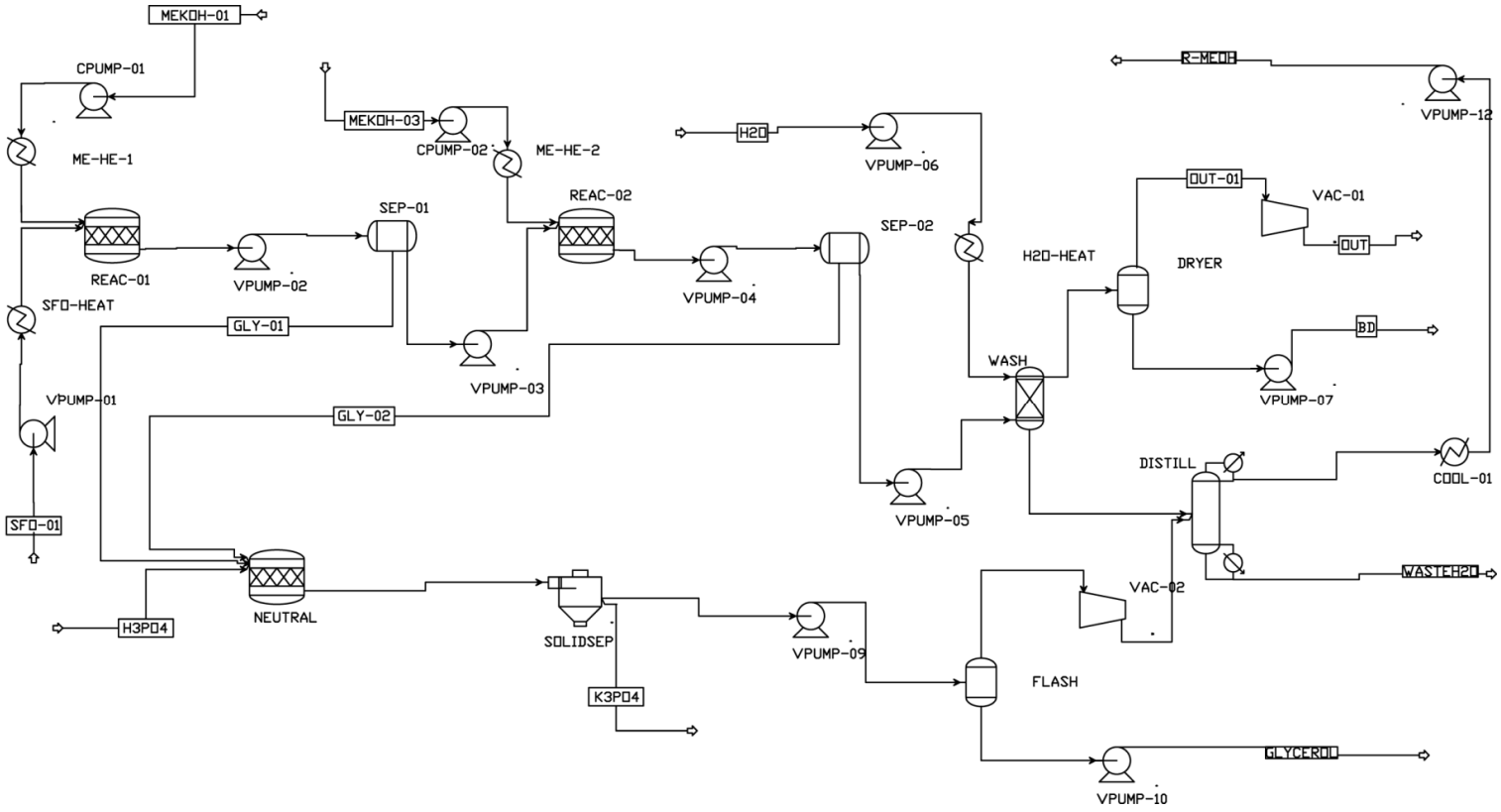

Figure 1 PROCESS-I layout

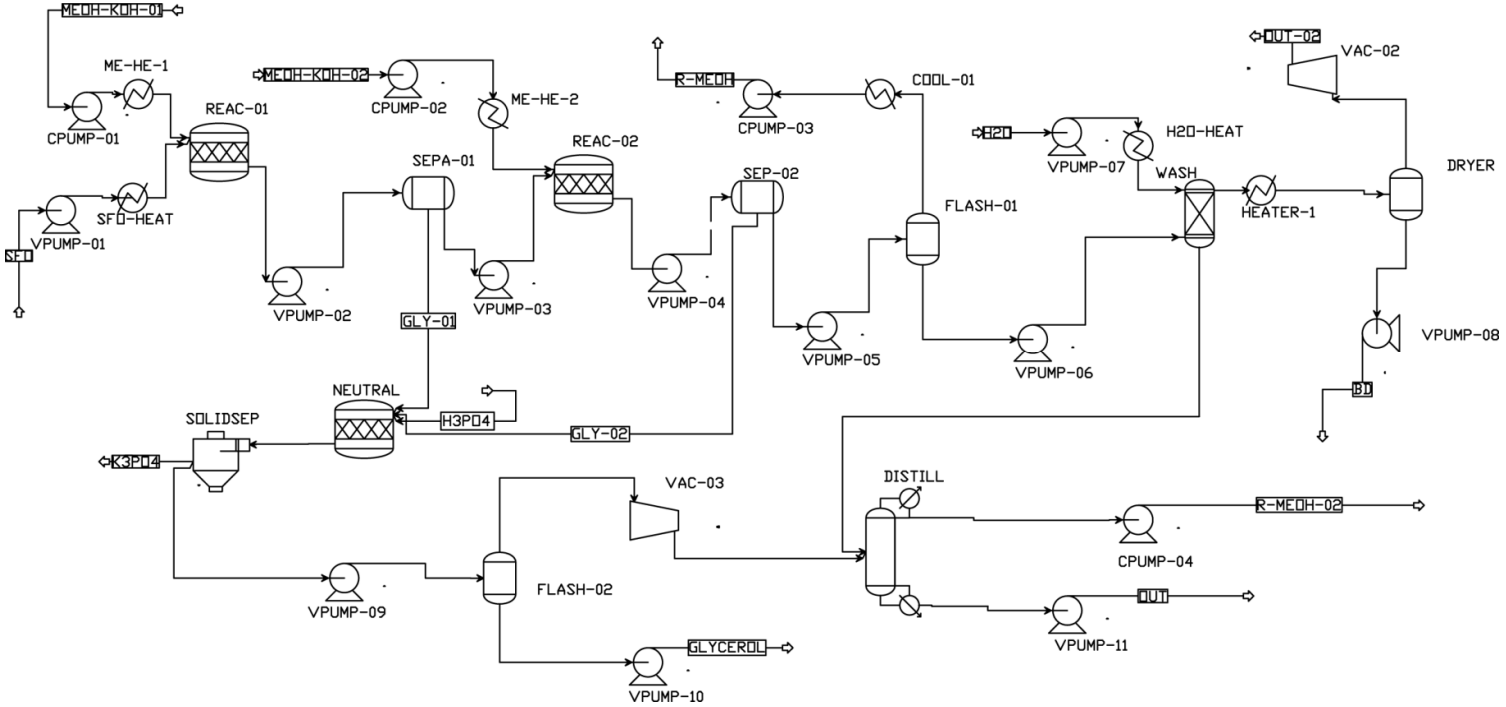

Figure 2 PROCESS-II layout

$$Y = \frac{\dot{m}_{BD} * x_{BD} + \dot{m}_{GLY} * x_{GLY} + \dot{m}_{MEOH} * x_{MEOH}}{\dot{m}_{BD} + \dot{m}_{GLY} + \dot{m}_{MEOH}} \quad (4)$$

$$Z = E_T \quad (5)$$

The constraints defined are those set by EN 14214 for biodiesel, and purity for the glycerol and methanol produced.

The optimization algorithm used is the multiobjective genetic algorithm. This algorithm uses an elitism operator able to preserve some excellent solutions without bringing premature convergence to local optimal frontiers (Abraham et al., 2005). The algorithm requires the identification of a space of solutions, from which the generations start. The starting domain is the one defined by the full factorial design algorithm.

The processes modeled were inspired by technical reports on the biodiesel production process in Alcala' de Henares for PROCESS-I (Ministerio de industria turismo y commercio, IDEA, 2005), and Bogotà for PROCESS-II (CORPODIB et al, 2003). PROCESS-I consisted of a two-step reactor with an intermediate decanter (SEP-01) for separating the glycerol from the biodiesel. The reactors are modeled as a stoichiometry reactor, where it is possible to identify the reactions of transesterification and the degree of conversion of each compound. The first reactor ensures an 86% conversion of vegetable oil, while with the second step of reaction 98% conversion is reached. The amount of methanol and catalyst delivered in each reactor is calculated starting from the proportion defined above, considering a flow rate of 2000 kg/h of vegetable oil for the first reactor. The flow rate considered for the second reactor is the amount of unreacted oil after the first step. The output from the second decanter (SEP-02) was delivered to a liquid-liquid extraction column (WASH), where water was used as the solvent to remove any residual glycerol and unreacted methanol from the biodiesel. After this treatment, the biodiesel was sent to a dryer (DRYER) to eliminate any residual water and thus comply with EN 14214. The separated glycerol was delivered to a neutralizing reactor (NEUTRAL), where the residual catalyst was removed. After neutralization, the methanol was extracted by a flash distillation unit (FLASH-01) and the glycerol obtained was delivered to a storage tank. The methanol extracted from the glycerol stream and the waste water from the liquid-liquid extraction column were sent to a distiller column (DISTILL), which is needed to further purify the methanol and enable its recovery and reuse. On the contrary, in PROCESS-II once the glycerol was separated from the biodiesel, the unreacted methanol was extracted from the reaction mixture by means of a flash distillation unit (FLASH-01), and the biodiesel was treated in a liquid-liquid extraction column. To comply with legal requirements, the biodiesel was then dried (DRYER). The dryer defined is a flash evaporator. In this case the operating pressure is fixed at 80 kPa. The operating temperature was considered a variable

to be optimized, as shown in table 1. The separated glycerol was delivered, after neutralizing (NEUTRAL) the catalyst, to a flash distilling unit (FLASH-02). Neutralization was performed in an equilibrium reactor using phosphoric acid, where the neutralization reaction is as follows:

$$3\ KOH + H_3PO_4 \leftrightarrow K_3PO_4 + 3\ H_2O \quad (6)$$

The phosphoric acid delivered to the reactor is mixed with water and has a total flow rate of 18 kg/h, with an acid concentration of 85% in weight.
The methanol extracted and the waste water were delivered to a distilling column (DISTILL) to ensure the maximum methanol quality and the minimum methanol content in the waste water. The variables and their range of variability for each process are listed in table 1.

Table 1 Variables influencing the optimization algorithm

PROCESS-I				
		Lower Value	Intermediate Value	Upper Value
T_{Water}	[°C]	30	65	100
Reflux Ratio		0.8	2.9	5
N_{Tray}		10	20	30
T_{Flash}	[°C]	90	145	200
T_{Dryer}	[°C]	120	185	250
$\dot{m}_{Water}$	[kg/h]	70	185	300
PROCESS-II				
		Lower Value	Intermediate Value	Upper Value
T_{Water}	[°C]	30	65	100
Reflux Ratio		0.75	1.12	1.5
$T_{Flash-01}$	[°C]	75	112	150
$T_{Flash-02}$	[°C]	75	112	150
T_{Dryer}	[°C]	120	185	250
$\dot{m}_{Water}$	[kg/h]	100	400	700

The outcome of optimization is a set of solutions representing the Pareto frontier, which is given in figure 3 for PROCESS-I and in figure 4 for PROCESS-II. The Pareto frontier obtained represents the energy requirements for a given process configuration.

RESULTS AND DISCUSSION

The Pareto charts obtained plot the energy requirements against the quality of the material produced for each configuration. To identify the process with the smallest amount of energy consumed, a specific energy consumption was calculated. The specific energy consumption is obtained through dividing the energy consumption by the flow rate of biodiesel output for each process.

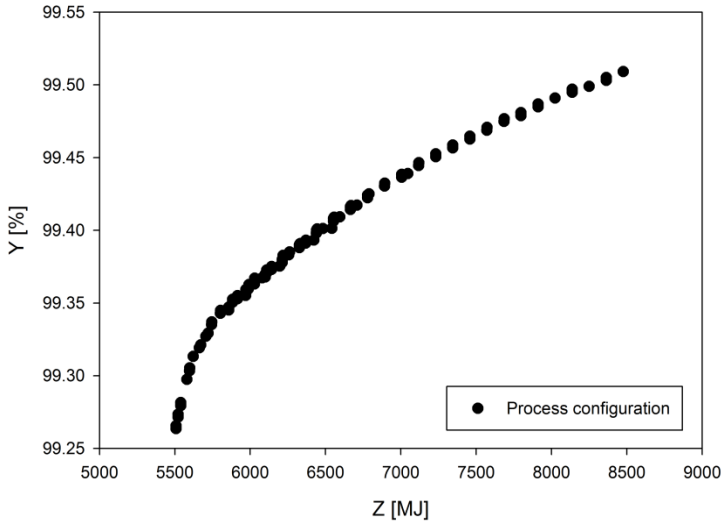

Figure 3 PROCESS-I Pareto Frontier

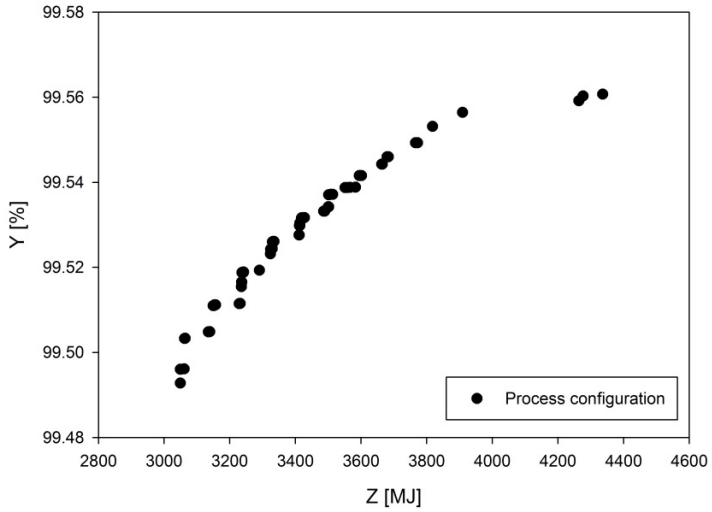

Figure 4 PROCESS-II Pareto Frontier

The configuration used for each process, is the one identified by the intersection of the minimum energy consumed and the maximum quality of material produced. The configurations identified and the technical results obtained are shown in table 2.

Table 2 Process configurations and technical results

PROCESS-I			PROCESS-II		
T_{Water}	[°C]	36	T_{Water}	[°C]	32.5
Reflux Ratio		2.8	Reflux Ratio		0.84
N_{Stage}		17	$T_{Flash-01}$	[°C]	75.5
T_{Flash}	[°C]	90	$T_{Flash-02}$	[°C]	148
T_{Dryer}	[°C]	199	T_{Dryer}	[°C]	250
$\dot{m}_{Water}$	[kg/h]	70	$\dot{m}_{Water}$	[kg/h]	114

Stream	Flow rate [kg/h]	Purity [%]	Stream	Flow rate [kg/h]	Purity [%]
Biodiesel	1987	99.5	Biodiesel	1984	99.4
Glycerol	246	95.4	Glycerol	216.6	97.7
Methanol	500	98	Methanol	515.3	99.4

Energy consumption	Total [MJ/h]	Specific [MJ/kg]	Energy consumption	Total [MJ/h]	Specific [MJ/kg]
E_T	5507	2.77	E_T	3049	1.53

CONCLUSION

In this work we have compared and optimized two possible processes for the production of biodiesel. The processes were first analyzed in ASPENPLUS to define the flow sheet and the equipment needed and subsequently optimized using modeFRONTIER. The results of the optimization are Pareto frontiers, that represent all the possible configurations with the best trade-off between energy consumption minimization and material quality maximization. These optimal configurations require a specific energy consumption of 2.7 MJ/kg for PROCESS-I and 1.5 MJ/kg for PROCESS-II. The quality of biodiesel produced satisfies the standards required for each layout. According to the Pareto frontier the process with the lowest specific consumption is PROCESS-II.

NOTATION

$\dot{m}$	Mass flow rate, kg/h
x	Material purity, %
Y	Objective function, %
Z	Objective function, MJ
E	Energy, MJ
N	Number
T	Temperature
VPUMP	Volumetric pump
CPUMP	Centrifugal pump
VAC	Vacuum pump
REAC	Reactor
SEP	Decanter
NEUTRAL	Neutralization reactor
SOLIDSEP	Separator of solid compound
FLASH	Flash distillation unit
WASH	Liquid-liquid extraction column
DISTILL	Distillation column
DRYER	Dryer
ME-HE	Heater of methanol stream
H2O-HEAT	Heater of water stream
SFO-HEAT	Heater of vegetable oil
COOL	Methanol condenser
MEKOH	Mixture methanol-potassium hydroxide
SFO	Vegetable oil stream
H3PO4	Phosphoric acid
K3PO4	Potassium phosphate
BD	Biodiesel
GLY	Glycerol stream to be purified
GLYCEROL	Glycerol output
R-MEOH	Recycled methanol
WASTEH2O	Waste water from distillation column

Subscripts

BD	Biodiesel
GLY	Glycerol
MEOH	Methanol
T	Thermal
Tray	Distillation column tray

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