CHEMICAL ENGINEERING TRANSACTIONS
VOL. 29, 2012
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at: www.aidic.it/cet
Guest Editors: Petar Sabev Varbanov, Hon Loong Lam, Jiří Jaromír Klemeš

ISBN 978-88-95608-20-4; **ISSN** 1974-9791
DOI: 10.3303/CET1229191

Energy Efficient Recovery of Methanol and Glycerol in Biodiesel Production

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Biodiesel is a renewable fuel that consists of fatty acids methyl esters – currently produced by trans-esterification of glycerides with methanol. After the biodiesel synthesis, the downstream processing steps involve the purification of crude glycerol, as well as the separation of excess methanol (recyclable), glycerol by-product and water (from washing and pre-treatment step). The separation of the ternary mixture methanol-water-glycerol is carried out in a conventional direct sequence that requires two distillation columns and rather high amounts of energy.
This study proposes an efficient process intensification method for this ternary separation, namely the use of a dividing-wall column (DWC) that is able to separate all products at high purity, in only one equipment unit. AspenTech Aspen Plus was used as a computer aided process engineering tools to perform the rigorous steady-state simulations, as well as the optimization of the new DWC separation alternative. In order to allow a fair comparison, all designs were optimized using the state of the art sequential quadratic programming (SQP) method. Remarkable, the results show that the proposed DWC system requires 27 % less energy and 12 % lower investment costs, thus having a significant contribution towards inexpensive biodiesel production.

1. Introduction

Biodiesel is one of the most promising clean and renewable fuels – consisting of fatty acid methyl esters (FAME) – and represents an alternative for petroleum diesel. Currently, biodiesel is produced from green sources such as vegetable oils, animal fat or waste cooking-oils (Bowman et al., 2006; Lam et al., 2010; Leung et al., 2010). The most widespread manufacturing technologies use homogeneous catalysts, in processes where both reaction and separation steps can create bottlenecks. Although reactive separations were recently proposed for the esterification of free fatty acids (FFA) to FAME (Kiss, 2010, 2011; Kiss and Bildea, 2011, 2012), the vast majority of existing biodiesel plants are based on trans-esterification of tri-glycerides leading to biodiesel and glycerol by-product (Meher et al., 2006; Qiu et al., 2010, Leung et al., 2010).
The biodiesel production by trans-esterification requires several expensive downstream processing steps such as the purification of biodiesel, as well as the separation of excess methanol, glycerol by-product and water – from the washing and FFA pre-treatment steps (Dunford, 2007; Fjerbaek et al., 2009; Helwani et al., 2009; Chemstations, 2010; Balat and Balat, 2010; Atadashi et al., 2011). In practice, the separation of the ternary mixture methanol-water-glycerol is carried out in a conventional direct sequence that requires two distillation columns and demands plenty of energy – see flowsheet illustrated in Figure 1, left (Dunford, 2007; Helwani et al., 2009; Chemstations, 2010).
In order to overcome this problem, several energy efficient distillation solutions based on process integration and intensification techniques (heat-integrated distillation column, reactive distillation,

Please cite this article as: Ignat R. M. and Kiss A. A., (2012), Energy efficient recovery of methanol and glycerol in biodiesel production, Chemical Engineering Transactions, 29, 1141-1146

thermally coupled columns) were studied (Asprion and Kaibel, 2010; Harmsen, 2010; Dejanović et al., 2010; Kiss and Bildea, 2011; Yildirim et al., 2011). One of the most promising process intensification technologies in distillation is the dividing-wall column (DWC), as it allows significantly lower investment and operating costs while also reducing the equipment footprint. In this study we propose a new separation alternative for the ternary mixture methanol-water-glycerol, based on DWC as the key separation unit for the large scale biodiesel production (Figure 1, right). AspenTech Aspen Plus was used as a powerful computer aided process engineering tool in order to perform rigorous simulations of the classic sequence of two distillation columns and the alternative based on DWC. These scenarios were both optimized using the state of the art sequential quadratic programming (SQP) method in terms of minimizing the total heat duty of the sequence, constraint by the required purity and recovery of the products, using several optimization variables: total number of stages, feed stage and side stream location, reflux ratio, liquid and vapor split.

2. Problem statement

The biodiesel production by trans-esterification requires several expensive downstream processing steps such as the purification of crude glycerol, as well as the separation of excess methanol (recyclable stream), glycerol by-product and water (from the washing and FFA pre-treatment step). The problem is that the separation of the ternary mixture methanol-water-glycerol is still carried out in a conventional direct sequence that requires two distillation columns (Figure 1, left), a quite large footprint and significantly high amounts of energy. To solve this problem, this study proposes an efficient process intensification method for this ternary separation, namely the use of a dividing-wall column (DWC) that is able to separate all products at high purity, in only one equipment unit (Figure 1, right).

3. Results and discussion

In this study we consider the separation of the ternary mixture methanol-water-glycerol as described in the literature (Dunford, 2007; Helwani et al., 2009; Chemstations, 2010). For the base case (direct distillation sequence) and the DWC alternative the feed basis is 2900 kg/h – equivalent to a biodiesel production rate of about 100 ktpy. The target product purity considered for each product cut is min. 99.5 %wt. Note that the reactants and product amounts for trans-esterification are in the mass ratio of 100:22:11 for biodiesel: methanol:glycerol, meaning that 11 kg of glycerol is synthesized per each 100 kg of biodiesel produced (Dunford, 2007). Typically, the weight amounts of methanol and glycerol are similar, while water is present in lower quantities (Dunford, 2007; Chemstations, 2010). Steady-state simulations were carried out in AspenTech Aspen Plus® using the rigorous RADFRAC unit enhanced with the RateSep (rate-based) model.

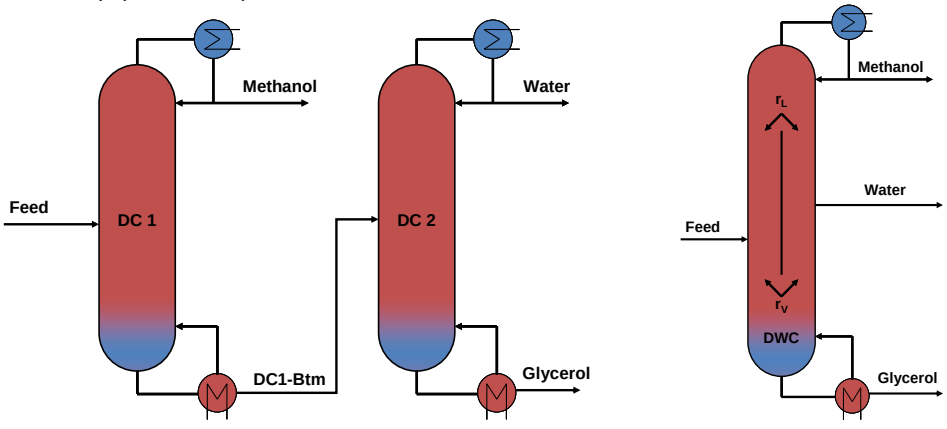

Figure 1. MeOH-water-glycerol separation in a direct sequence (left) and a dividing-wall column (right)

Table 1. Design parameters of an optimal direct sequence of two columns

Design parameters	DC1	DC2	Unit
Flowrate of feed stream	2900	1531.5	kg / h
Feed composition (mass fractions)			
Methanol : Water : Glycerol	0.473 : 0.054 : 0.473	0 : 0.102 : 0.898	–
Temperature of feed stream	60	122.7	°C
Pressure of feed stream	1.2	0.53	bar
Operating pressure	0.5	0.5	bar
Column diameter	0.9	0.4	m
Total number of stages	14	12	–
Feed stage	9	7	–
Reflux ratio	1.4	0.2	kg / kg
Methanol product purity	99.9 / 99.9	-	%wt / %mol
Water product purity	-	99.6 / 99.8	%wt / %mol
Glycerol product purity	-	99.9 / 99.9	%wt / %mol
Reboiler duty DC1	1080	250	kW
Condenser duty DC1	–1029	-120	kW

Due to the nature of the components involved in the separation, UNIQUAC was selected as the most accurate property model (Kiss et al., 2012; Kiss and Bildea, 2012). Both configurations (base case and DWC alternative) described hereafter were optimized in terms of minimal energy demand using the sensitivity analysis tool and the state of the art sequential quadratic programming (SQP) method available in Aspen Plus (Bartholomew-Biggs, 2008). This can be linked to minimizing the total heat duty of the sequence, constrained by the required purity and recovery of the products, using sensitivity analysis and the SQP optimization tool from Aspen Plus. Several optimization variables were used: total number of stages, feed-stage location, side-stream location, location and length of the dividing wall, reflux ratio, liquid and vapor split (Kiss and Suszwalak, 2012).

3.1 Direct distillation sequence

Figure 1 (left) shows the direct distillation sequence as the conventional industrial practice for methanol recovery and glycerol separation (Dunford, 2007; Helwani et al., 2009; Chemstations, 2010). Methanol is collected as top distillate from the first distillation column (DC1), while the bottom product – consisting of water and glycerol – is fed to the second distillation column (DC2). The recovered methanol is typically recycled back to the trans-esterification reactor. High purity glycerol is obtained as bottom product, and water as distillate product of DC2, respectively. Both distillation columns are operated at 0.5 bar in order to keep the temperature in the reboiler sufficiently low to prevent the glycerol degradation. Table 1 provides the optimal design parameters for this base case, while Figure 2 conveniently plots the liquid composition profiles.

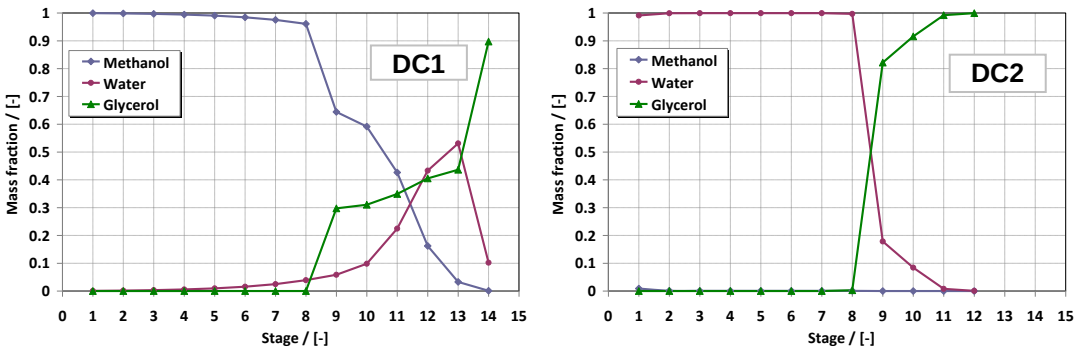

Figure 2. Composition profile in DC1 and DC2 units of the conventional direct distillation sequence

Table 2. Design parameters of an optimal dividing-wall column

Design parameters	Value	Unit
Flowrate of feed stream	2900	kg / h
Feed composition (mass fractions)		
Methanol : Water : Glycerol	0.473 : 0.054 : 0.473	–
Temperature of feed stream	60	°C
Pressure of feed stream	1.2	bar
Operating pressure	0.5	bar
Column diameter	1.1	m
Number of stages pre-fractionator side	10	–
Total number of stages DWC	30	–
Feed stage pre-fractionator	7	–
Side stream withdrawal stage	22	–
Wall position (from / to stage)	15-25	–
Reflux ratio	0.83	kg / kg
Liquid split ratio (r_L)	0.42	kg / kg
Vapor split ratio (r_V)	0.25	kg / kg
Methanol product purity	99.9 / 99.8	%wt / %mol
Water product purity	99.6 / 99.8	%wt / %mol
Glycerol product purity	99.9 / 99.9	%wt / %mol
Reboiler duty	975	kW
Condenser duty	–793	kW

3.2 DWC alternative

The DWC was designed according to the rules described in the literature (Rangaiah et al., 2009; Dejanović et al., 2010; Rong, 2011; Yildirim et al., 2011). A sequence of two rigorous RADFRAC units was used to model the DWC as no off-the-shelf DWC unit is available in the current commercial process simulators. This configuration is thermally equivalent to a DWC, as long as the temperature difference on both sides of the wall indicates that there is no heat transfer between the two sides (Dejanović et al., 2010; Yildirim et al., 2011).

The state-of-the-art SQP method and the efficient sensitivity analysis tool from Aspen Plus were also employed. Methanol is recovered as top distillate, glycerol as bottom product and water is withdrawn as side stream of the main column. Figure 3 plots the temperature and liquid composition profiles in the DWC unit, while the key parameters of the optimal design are presented in Table 2. Remarkable, the temperature difference between the two sides of the wall is very low – less than ~25 °C – such conditions being easily achievable in the practical application with little heat transfer expected and negligible effect on the column performance (Dejanovic et al., 2010; Yildirim et al., 2011).

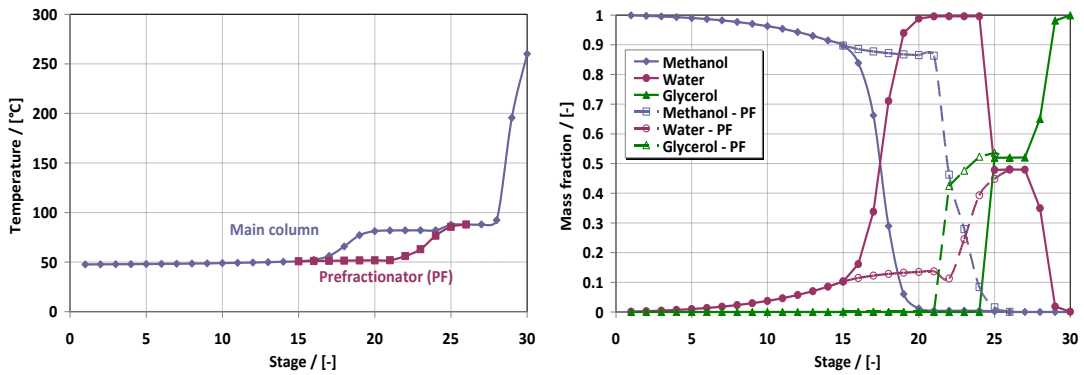

Figure 3. Temperature and composition profile in the dividing-wall column (dotted line means the pre-fractionator or the feed section of the column)

Table 3. Head-to-head comparison of conventional vs DWC alternative

Key performance indicators	Conventional process	DWC alternative	Savings
Total investment cost (TIC)	$ 563,429	$ 499,087	11.8 %
Total operating costs (TOC)	$ 280,491	$ 208,402	27.0 %
Total annual costs (TAC)	$ 336,834	$ 258,310	24.4 %
Energy requirements (kW·h/t glycerol)	967.50	709.30	26.7 %
CO_2 emissions (kg CO_2/h·t glycerol)	135.31	99.19	26.7 %

3.3 Process comparison

In order to perform a fair comparison of the two process alternatives, the total investment costs (TIC), total operating costs (TOC) and total annual costs (TAC) were calculated. The equipment costs are estimated using correlations from the Douglas textbook to the price level of 2010, as described by Dejanović et al. (2010). For the TAC calculations, a plant lifetime of 10 years was considered. While the accuracy of the correlations is in the range of acceptable and realistic ± 30 %, this figure of the accuracy is less important when comparing design alternatives since the error is consistent in all cases. Table 3 provides a head-to-head comparison of the key performance economic indicators, while Figure 4 conveniently illustrates the costs of the processes considered. The DWC alternative is the most efficient in terms of energy requirements allowing energy savings of 27 % while also being the least expensive in terms of investment and operating costs – leading to 25 % lower total annual costs.

The energy requirements are closely linked to the CO_2 emissions, but only when no heat integration is considered. When part of the process heat is reused instead of primary energy, then the CO_2 emissions are lower as compared to the figure expected from the energy data. The CO_2 emissions were calculated according to previously described methods (Kiss and Suswalak, 2012). Table 3 also lists the specific amount of CO_2 emissions per ton of glycerol. Since these emissions are closely linked to the amount of energy required, it comes as no surprise that the DWC alternative is again in pole position exhibiting the lowest carbon footprint.

4. Conclusions

Compared to an optimized conventional direct sequence of two distillation columns, the results of the rigorous simulations performed in Aspen Plus show that significant savings – of 27 % in the energy requirements and 12 % in the investment cost – are possible for the process intensification alternative based on the novel proposed DWC. Notably, the new separation scheme also requires less equipment units and reduced plant footprint. Based on these results, the use of a DWC in biodiesel production is especially interesting in case of building new large biodiesel plants, but also in the case of revamping existing plants – where the equivalent Petlyuk setup should be certainly taken into consideration.

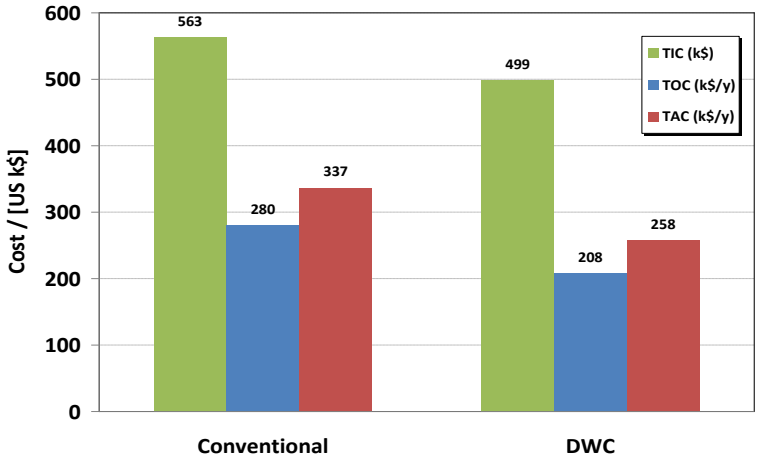

Figure 4. Comparison of conventional and DWC alternatives in terms of key performance indicators: total investment, operating and annual costs

Acknowledgments

The financial support from the Sector Operational Program Human Resources Development 2007-2013 of the Romanian Ministry of Labor, Family and Social Protection through the Financial Agreement POSDRU/88/1.5/S/61178 is gratefully acknowledged.

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