Article

Modelling the Effect of Water Removal by Reverse Osmosis on the Distillation of Mixtures of Short-Chain Organic Acids from Anaerobic Fermentation

Serena Simonetti and Davide Dionisi *

Materials and Chemical Engineering Group, School of Engineering, University of Aberdeen, Aberdeen AB24 3UE, UK; serena.simonetti23@gmail.com
* Correspondence: davidedionisi@abdn.ac.uk; Tel.: +44-(0)-1224-272814

Abstract: Anaerobic fermentation (AF) to produce sustainable short-chain organic acids (SCOAs) has found no commercial application so far. This is due to several limitations, including the high energy consumption of the SCOAs' separation from water by distillation. This study used AspenPlus simulations to investigate the benefits of reverse osmosis (RO) to remove water and concentrate the SCOAs from AF before their separation by distillation. The effect of RO on distillation reflux ratio, heat energy requirements, column diameter and equipment costs was simulated for the processing of model SCOA-containing streams, representing AF effluents. A total of 90 simulations were carried out, investigating three different SCOA compositions, corresponding to different ratios of lactic, acetic and propionic acids, three different concentrations of the total SCOAs (10, 50, 100 g/kg in the stream entering RO) and different extents of water removal by RO. RO brought a reduction in the distillation reboilers' duty of up to more than 90%, with a reduction of column diameter of up to more than 70%. The total energy consumption, equipment cost and NPV (net present value) of the RO plus distillation process were in all cases more favourable than for the process without membranes.

Keywords: anaerobic fermentation; reverse osmosis; distillation; short-chain organic acids

1. Introduction

Anaerobic fermentation (AF) has been proposed as a process to produce short-chain organic acids (SCOAs), e.g., acetic, butyric, propionic, lactic acid [1,2]. SCOAs are produced in millions of tonnes per year globally for a variety of uses in the food and in the chemical industries [3–5]. Current production processes for SCOAs mainly use fossil resources as feedstocks and are mainly based on high-temperature chemical processes with metal catalysts [6], causing concerns about their sustainability. On the other hand, AF can produce SCOAs from organic waste using open mixed microbial cultures. AF is the same process as the well-known and widely used anaerobic digestion (AD) process but with the operating conditions controlled to avoid the conversion of the SCOAs to methane, the final digestion product. Compared with current processes for SCOA production from fossil resources, SCOA production with AF has the advantages of using biomass or organic waste, which are renewable resources, of using temperature close to ambient values and of not requiring external addition of metal catalysts which are too a non-renewable resource [6].

Despite the advantages of AF for the production of SCOAs, no commercial plant currently uses this process to produce SCOAs. Indeed, production of SCOAs via AF also brings several disadvantages that have so far prevented its full-scale commercialization. The reaction rate of biological processes is slower than that of chemical processes, and therefore AF requires large reactor volumes. AF produces mixtures of SCOAs rather than the pure substances from chemical processes, therefore requiring a higher extent of separation and purification. Furthermore, the mixtures of SCOA from AF are diluted in water that accounts for most of the mass of AF effluents. SCOAs are present in AF effluents

in a wide range of concentrations, from a few g/L to over 100 g/L [7]. The separation and purification of SCOAs from AF effluents is one of the main challenges towards the development of AF processes at commercial scale.

Many processes have been proposed for the separation and purification of mixtures of SCOAs in water [8,9], e.g., precipitation, chromatography, liquid–liquid extraction. Although these processes have found application in some cases, they are not considered suitable for the diluted mixtures of SCOAs in water produced by AF.

Distillation and membrane filtration are the separation and purification processes considered in this study. Distillation can be used to separate SCOA mixtures; however, its application is limited by the presence of azeotropes, by the thermal instability of some SCOAs (e.g., lactic acid) and by the diluted nature of AF effluents with consequent high energy costs due to the need to vaporize large volumes of water [10]. Membrane processes have also been investigated for the separation and purification of SCOAs from AF: nanofiltration (NF) membranes were used successfully to concentrate diluted solutions of acetic and butyric acid in water [11]; the concentration of diluted solutions of acetic acid with various types of membranes, including NF and reverse osmosis (RO), was reviewed showing several examples of successful application [5]; NF and RO were successfully used to concentrate solutions of SCOAs from AF showing, under the optimum conditions, only very little losses of SCOAs in the permeate [12,13]; RO was also used successfully to concentrate mixtures of acetic acid and sugars, showing that retention of acetic acid is very dependent on the RO operating conditions [14].

This study investigated, by means of process simulations, the combination of RO and distillation to remove water and purify the SCOAs from AF. To the best of our knowledge, there is no investigation in the literature about the combination of RO and distillation for the separation of these types of mixtures. In the process concept considered in this study, RO is used on the AF effluents, after removal of the suspended solids, to remove water and concentrate the SCOAs, prior to removal of the remaining water and separation of the acids by distillation. The investigated process is expected to have several benefits. The water removal and concentration of the SCOAs in the RO process is expected to reduce the energy consumption and equipment size of the distillation process. In addition, RO only uses electricity as energy input while distillation typically uses natural gas as energy source and steam as energy vector in reboilers. Since electricity is more easily obtainable than steam from renewable resources, the investigated process would contribute to improving the sustainability of SCOA production from AF.

This study used simulations to calculate the benefits of water removal by RO on energy use, equipment size and economic feasibility of the combined RO-distillation process. It is important to observe that most of the process conditions simulated in this study have not been experimentally investigated yet. Indeed, the experimental study of RO of SCOA mixtures is limited to the studies cited above and to the preliminary investigation carried out in our group with diluted SCOA mixtures (Supplementary Materials, Figure S1, [15]). Similarly, the study of distillation for the separation of SCOA mixtures has been limited by the high energy costs required for the removal of large volumes of water, as discussed above.

The value and novelty of this study is to provide quantitative results on which process configurations are expected to be more beneficial and more sustainable for the separation and purification of SCOAs. It is then expected that the most promising configurations will be investigated at lab and pilot scale to verify the model predictions and to develop the process further towards commercialization. This study uses a simple distillation model at atmospheric pressure which does not include azeotropes or thermal degradation effects. These effects can be important and should be accounted for in further model development and in the experimental trials of this process.

2. Methodology

2.1. Streams and Process Scheme

The simulations were based on the process scheme in Figure 1. The anaerobic fermenter coverts biomass or organic waste into a mixture of SCOAs. After removal of the suspended solids, the liquid stream is sent to RO membranes for water removal and SCOA concentration. The SCOA-rich concentrate is sent to distillation for the removal of the residual water and the separation and purification of the acids. It was assumed that the SCOAs are completely retained by RO with the permeate composed of pure water. The simulations considered only RO and distillation (dashed block in Figure 1).
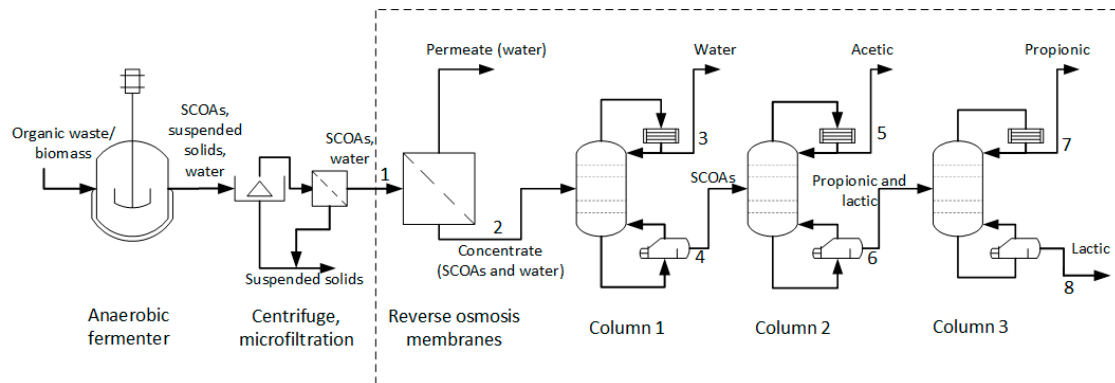
Figure 1. Process scheme considered in this study. The model simulations refer to the dashed block only (RO plus distillation).

In our simulations, the stream entering the membrane RO process (stream 1 in Figure 1) was assumed in all cases to have a total mass flow rate of 1.0×10^6 kg/d (1000 t/d). This represents the output of a large fermenter or of multiple fermenters. The size of anaerobic digesters can vary in a wide range, from a few hundred up to several thousands m^3 [16]. We have chosen to simulate the output of a large fermenter or of multiple joint fermenters because the production of SCOAs is expected to benefit from economies of scale and larger production volumes. Since this study was aimed to simulate the process of RO and distillation for a range of AF effluents, three compositions and three concentrations were assumed and simulated in this study (Table 1). For modelling purposes, the components of stream 1 were assumed to be water (boiling point 100 °C at atmospheric pressure), acetic (118 °C), propionic (141 °C) and lactic acid (217 °C) in different proportions. A large number of SCOAs are present in AF effluents, in this study acetic and lactic acid were chosen because they are often the most abundant under different fermentation conditions, and propionic acid was chosen as representative of acids of intermediate chain length and boiling point. Butyric acid is also often an important component of SCOAs from AD; however, we noted that the inclusion of this acid led to incorrect vapour–liquid equilibrium results with the thermodynamic model and the software (Aspen Plus v.12.1) used in this study. In addition, the inclusion of butyric acid would not have changed the main results of this study significantly. Therefore, we did not include butyric acid among the model SCOA components. In composition 1, lactic acid is the most abundant SCOA, with minor amounts of acetic and propionic. This composition represents effluents of AF carried out at low pH, where lactic acid is often the main product [17]. In composition 2, lactic acid is still the main product but there is a higher fraction of acetic and propionic. This composition still represents effluents from acidic AF, but with a more balanced SCOA composition. In composition 3, acetic acid is the main component and there is no lactic acid. This composition represents effluents of AF carried out at approximately neutral or slightly acidic pH, for example, from dark fermentation processes with hydrogen production [18]. As far as the concentration of stream 1 is concerned, for each composition, the three total

SCOA concentrations of 10, 50 and 100 were modeled. These three concentrations were chosen based on the wide range of SCOA concentrations from AF processes [7].

Table 1. Composition and flow rates of SCOAs and water entering the RO process (stream 1 in Figure 1).

SCOAs		SCOA Composition (% *w/w* of Total SCOAs)	Mass Flow Rate (kg/d) of Each Component for Total SCOA Concentration of		
			10 g/kg	**50 g/kg**	**100 g/kg**
Composition 1	Acetic	10	1.00×10^3	5.00×10^3	1.00×10^4
	Lactic	80	8.00×10^3	4.00×10^4	8.00×10^4
	Propionic	10	1.00×10^3	5.00×10^3	1.00×10^4
	Water		9.90×10^5	9.50×10^5	9.00×10^5
Composition 2	Acetic	40	4.00×10^3	2.00×10^4	4.00×10^4
	Lactic	40	4.00×10^3	2.00×10^4	4.00×10^4
	Propionic	20	2.00×10^3	1.00×10^4	2.00×10^4
	Water		9.90×10^5	9.50×10^5	9.00×10^5
Composition 3	Acetic	60	6.00×10^3	3.00×10^4	6.00×10^4
	Lactic	0	0	0	0
	Propionic	40	4.00×10^3	2.00×10^4	4.00×10^4
	Water		9.90×10^5	9.50×10^5	9.00×10^5

2.2. Distillation Simulations

Distillation simulations were carried out with the software Aspen Plus v12.1. Each of the three distillation columns in Figure 1 was set up with 30 theoretical stages, the condenser being stage 1 and the kettle reboiler being stage 30, with feed entering at the middle stage. The choice of 30 theoretical stages was done after preliminary simulations indicated that this number of stages was enough to obtain the desired purity of the acids with, in most cases, a relatively low reflux ratio. In this study the primary aim was to minimise energy consumption rather than capital costs, therefore a relatively large number of stages was chosen. The simulations were performed in all cases at atmospheric pressure.

The specifications were set as follows:

- In each column, the distillate flow rate was set equal to the mass flow rate entering the distillation process of the component to be purified as distillate, i.e., water in column 1, acetic acid in column 2 and propionic acid in column 3.
- The purity of each of the acids was set as 99.00 (% *w/w*) or higher.
- The reflux ratio in each column was varied manually to find the minimum value that ensured the required purity of all acids.

The NRTL-HOC (Non-Random Two Liquids with Hayden O'Connell correlation) model was used for the vapour-liquid equilibrium (VLE) in all cases. This model was used in a number of studies simulating the VLE of SCOAs, e.g., [19,20].

For each of the three compositions and for each of the three concentrations in Table 1, 10 distillation simulations were performed for 10 values of the water removed by the RO process (0–900 t/d with intervals of 100 t/d). Therefore, a total of 90 distillation simulations was performed.

2.3. Equipment Sizing

The column diameter was obtained from the AspenPlus simulations, assuming sieve trays and 80% approach to flooding. Each column was split into two sections of different diameter, above and below the feed stage. The column total height was the same in all cases and was equal to 17.07 m, obtained assuming a tray spacing of 0.6096 m for 28 trays (30 stages minus the condenser and reboiler).

The shell mass of the distillation columns was calculated from the column diameter and column height assuming cylindrical shape:

$$Shell\ mass\ (kg) = \pi DHt\rho \tag{1}$$

where D (m) = column diameter, calculated in each case from AspenPlus simulations; H (m) = column height; t (m) = thickness of the vessel walls, assumed to be 0.03 m in all cases; r = density of stainless steel, assumed to be 800 kg/m^3.

Since the columns were split into two sections of different diameter, Equation (1) was applied to each section and then the total mass was calculated as the sum.

The reboiler heat transfer area (A) was calculated from the reboiler duty obtained from the AspenPlus simulations, according to Equation (2):

$$A = \frac{Q}{U \cdot \Delta T} \tag{2}$$

where Q (W) = reboiler duty; U (W m^{-2} °C^{-1}) = heat transfer coefficient in the reboiler, assumed in all cases to be 2270 W m^{-2} °C^{-1} [21]; DT = temperature difference between the steam and the boiling fluid, assumed in all cases to be 5 °C.

The membrane area required (A_{memb}, m^2) was calculated from Equation (3):

$$A_{memb} = \frac{Q_{memb}}{Flux} \tag{3}$$

where Q_{memb} (m^3/d) = water flow rate of the permeate across the RO membranes, which was calculated from the mass flow rate assuming a water density of 1000 kg/m^3; Flux (m^3 m^{-2} d^{-1}) = trans membrane flux, assumed to be 0.24 m^3 m^{-2} d^{-1} on the basis of our preliminary experiments in Supplementary Materials, Figure S1.

2.4. Economic Calculations

The equipment cost of distillation columns and reboilers was estimated according to the Equation (4), from [22] (reference [22] was also used for the numerical values in this equation):

$$C = a + b \cdot S^n \tag{4}$$

For the distillation columns, S was the shell mass (in kg) and the factors were a = 15,000, b = 0.68, n = 0.85. For the reboilers, S was the heat transfer area (in m^2) and the factors were a = 25,000, b = 340, n = 0.90. For the reboilers, since Equation (4) is limited to heat transfer areas of up to 500 m^2, multiple reboilers in parallel were assumed if the total heat transfer area from Equation (2) was higher than 500 m^2. The cost C was obtained in 2013 USD and was converted into 2023 GBP by multiplying by the factor 1.147, obtained from online sources.

The equipment cost of membranes was calculated by multiplying the required membrane area from Equation (3) by the factor GBP 49.53/m^2 calculated from [21].

The NPV (net present value, GBP) was calculated according to the formula:

$$NPV = \sum_{t=0}^{n} \frac{R_t}{(1+i)^t} \tag{5}$$

where R_t was the net cash flow for year t, i was the interest rate (assumed to be 10%) and n was the life span of the plant assumed to be 25 years.

R_t was calculated as follows for every operating year, every term being in GBP:

$$R_t = M_{SCOAs} - C_{cap,dist} - C_{cap,memb} - C_{heat,reb} - C_{util,dist} - C_{pump,memb} - C_{util,memb} - C_{replac,memb} - C_{fixed\ costs\ and\ labor}$$

where each term was defined and calculated as follows, the numerical values refer to the base case with some values being changed in the sensitivity analysis described at the end of this section:

M_{SCOAs} = total market revenue of the SCOAs, calculated as the sum of the products of market value of each acid times their annual production rate with the process. The market values were assumed to be (GBP/kg): 0.729 for lactic, 1.00 for acetic and 2.74 for propionic, calculated by the authors from data in [23].

$C_{cap,dist}$ = total capital cost of the distillation plant, calculated as twice the sum of the equipment costs of the distillation columns and of the reboilers. The factor of 2 between the distillation equipment cost and the cost of distillation columns and reboilers was assumed after preliminary cost analysis with Aspen Process Economic Analyser (APEA).

$C_{cap,memb}$ = total capital cost of the membrane plant, calculated by multiplying the membrane area from Equation (3) by the factor 939.9 GBP/m^2, calculated by the authors from data in [24]. Note that the total capital cost of the membrane plant is higher than the equipment cost of membranes calculated earlier, as the former includes any capital costs associated with the membrane plants, e.g., building, land, ancillary equipment.

$C_{heat,reb}$ = cost of reboiler heat energy, calculated as the reboiler energy requirement from AspenPlus simulations multiplied by heat energy cost, which was assumed to be 7.03 p/kWh (average price of natural gas for industrial uses, UK first quarter 2023 [25])

$C_{util,dist}$ = utility cost of the distillation plant other than the reboiler costs, assumed to be equal to 10% of $C_{heat,reb}$.

$C_{pump,memb}$ = cost of pumping energy for the RO plant, calculated from the pumping energy consumption (assumed to be 5 kWh/m^3, within the range given in [26]) times the permeate flow rate, assuming an electricity cost of GBP 0.2151/kWh [25].

$C_{util,memb}$ = membrane utility costs other than pumping, assumed to be equal to 10% of $C_{pump,memb}$.

$C_{repl,memb}$ = membrane replacement costs. It was assumed that membranes are replaced every 5 years at a cost of GBP 15.86/m^2 [21]

$C_{fixedcost\ and\ labour}$ = other fixed costs, e.g., maintenance and labour, assumed to be 10% of the total capital costs $C_{cap,dist}$ + $C_{cap,memb}$.

Due to the uncertainties in the estimation of many numerical values for the cost analysis, a sensitivity analysis on the NPV has been carried out varying several cost parameters. The cost parameters that were varied in the sensitivity analysis were interest rate; total capital costs (distillation plus membranes); unit steam cost; unit electricity cost; other costs (sum of utility cost for distillation, utility cost for membranes, fixed and labour costs, membrane replacement costs). Each of the cost parameters was varied at 50, 200 and 400% the value of the same parameter in the base case (100% of the parameter value).

3. Results and Discussion

The simulation results of distillation without membrane concentration are presented in Section 3.1, the results of distillation with previous membrane concentration are presented in Section 3.2. Detailed simulation results (reflux ratios, temperature and composition of all streams) are reported in Table S1 in the Supplementary Materials. The general discussion is presented in Section 3.3.
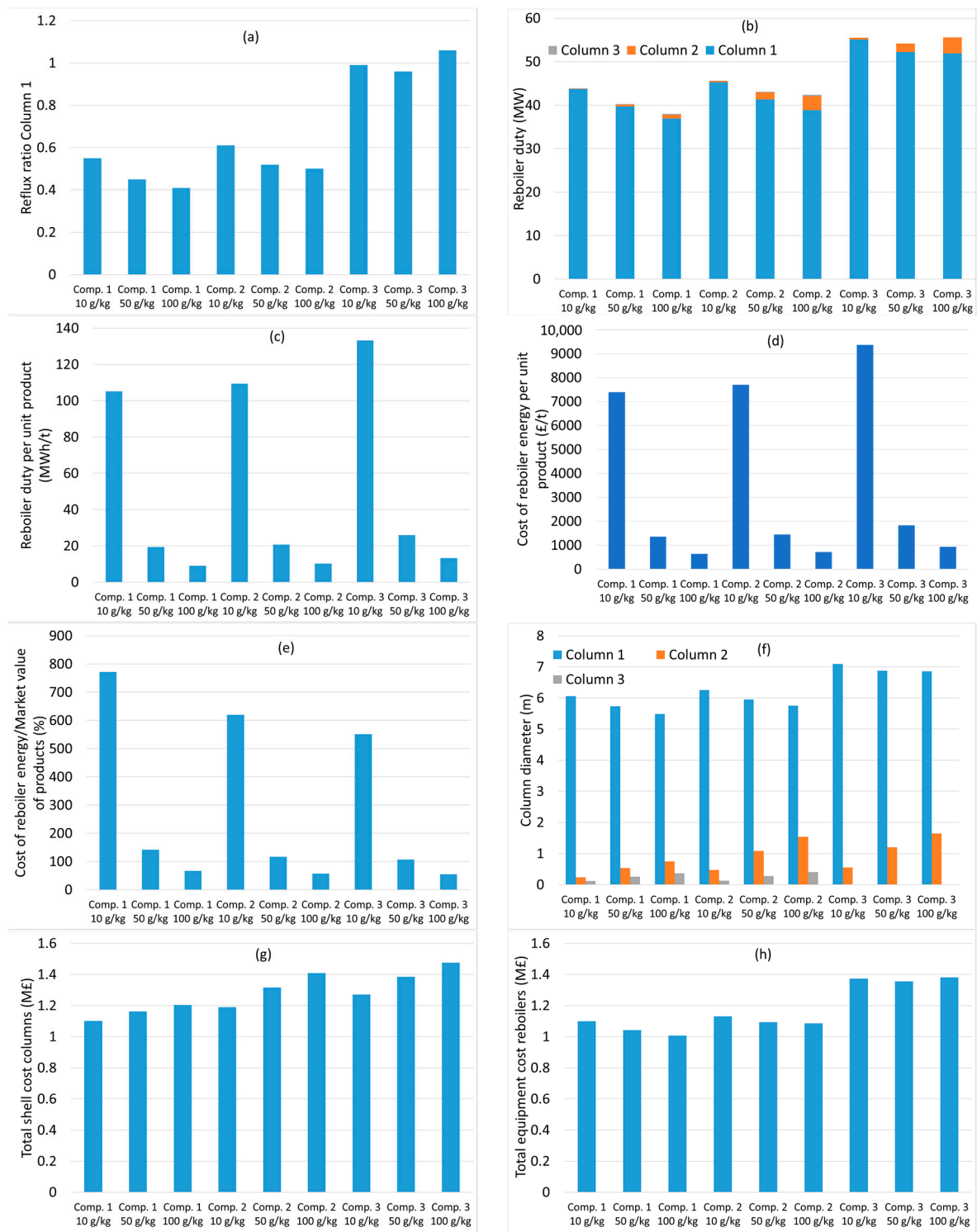
3.1. Distillation without Membrane Concentration

Figure 2 shows the model results for the case where distillation is performed directly on the AF effluents (after removal of the suspended solids) without any water removal with membranes. Figure 2a shows, for the various compositions and concentrations of the SCOAs, the minimum reflux ratio which was required in column 1 to satisfy the specification of the purity of the SCOAs. For a given feed concentration and composition, the reflux ratio is the key parameter that determines the equipment size and reboiler duty in distillation columns. Column 1 is considered in Figure 2a because it is expected to be the largest and the one with the highest energy demand due to the need to remove large volumes of water in this column. The reflux ratios required in columns 2 and 3 are less critical in terms of energy demand and equipment size due to the smaller volumes to be treated in these columns. The minimum reflux ratio required in column 1 is in the range

0.4–0.6 for compositions 1 and 2 and approximately equal to 1 for composition 3. The reason for the higher reflux ratio for composition 3 and also for the slightly higher reflux ratio for composition 2 than for composition 1 is the higher content of acetic acid. The main task of column 1 is the separation of water from acetic acid and feeds richer in acetic acid make this separation more difficult, requiring a higher reflux ratio. From Figure 2a it can also be observed that for compositions 1 and 2 the minimum reflux ratio in column 1 slightly decreases for more concentrated feeds. This is due to the fact that, as the total mass flow rate of SCOAs in the feed increases, it becomes slightly easier to satisfy the requirement of 99% recovery of each acid and slightly higher concentrations of acids in the water distillate of column 1 become acceptable, requiring lower reflux ratios.

Figure 2b shows the reboiler duty. In all cases, column 1 gives by far the largest contribution to the total reboiler duty, as discussed above. The reboiler duty is higher for composition 3 than for compositions 1 and 2 due to the higher reflux ratio required. For compositions 1 and 2 the reboiler duty decreases as the feed concentration increases due to the lower reflux ratio. Figure 2c shows the reboiler duty per unit mass of products, which as expected decreases by a large factor as the feed concentration increases. For a given concentration of the feed, the reboiler duty per unit mass of products is the highest for composition 3 due to the higher reflux ratio. Figure 2d, which shows the cost of the reboiler energy, follows the same trend as Figure 2c and confirms the benefits of having the highest possible SCOA concentration in the feed, i.e., the highest possible SCOA concentration in the AF effluents. Clearly, one of the requirements for an economically viable process is that the energy costs are considerably lower than the market value of the products. Therefore, Figure 2e shows the ratio between the reboiler energy costs and the market values of the products. For the lowest feed concentration of 10 g/kg, the reboiler energy costs are for all compositions much higher than the market values of the products, and therefore a separation process without membrane concentration is not in this case economically viable. For the intermediate feed concentration of 50 g/kg, the reboiler energy costs are slightly higher or slightly lower than the market value of the products and therefore the process without membranes is also in this case economically unfeasible. For the highest feed concentration of 100 g/kg, the reboiler energy costs are in the range 45–55% of the market value of the products and, although this represents a high energy cost, the process may be economically viable without membranes. Figure 2f shows the diameter of each distillation column. It is confirmed that column 1 is by far the largest of the three columns, due to the water removal, with a diameter in the range 5.5–7.1 m depending on the feed composition and concentration. For column 1, composition 3 requires the largest diameter due to the higher reflux ratio, while the diameter of column 1 decreases as the feed concentration increases due to the lower reflux ratio and the lower flow rate of water to be removed. The diameter of columns 2 and 3 increase as the feed concentration increases, due to the larger volumes of SCOAs to be separated, reaching a maximum value of 1.65 m for column 2 with composition 3 100 g/kg. The total shell cost (Figure 2f) is estimated to be in the range GBP 1.0–1.5 M and slightly increases with the feed concentration due to the higher diameter required for columns 2 and 3.

Overall, the reboiler energy consumption for distillation in the process without membrane concentration is very high in all cases. To the best of our knowledge, there are no publicly available quantitative data on the energy consumption of conventional processes for organic acids' production. For other biotechnology-based processes, the distillation energy consumption of bioethanol purification has been calculated as approximately 0.25 MWh/t for extractive distillation [27], much lower than the values shown in Figure 2 (although the market value of SCOAs is higher than of bioethanol), which indicates the need for reducing the energy consumption, as presented in Section 3.2.

Figure 2. Main simulation results for distillation without previous membrane concentration. (**a**) Minimum required reflux ration for column 1. (**b**) Reboiler duty for columns 1, 2, 3. (**c**) Reboiler duty per unit of total SCOA products. (**d**) Cost of reboiler energy per unit of total SCOA products. (**e**) Ratio between the cost of the reboiler energy and the total market value of the SCOA products. (**f**) Column diameter for columns 1, 2 and 3. (**g**) Equipment cost (shell cost) for columns 1, 2, 3. (**h**) Total equipment cost for the reboilers of columns 1, 2, 3.

3.2. Distillation after Water Removal with Membranes

The aim of the RO membrane process is to reduce the water entering the distillation process, aiming to reduce the distillation energy consumption and costs. Figure 3a shows how the water entering the distillation process reduces as the water removed as permeate in the membrane process increases. For a given permeate flow rate, the water entering the distillation process is lower for the more concentrated feeds, due to their lower water content as they left the AF process. Figure 3b–d show the effect of the water removal in the membrane process on the minimum reflux ratio required in column 1 to satisfy the purity specification of the acids. The reflux ratio in column 1 is a key parameter in determining the energy and capital costs of the distillation process. As the water removed as permeate by the membranes increases, two competing effects influence the minimum reflux ratio. On the one hand, more concentrated feeds tend to require a higher reflux ratio to achieve the same purity of the produced acids. On the other hand, more concentrated feeds allow for the water in the distillate to contain a slightly higher concentration of acids than more diluted feeds while still achieving the specified purity and recovery of the acids. This latter effect allows for the use of a lower reflux ratio in column 1. As a result of these competing effects, for composition 1 the reflux ratio tends to decrease as the water removal by the membranes increases, while for compositions 2 and 3 the reflux ratio increases or decreases depending on the initial concentration in the feed. While the reduction in the water entering the distillation process, shown in Figure 3a, is expected to have a major effect on the reduction of distillation costs, the reflux ratio also plays an important role and the significant increase in the reflux ratio observed (Figure 3d) for composition 3 at 50 and 100 g/kg will reduce the benefits brought by the lower water flow rate entering the distillation. On the other hand, for composition 1, where the minimum reflux ratio decreases as the water removal by the membranes increases (Figure 3b), the benefits of lower water entering distillation and lower reflux ratio will add up.
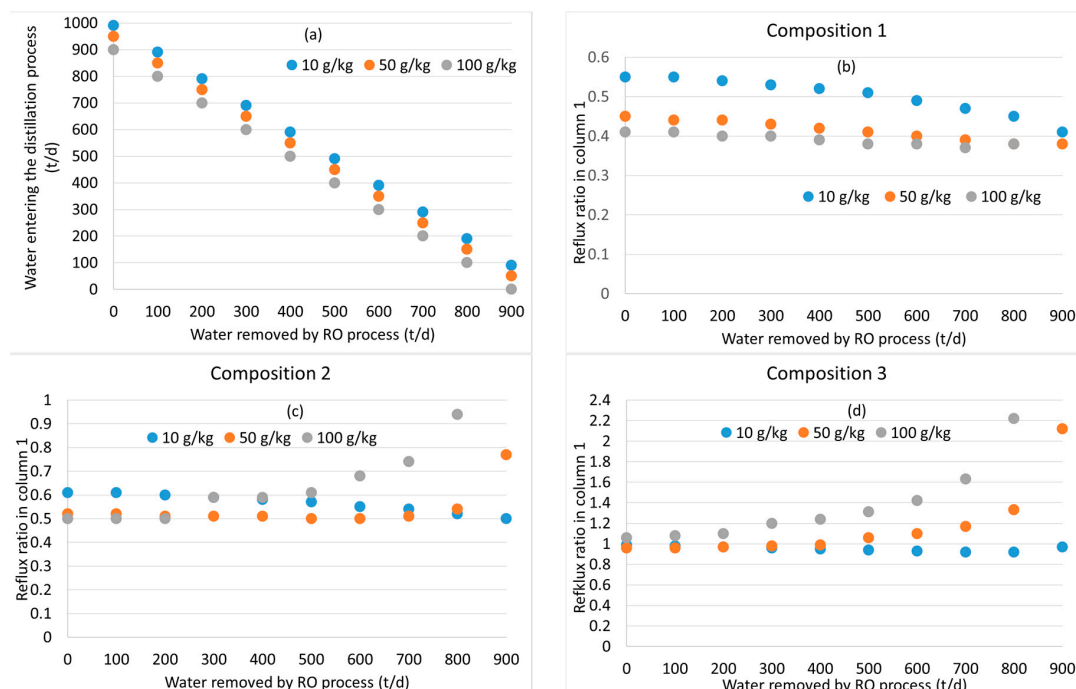
Figure 3. Distillation with previous membrane concentration. Results presented as a function of the water removed in the RO process. (**a**) Water entering the distillation process. (**b**) Minimum reflux ratio required in column 1 for composition 1, for each total SCOA concentration in stream 1. (**c**) Minimum reflux ratio required in column 1 for composition 2, for each total SCOA concentration in stream 1. (**d**) Minimum reflux ratio required in column 1 for composition 3, for each total SCOA concentration in stream 1.

Figure 4a–c show how the water removal by the membranes reduces the reboiler duty in the distillation columns. The reboiler duty decreases from the values of 38–56 MW in the absence of membranes to less than 5 MW for the highest water removal considered here, 900 t/d. This reduction in reboiler duty is very considerable and shows the main benefit of the membrane process. The reboiler duty per unit mass of products (Figure 5a–c) shows the same trend observed in Figure 4, with the values being much lower for the more concentrated feeds than for the more diluted feeds, as expected. The ratio between the reboiler energy costs and the market value of the products becomes much more favorable as the water removed by the membranes increases (Figure 6). For the most diluted feed of 10 g/kg, this ratio becomes lower than 100% for the highest water removals of 800–900 t/d. For the most concentrated feed of 100 g/kg, this ratio reduces from 47–55% in the absence of membranes to 1–2% for the highest water removal of 900 t/d. In all cases, Figure 6 shows the very significant benefits of the membrane process in reducing the reboiler duty.
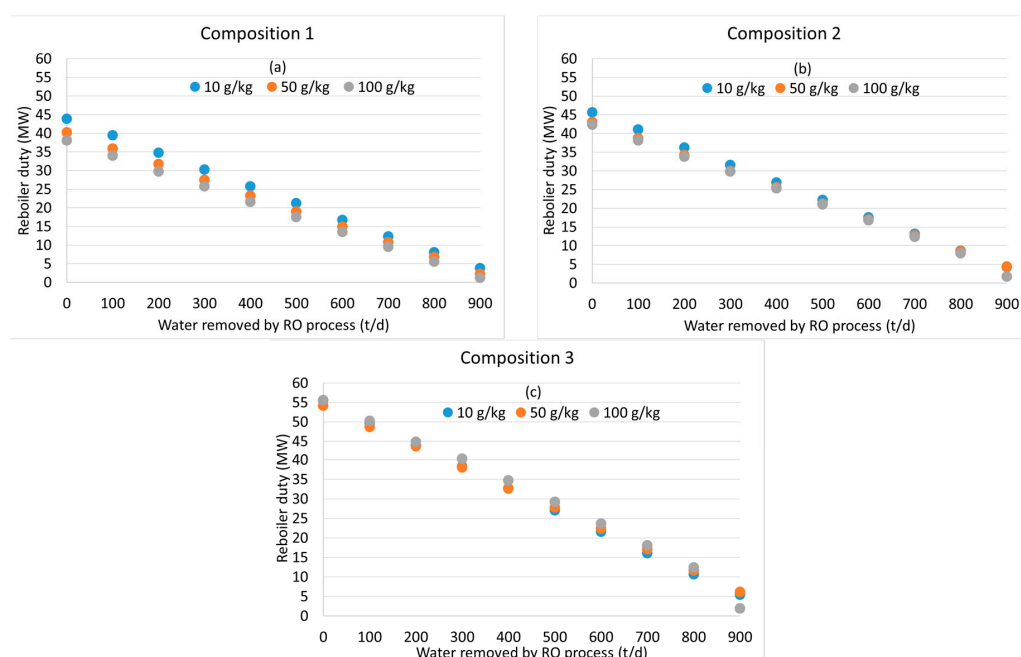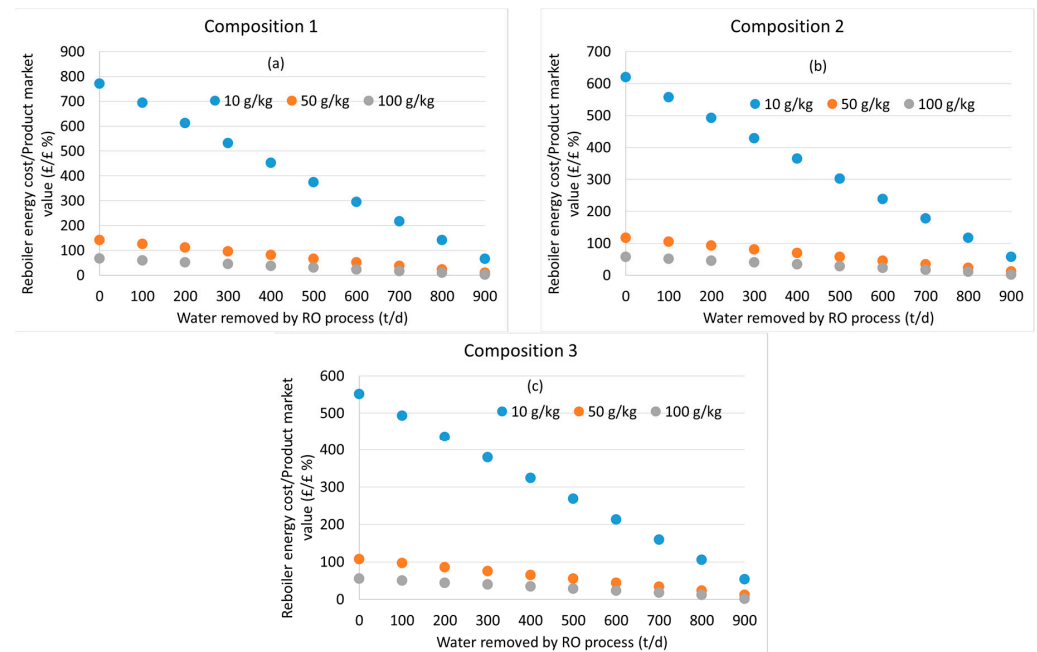

Figure 4. Distillation with previous membrane concentration. Total reboiler duty in columns 1, 2 and 3 reported as a function of the water removed in the RO process, for each value of the total SCOA concentration in stream 1. (**a**) Composition 1. (**b**) Composition 2. (**c**) Composition 3.

Figure 7 shows the effect of membranes on the size of the capital equipment. The area of the membranes is linearly proportional to the permeate flow rate (Figure 7a). Membranes bring a large reduction in the diameter of column 1 (Figure 7b), which is by far the largest of the three columns. The diameter of column 1 reduces from 6–7 m without membranes to 1–2 m. The largest diameters are in most cases obtained for the most diluted feed, 10 g/kg, due to the combined effect of the volume of water entering distillation and of the reflux ratios (Figure 3). Figure 8 shows the effect of membranes on equipment costs. The equipment cost of membranes is estimated to increase linearly (Figure 8a) with the permeate flow rate, due to the assumption of constant membrane flux for all simulations. The total shell cost of the three distillation columns decreases very significantly as the water removed by the membranes increases due to the reduction in the water to be treated by distillation. Compared to the base case without membranes, the reduction in the shell cost is higher than 50% for the highest considered permeate rate of 900 t/d. Generally, the shell cost is slightly higher for the more concentrated feed of 100 g/kg due to the higher contribution of columns 2 and 3, which have a higher role for the most concentrated feed (Figure 2f,g). Considering the combined equipment cost of membranes plus distillation columns (Figure 9), the addition of membranes brings a clear reduction. Indeed, with the

assumptions of this study, the equipment cost of membranes is significantly lower than the cost of distillation columns and the cost reductions brought by membranes on distillation columns outweigh by a large factor the equipment cost of membrane systems.
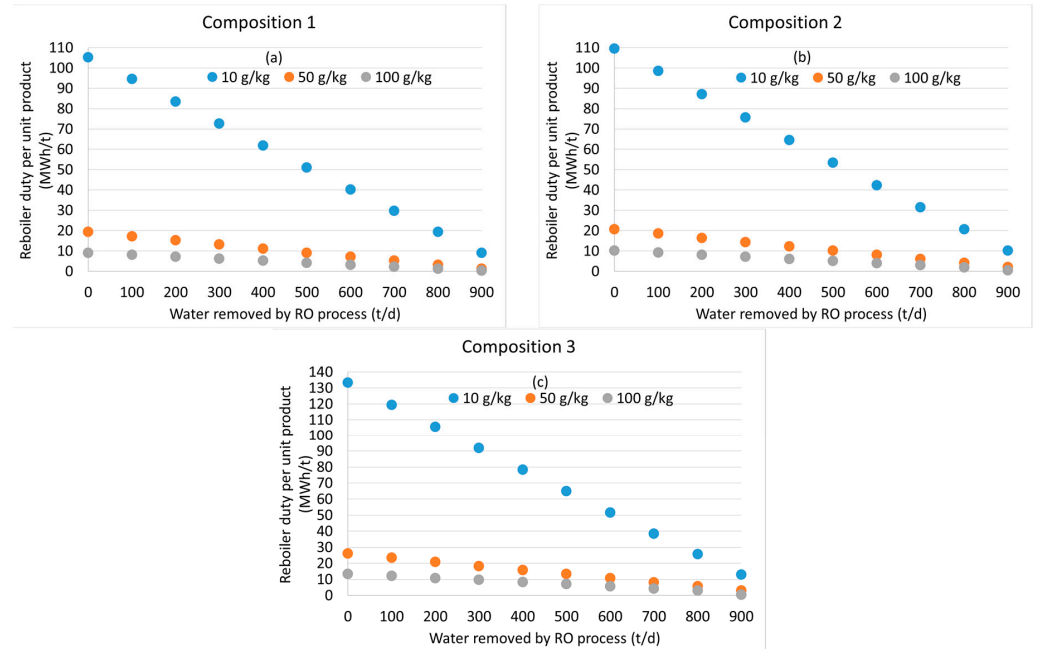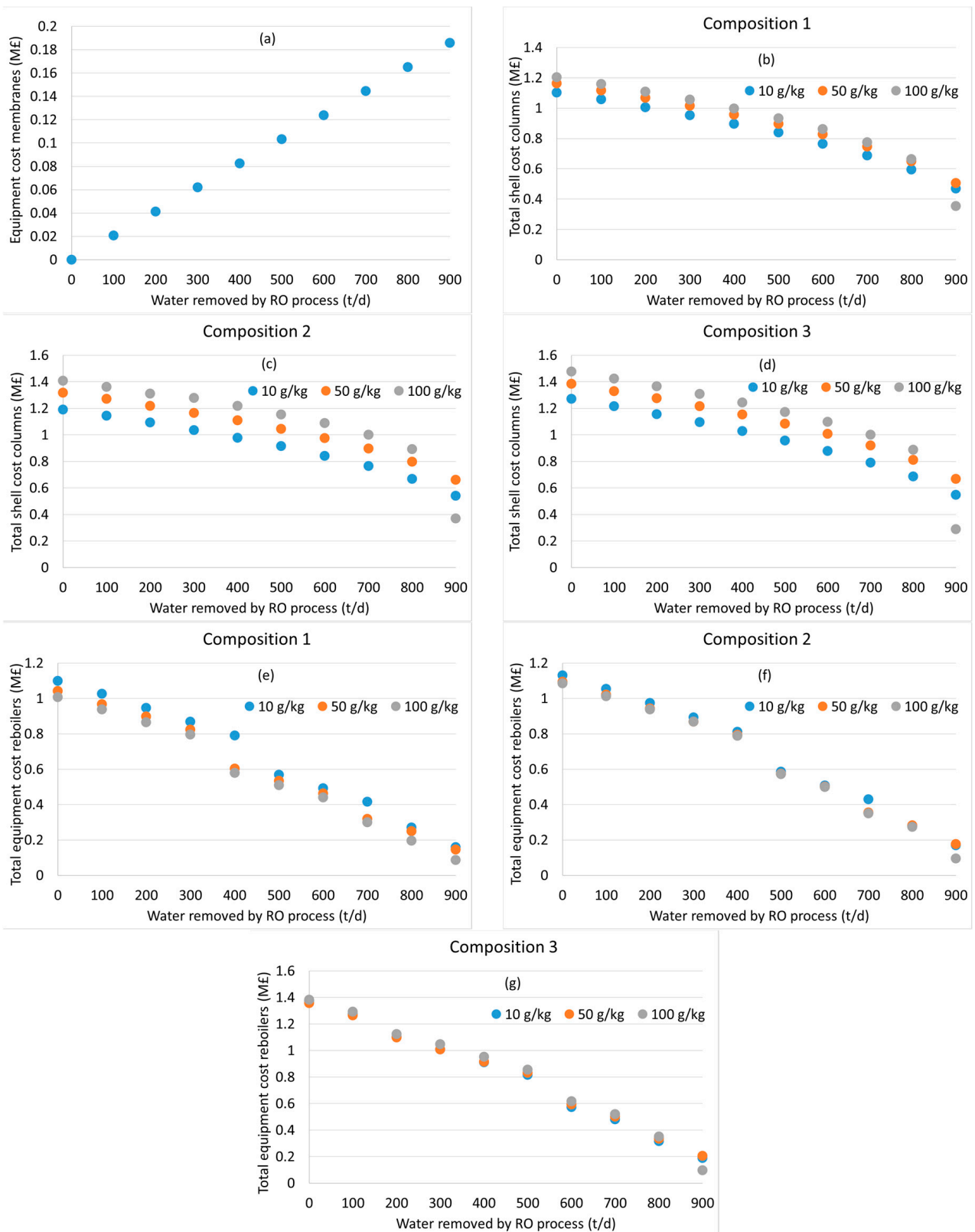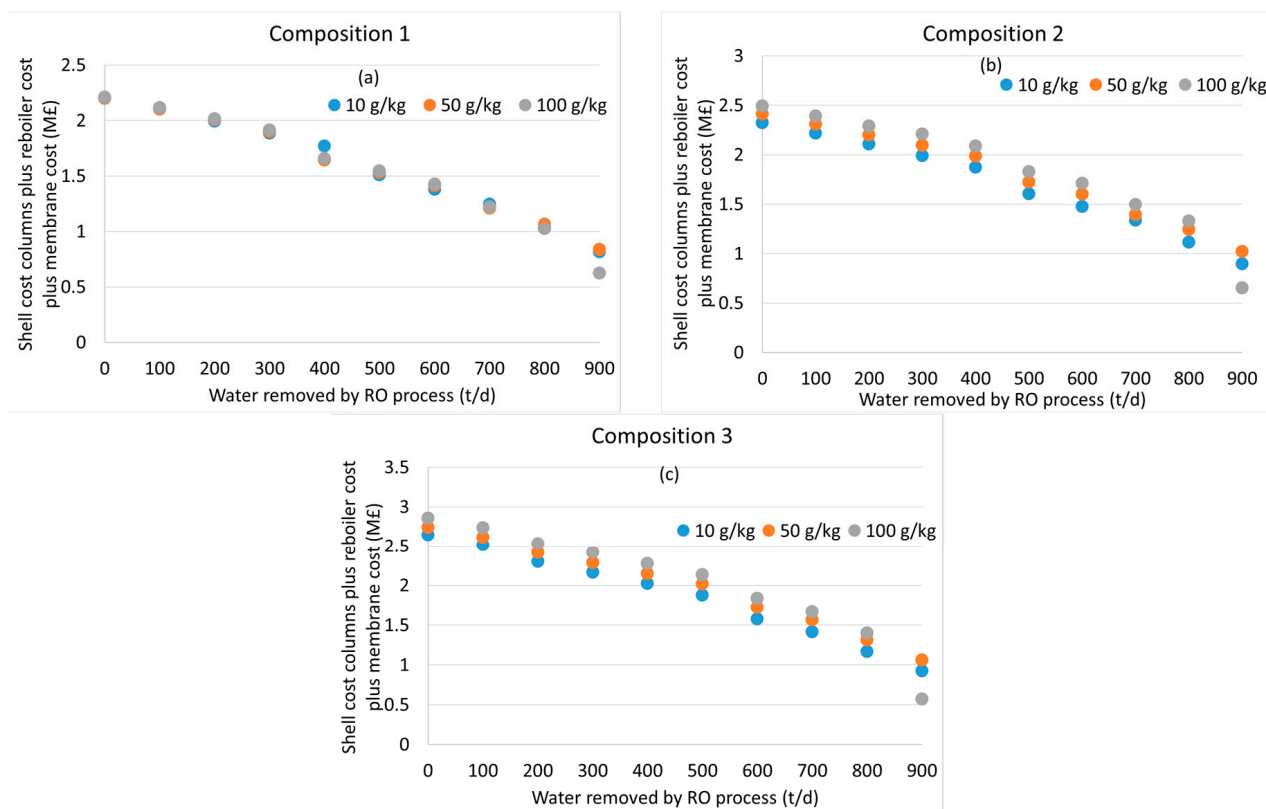

Figure 5. Distillation with previous membrane concentration. Total reboiler duty in columns 1, 2 and 3 per unit of total SCOA products reported as a function of the water removed in the RO process, for each value of the total SCOA concentration in stream 1. (**a**) Composition 1. (**b**) Composition 2. (**c**) Composition 3.

Figure 6. Distillation with previous membrane concentration. Ratio between the total reboiler energy cost and the total market value of the SCOA products, for each value of the total SCOA concentration in stream 1. (**a**) Composition 1. (**b**) Composition 2. (**c**) Composition 3.
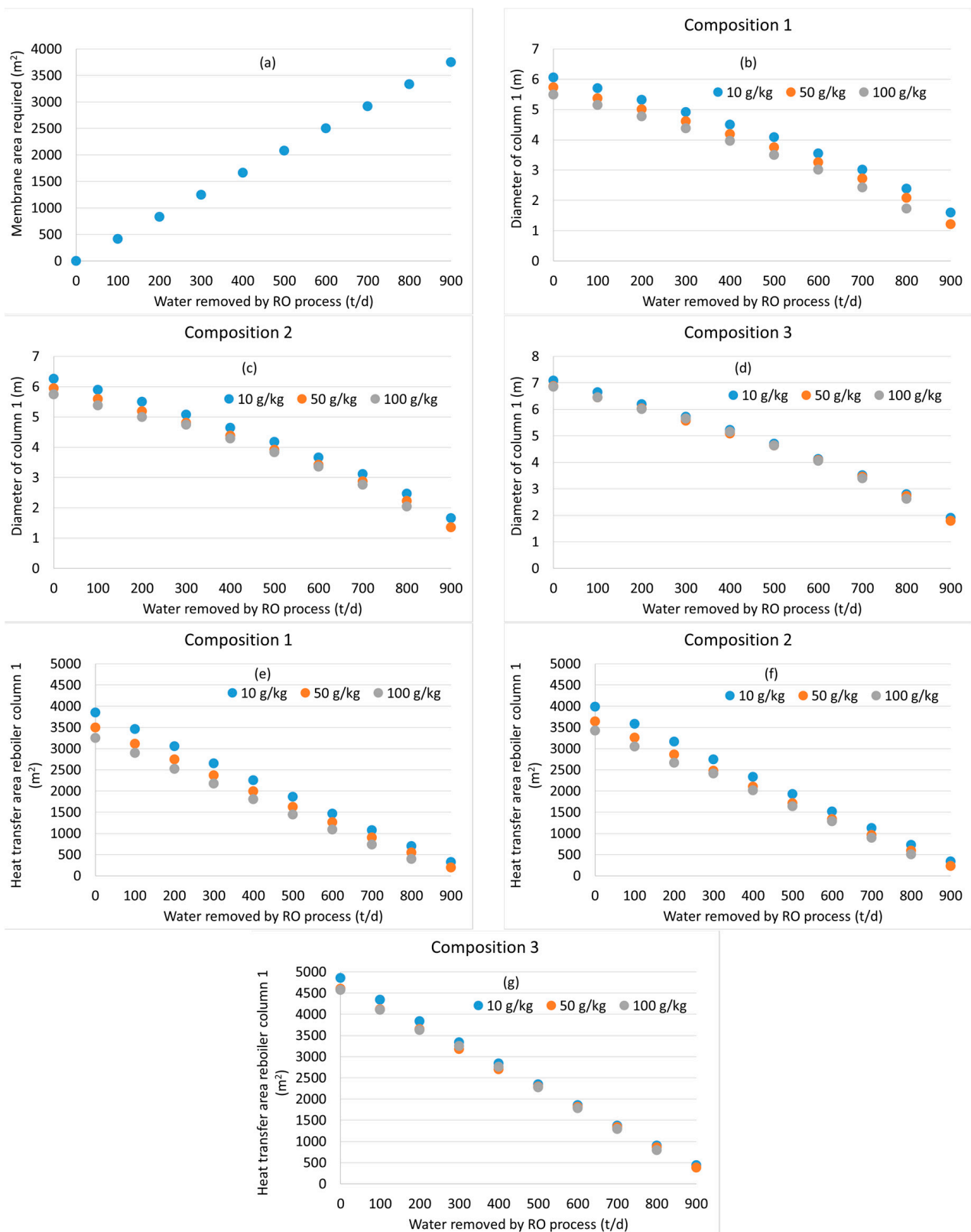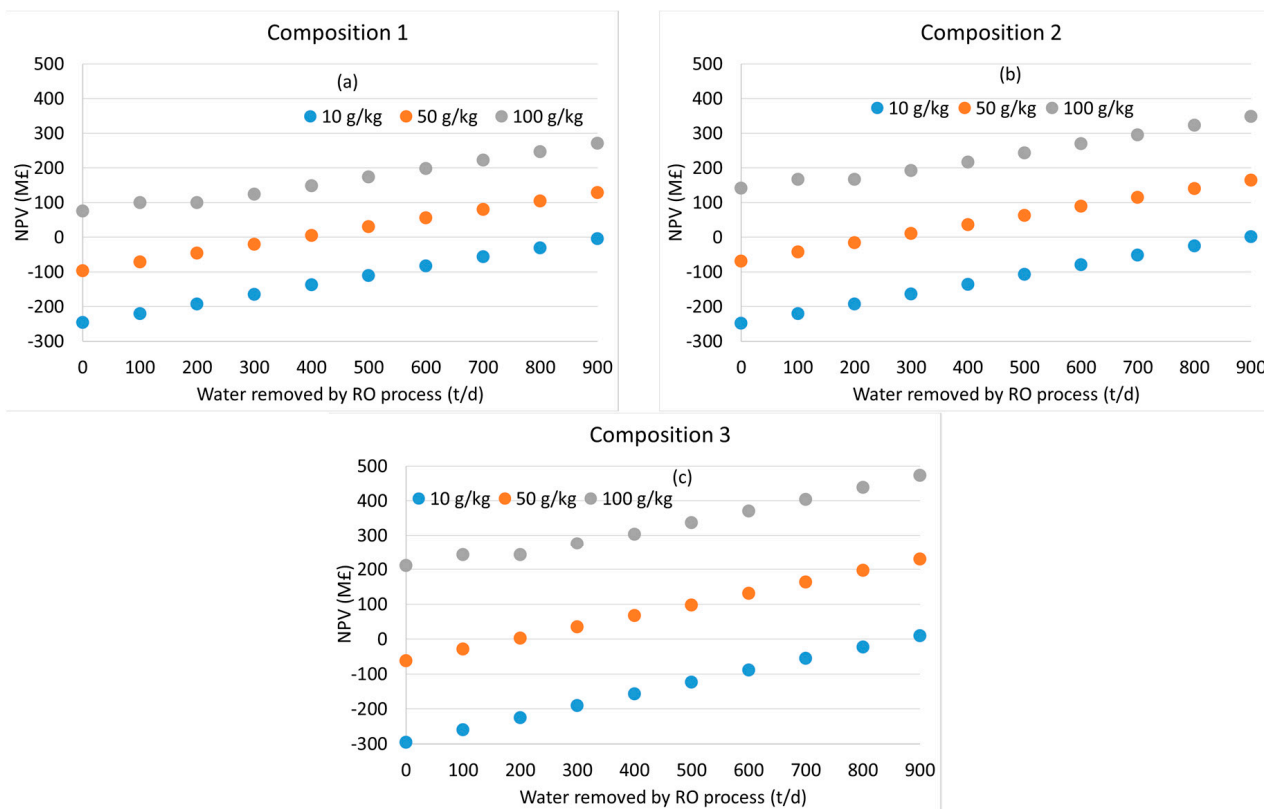
Figure 7. Distillation with previous membrane concentration. Equipment sizing as a function of the water removed in the membrane process, for each value of the total SCOA concentration in stream 1. (**a**) Membrane area. (**b**–**d**) Diameter for column 1 (largest of the diameters of the two sections) for compositions 1–3. (**e**–**g**) Required reboiler heat transfer area for compositions 1–3.

Figure 8. Distillation with previous membrane concentration. Equipment costs as a function of the water removed in the membrane process, for each value of the total SCOA concentration in stream 1. (**a**) Membranes. (**b**–**d**) Total shell cost for columns 1, 2, and 3 for compositions 1–3. (**e**–**g**) Total reboiler cost for columns 1, 2, and 3 for compositions 1–3.

Figure 9. Distillation with previous membrane concentration. Sum of the equipment cost of distillation (columns and reboilers) and of membranes, for each value of the total SCOA concentration in stream 1. (**a**) Composition 1. (**b**) Composition 2. (**c**) Composition 3.

Combining the capital and operating costs together, Figure 10 simulates the effect of the permeate flow rate on the NPV. In all cases the NPV increases with the addition of membranes and with the increase of the water removed by the membranes. This indicates that the RO process prior to distillation has in all cases a positive economic effect. For the most diluted feeds of 10 g/kg, the NPV is negative in almost all cases, turning slightly positive only for the highest value of the water removed by RO of 900 t/d. This indicates that diluted effluents from AF cannot in practice be made profitable with the processes considered in this study. For the intermediate concentration of 50 g/kg, the NPV turns positive for relatively low values of the water removed, while for the highest feed concentration of 100 g/kg, the NPV is positive in all cases. These considerations confirm the importance of producing SCOA effluents from AF at the highest possible concentration. Considering the unavoidable uncertainty in the cost parameters and therefore in the NPV, Figure 11 shows the sensitivity of the NPV to variations in the cost parameters. The sensitivity analysis is shown for the intermediate case of concentration 50 g/kg, composition 1. The largest effect on the NPV is the unit cost of steam, Figure 11c. This is understandable considering the high energy consumption of the distillation process, especially for low water removal by RO. Higher steam costs make the NPV significantly more negative; however, it is important to observe that with high water removal by RO the NPV becomes positive even for an increase in steam costs of 400% compared to current values. This confirms the importance of SCOA concentration by RO in reducing the energy requirements by the process. The variations in the other cost parameters also have an effect on the NPV. Increases in the interest rate (Figure 11a) and in the other costs (Figure 11e) make the NPV less positive but in all cases the NPV is positive for large values of the water removal by RO. Variations in the capital costs have a relatively little impact on the NPV, which is understandable considering that the major role in the NPV is played by the steam costs and by the market value of the

SCOAs. Changes in the unit electricity costs (Figure 11d) give almost no effect on the NPV, which is due to the fact that in the considered process heat energy consumptions in the reboiler is much larger than the electricity consumption in the membrane unit.

Figure 10. Distillation with previous membrane concentration. NPV as a function of the water removed in the membrane process, for each value of the total SCOA concentration in stream 1. (**a**) Composition 1. (**b**) Composition 2. (**c**) Composition 3.

Overall, addition of SCOA concentration with RO has been shown to significantly reduce the energy consumption of the distillation process. For the best conditions calculated in this study, i.e., SCOA concentration of 100 g/kg in the AF effluents and the highest water removal by RO (900 t/d), the total reboiler duty in the distillation is in the range 0.30–0.50 MWh/t, depending on the SCOA composition. These values make the considered SCOA recovery process more attractive and bring the estimated energy consumption by distillation in the same range of bioethanol distillation [28] or of an innovative proposed sustainable process for acetic acid production from methanol carboxylation with an estimated energy consumption of 0.2–0.6 MWh/t [28]. It is important to observe that the low energy consumption reported by [28] was obtained with energy integration and heat recovery schemes that have not been considered for the process considered in this study, although they are also applicable to it.
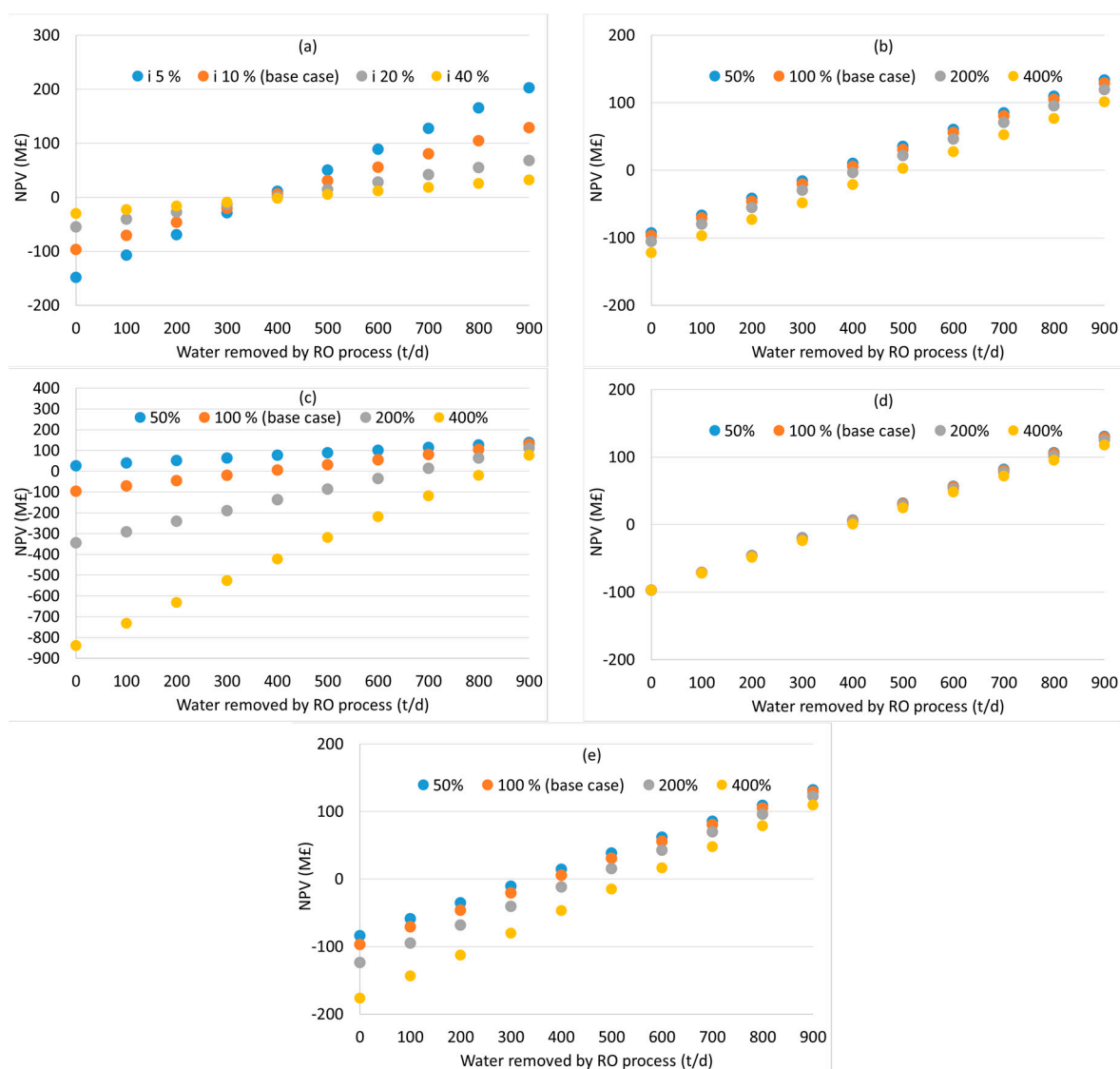
Figure 11. Distillation with previous membrane concentration. Sensitivity analysis on the NPV for composition 1, 50 g/kg. The values of 50, 100, 200 and 400% refer to the deviation from the base case (100%). (**a**) Effect of the interest rate. (**b**) Effect of the total capital costs (distillation plus membranes). (**c**) Effect of the unit cost of steam. (**d**) Effect of the unit cost of electricity. (**e**) Effect of the other costs (sum of utility costs of distillation and membranes, fixed costs and membrane replacement costs).

3.3. General Discussion and Model Limitations

The simulations in this study indicate that using RO to remove water from AF effluents can bring an important reduction, of up to more than 90%, in the energy consumption for the distillation of SCOA mixtures. The benefits in the reduction of energy consumption are even more evident if we consider that the pumping energy for RO is provided by electricity, while the reboiler energy is usually provided by natural gas, and it is easier to produce electricity than heat from renewable resources, e.g., wind and sun. In addition to the benefits in energy reduction, water removal by RO brings a reduction in equipment size and capital costs of the distillation process, which have been quantified in this study and bring additional benefits to the economics and to the sustainability of SCOA production from organic waste via AF.

This study, which to the best of our knowledge was the first to quantitively investigate the coupling of RO and distillation for this type of effluents, was based on an ideal simplified model. Therefore, like for all models, all the simulations done in this study need to

be verified experimentally to quantify the effect of RO on SCOA distillation with real life examples and to develop more accurate models. There are several aspects where experimental simulation is needed:

Efficiency of RO for concentration of water based SCOA mixtures in a wide range of SCOA concentrations. Although there are promising early experimental findings, only a limited range of SCOA concentrations has been investigated experimentally. Depending on the operating conditions of pH, type of membrane and applied pressure, successful retention of SCOAs with RO membranes was obtained with acetic-butyric mixtures at 1–2 g/L [11], with mixtures of various SCOAs at 20–30 g/L [12], with acetic, propionic, butyric acids at total concentration of up to 5 g/L [13] and with acetic acid at up to 10 g/L in solution with sugars [14]. In the preliminary experiments in our group reported in Supplementary Materials (Figure S1), the feed concentration of SCOAs was 7.4 g/L. Since the SCOA concentration in AF effluents can be higher than 100 g/L [7], and only high concentrations are likely to be economically viable, there is need to investigate RO retention of SCOAs at higher concentrations than has been reported so far.

Distillation of SCOA mixtures typical of AF effluents. While distillation is performed at commercial scale for the purification of organic acids from conventional processes based on fossil resources [29], the characteristics of AF effluents are significantly different. The model used in this study is a simple model and does not take into account several effects that may happen in the distillation of water based SCOA mixtures: acetic acid may present an azeotrope at high water concentrations, which may need the use of azeotropic distillation rather than direct distillation [5]; lactic acid degrades at high concentrations in water and at high temperatures because of which lactic acid purification by distillation may need to be carried out under vacuum [30]. However, these findings relate to solutions of single organic acids in water, rather than to mixtures of SCOAs as for AF effluents.

Based on the considerations above, the process simulated in this study needs to be investigated experimentally to test the validity of the model and to identify the actual operating conditions of RO and distillation that will lead to the predicted savings in energy requirements for the separation and purification of the SCOAs in AF effluents. It is hoped that the model developed in this study will foster further studies on this topic, helping to move SCOA production via AF closer to commercial realization.

4. Conclusions

Considering SCOA-rich effluents from AF, we have shown and quantified the benefits of the combination of RO and distillation for water removal and for the separation and purification of the SCOAs. With the process and model considered in this study, water removal by RO can bring down the reboiler energy consumption in the distillation process by more than 90% with additional benefits in terms of reduction of distillation columns' size, mass and cost. The energy consumption by RO is small compared to the energy savings in reboiler heat. Furthermore, the energy required for RO is mainly electricity, which can be generated more easily from renewable resources (e.g., wind or sun) than the heat required by distillation. Overall, the combined RO-distillation process is expected to significantly increase the NPV and the economic feasibility of SCOA separation and purification. It is hoped that this study will stimulate experimental investigations on the combination of RO and distillation to bring the production of SCOAs from organic waste and biomass via AF closer to commercialisation.

Data Availability Statement: Data is contained within this article and in the Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

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