Waste Heat Recovery through Organic Rankine Cycles in the Bioethanol Separation Process

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ABSTRACT: The huge use of heating utilities is one of the main drawbacks associated with the azeotropic separation process for the bioethanol production. In this context, process integration through heat exchanger networks can be used to integrate the involved streams; however, the main problem in this scheme is that the streams that require cooling are at lower temperature than the ones that require heating, yielding very small opportunities for energy integration. Recently, the organic Rankine cycle has been proposed as an alternative for waste heat (i.e., heat at low temperature) recovery producing electric power. Therefore, in this paper is presented an optimization study for the energy integration in the azeotropic bioethanol separation process involving energy integration through heat exchanger networks incorporated into an organic Rankine cycle. A proper optimization approach is proposed to yield the solution with the minimum separation cost. Several separation sequences are used to demonstrate that incorporation of the organic Rankine cycle to energy integration in bioethanol production yields significant economic benefits. Furthermore, this integrated scheme improves the energy efficiency for the waste heat recovery, making more attractive the use of bioethanol.

INTRODUCTION

Decreasing greenhouse gas emissions (GHGE) has become an important global issue because the effects of climate change have negatively affected the whole world. The main source of GHGE is the use fossil fuels for heating, electricity generation, and transportation. One alternative to reduce these emissions is to substitute totally or partially fossil fuels with bioethanol,^{1,2} which is obtained from renewable resources. Furthermore, bioethanol can be implemented easily in the existing infrastructure and can substitute for methyl *tert*-butyl ether (MTBE) as an octane enhancer in gasoline engines.³ Nowadays, the largest bioethanol producer in the world is the United States, where bioethanol is produced mainly from corn,⁴ followed by Brazil, where the feedstock is sugar cane.⁵ However, the current methods for producing bioethanol (see Figure 1) use large amounts of energy in the separation process associated with the ethanol–water azeotropic mixture (because the ethanol–gasoline blend has low water tolerance).^{6–8} Traditionally, the separation of the ethanol–water mixture is carried out through azeotropic distillation using benzene, pentane, or diethyl ether as solvent; another alternative is extractive distillation using ethylene glycol or gasoline.^{9,10} Furthermore, these technologies involve large capital and operating costs.^{7,8,11–15} In addition, bioreactors usually yield low concentrations of bioethanol,^{16,17} and huge utilities are required in the process (i.e., electricity, steam, and cooling water). For these reasons, until now bioethanol has not been yet economically competitive with respect to fossil fuels.

The azeotropic distillation process for the bioethanol–water mixture has associated several hot streams that require cooling and cold streams that require heating (Figure 1).^{6–10} In this context, energy integration through heat exchanger networks can be an attractive solution for reducing the external energy

consumption in the separation process.^{18–25} Therefore, recently Vázquez-Ojeda et al.²⁶ proposed integrating energetically the process streams involved in the bioethanol separation process through the SYNHEAT model.^{27–31} The main problem with this previous approach is that in the bioethanol separation process the hot streams are at low temperature, which decreases drastically the possibility of using these streams to heat the cold process streams that are at higher temperatures. In the approach by Vázquez-Ojeda et al.²⁶ the integrated energy is low and so the reduction in the consumption of utilities. On the other hand, recently the organic Rankine cycle (ORC) has been proposed to recover waste heat and produce electric power; this unit is similar to the steam Rankine cycle (SRC), but it uses a refrigerant as working fluid.^{32–36} Desai and Bandyopadhyay³⁷ have proposed integrating an ORC to a heat exchanger network (HEN) for waste heat recovery, and then Hipólito-Valencia et al.^{38–40} proposed superstructures and mathematical programming models for waste heat recovery through ORC in the synthesis of HEN. These approaches have shown that the ORC is able to recover a significant amount of waste heat, producing electric power and yielding significant economic improvements. Therefore, this paper proposes the use of an ORC integrated to HEN for energy integration during the bioethanol separation process. In this way, several optimized separation sequences using different solvents and configurations^{26,41} are integrated energetically involving the use of an ORC and using a new method for the energy integration.

Received: December 11, 2013

Revised: March 17, 2014

Accepted: March 26, 2014

Published: March 26, 2014

Figure 1. Schematic representation of the addressed problem.

■ OPTIMIZATION METHODOLOGY

The implemented approach can be stated as follows: bioethanol separation processes designed previously and reported in the literature have been taken (in this case were considered the sequences reported by Vázquez-Ojeda et al.,⁴¹ where the operating conditions were optimized using evolutionary algorithms, and the sequences reported by Segovia-Hernandez et al.⁴²). From these designs are identified their hot and cold process streams as well as the flow rates, temperatures, and physical properties; these streams are then incorporated to the superstructure reported by Hipólito-Valencia et al.,³⁸ which includes an ORC to recover waste heat and produce electric power (HEN-ORC model). The superstructure is divided in stages (the number of stages corresponds to the maximum number of hot or cold process streams), and in each stage is allowed the heat exchange between any pair of hot and cold process streams (allowing in this way series, parallel, and series-parallel arrangements). The superstructure also has two major

Table 1. Parameters for Optimization

concept	value
working fluid in the ORC	R245fa
factor used to annualize the inversion k_F (year ⁻¹)	0.23
hours of operation per year (h/year)	8000
$\Delta T_{\min}$ (°C)	1
exponent for the function of capital cost of exchangers (dimensionless)	0.65
unit cost for cooling utility (U.S.\$/kWh)	1.27×10^{-3}
unit cost for heating utility (U.S.\$/kWh)	0.024
electricity cost, buy (U.S.\$/kWh)	0.08
electricity cost, sell (U.S.\$/kWh)	0.065
efficiency for energy production for the ORC	0.144
overall efficiency for the pump of the ORC	0.05
overall efficiency for the regenerator of the ORC	0.04
unit fixed cost for heat exchangers (U.S.\$)	0
unit variable cost for heat exchangers (U.S.\$/m ²)	1650

Table 2. Data for Examples

Example 1													
	DWC			CED			SVS						
	TIN ^a	TOUT ^b	FCp ^c	TIN	TOUT	FCp	TIN	TOUT	FCp				
HPS1 ^d	78.19	77.19	2568	78.25	77.25	2646	78.19	77.19	2640				
HPS2	78.31	77.31	1982	78.31	77.31	1196	78.3	77.3	1100				
HPS3	100.58	99.58	31	99.78	98.78	121							
AE	198.08	30	4.075	288	30	3.22	288.71	30	3.057				
CPS1 ^e	99.95	100.95	3833	100.02	101.02	3917	99.98	100.98	3902				
CPS2	197.08	198.08	1786	157.75	158.75	488	287.71	288.71	982				
CPS3				287	288	743							
CU	29	39		29	39		29	39					
HU	300	299		300	299		300	299					
Example 2													
	I			II			III			IV			
	TIN	TOUT	FCp	TIN	TOUT	FCp	TIN	TOUT	FCp	TIN	TOUT	FCp	
CSS													
HPS1	78	77	2400	78	77	2400	78	77	2400	78	77	3100	
HPS2	78	77	1320	78	77	1320	78	77	1320	78	77	1300	
HPS3	100	90	30	149	95	2.7	139	94	2.2	135	92	6.97	
AE	192	25	4.91	190	25	6	185	25	3.25	185	25	13.125	
CPS1	100	101	3120	100	101	3120	100	101	1380	100	101	10 100	
CPS2	109	147	45	124	165	28.5	122	158	17.2	123	160	64.86	
CPS3	177	192	29.3	181	190	27.7	172	185	11.53	173	185	41.6	
CU	18	32		18	32		18	32		18	32		
HU	300	250		300	250		300	250		300	250		
OSS													
HPS1	85	80	364	85	80	246	87	81	1150	91	82	411.11	
HPS2	78	77	2240	78	77	1500	78	77	7200	78	77	3200	
HPS3	103	95	121.25	108	95	51.53	99	93	716.6	100	99	2500	
AE	188	25	3.19	192	25	2.33	185	25	15.625	196	25	7.6	
CPS1	98	132	76.47	99	139	47	98	143	293.3	100	137	232.432	
CPS2	102	112	245	101	113	137.5	103	114	736.36	105	112	514.285	
CPS3	153	188	32.28	167	192	31.6	148	185	135.135	191	196	600	
CU	18	32		18	32		18	32		18	32		
HU	300	250		300	250		300	250		300	250		
CSS-EI													
HPS1	78	77	1820	78	77	2410	78	77	680	78	77	3100	
HPS2	78	77	2240	78	77	620	78	77	340	78	77	1300	
HPS3	100	90	58	149	95	2.96	139	94	2	135	92	8.53	
AE	192	25	4.19	190	25	6.06	185	25	3.312	185	25	13.125	
CPS1	100	101	2520	100	101	3120	100	101	1380	100	101	10 100	
CPS2	109	132	100.869	124	165	28.5	122	158	17.2	123	160	64.86	
CPS3	177	192	75.3	181	190	27.7	172	185	11.53	173	185	41.6	
CU	18	32		18	32		18	32		18	32		
HU	300	250		300	250		300	250		300	250		
OSS-EI													
HPS1	85	80	364	85	80	246	87	81	1150	91	81	370	
HPS2	78	77	2240	78	77	1500	78	77	7200	78	77	3200	
HPS3	103	95	121.25	108	95	51.53	99	93	710.5	100	99	2500	
AE	188	25	3.19	192	25	2.33	185	25	15.843	196	25	8.18	
CPS1	98	132	76.47	99	139	47	98	143	291.06	99	137	228.94	
CPS2	102	112	245	101	113	137.5	103	114	354.54	104	112	450	
CPS3	153	188	32.28	167	192	31.6	148	185	135.135	190	196	500	
CU	18	32		18	32		18	32		18	32		
HU	300	250		300	250		300	250		300	250		
Organic Rankine Cycle													
	condenser			evaporator			turbine			CU			
	TIN	TOUT		TIN	TOUT		TIN	TOUT		TIN	TOUT		
	40	30		40	100			50.7		10		20	

Table 2. continued

example 1 (kmol h ⁻¹)				CSS and CSS-EI (kmol h ⁻¹)				OSS and OSS-EI (kmol h ⁻¹)				FEED-II	
feed flow		solvent	feed flow		solvent		feed flow		solvent				
ethanol	water	glycol	ethanol	water	ethylene glycol	ethanol	water	ethylene glycol					
DWC	85	1609.24	86.87	I	6.8	38.56	6.8	I	6.8	38.56	6.8	octanol	5.06
CED	85	1609.24	48.7	II	4.54	40.82	8.44	II	4.54	40.82	8.44	octanol	4.16
SVS	85	1609.24	46.28	III	2.27	43.09	4.55	III	2.27	43.09	4.55	iso-octanol	4.43
				IV	0.91	44.45	1.8	IV	0.91	44.45	1.8	octanoic acid	4

^aTIN (°C), inlet temperature. ^bTOUT (°C), outlet temperature. ^cFCp (kW/°C), heat capacity flow rate. ^dHPS, hot process stream. ^eCPS, cold process stream.

Figure 2. Configurations for the WEIS sequences.

zones: a high-temperature zone in which there is heat exchange (i.e., process-to-process heat-exchange zone) and a low-temperature zone that considers the integration of the ORC into the process to generate shaft work. In this context, for the hot process streams there are potential heat exchangers that transfer waste heat from the HEN to run the organic Rankine cycle (evaporators), and in the cold process streams also there are potential heat exchangers that receive heat at low

temperature from the condenser of the ORC (condensers). The remaining heat exiting from the ORC is removed using cooling utilities. To satisfy the utility demands, there are considered at the cold and hot extremes of the superstructure auxiliary cooling and heating, respectively. The existences for the exchangers are optimized through binary variables. The temperatures for the process streams through the superstructure are optimization variables (continuous variables), and

Figure 4. Optimal solution for ethanol process using the HEN-ORC model.

cooling water at 29–39 °C was considered the cooling utility, whereas steam at 300 °C was considered the heating utility. For the second example, the cooling utility is at 18–32 °C, whereas the steam is at 300–250 °C. The unit steam price is U.S.\$0.024012/kWh, the unit electric power cost is U.S. \$0.065/kWh, and the unit cost for the electricity for the pump is U.S.\$0.08/kWh, the unit cooling water cost is U.S. 1.2744×10^{-3} /kWh. The working fluid in the ORC is R245fa, and the efficiency factors for ORC, pump of the ORC, and regenerator are 0.144, 0.05, and 0.04, respectively. $\Delta T_{\min} = 1$ °C, and the operation time for the plant is 8000 h/year. The economic information used is shown in Table 1, and the data for the involved streams are shown in Table 2.

Example 1. Figure 2 shows the following separation sequences without energy integration: (a) intensified extractive distillation sequence with dividing wall column and vapor side stream (DWC); (b) conventional extractive distillation sequence (CED); and (c) intensified extractive distillation sequence with vapor side stream (SVS). The streams that require heating and cooling are identified from these figures; then, the SYNHEAT model and the proposed HEN-ORC model are considered to integrate these streams. This way, Figure 3 presents the optimal designs using the SYNHEAT model to integrate the process, whereas Figure 4 shows the optimal solution obtained using the HEN-ORC model. Table 3 presents the energy consumptions of heating, cooling, and auxiliary equipment, the number of exchangers, the transferred total heat within the HEN, the transferred heat to the ORC, and the

produced power for the different scenarios with and without energy integration.

Reductions should be noted in the consumption of utilities in the separation sequences with the SYNHEAT model, specifically in the hot utility of 7.03, 11.67, and 11.72% for the DWC, CED, and SVS columns, respectively. These percentages are slightly higher than the ones obtained with the HEN-ORC model. However, the HEN-ORC model presents a major saving for the auxiliary equipment with 81.28, 89.74, and 89.63% for the DWC, CED, and SVS sequences, respectively (for the SYNHEAT model there are 55.18% DWC, 72.31% CED, and 72.4% SVS energy savings for auxiliary equipment (AE)). Then, although the total capital cost for the HEN-ORC solution is higher due to the ORC incorporated into the ethanol process, this obtains incomes for sales of electric power for all of the sequences (U.S.\$14561/year for DWC, U.S.\$11285/year for CED, and U.S.\$10630/year for SVS) and reduces the total operating cost by 6.86, 11.55, and 11.6% for DWC, CED, and SVS, respectively. These profits generate total annual costs that are 6.86, 11.55, and 11.6% lower than the WEIS solution and 0.4, 0.53, and 0.44% lower than the one incorporated into the SYNHEAT model for the DWC, CED, and SVS sequences, respectively. Finally, the incorporation of the ORC to the bioethanol separation process generates a return on investment of 107.54, 103.21, and 102.1% for the sequences DWC, CED, and SVS, respectively. Note that the cost for the ORC considers cooling, pumping, cooler, evaporators, pump, regenerator, and turbine. Table 4 shows the associated costs for example 1.

Table 3. Energy Requirements for the Conventional Separation Sequences for DWC, CED, and SVS Columns

concept/sequence	DWC	CED	SVS
WEIS (kW)			
heating	5619	5148	4884
cooling	4550	3963	3740
auxiliary equipment	716	831	791
SYNHEAT Model (kW)			
heating	5223.9	4547.1	4311.3
cooling	4550	3963	3740
auxiliary equipment	320.9	230.1	218.3
no. of heat transfer units	1	1	1
total heat transferred with HEN	395	600.8	572.6
HEN-ORC Model (kW)			
heating	5231.5	4553	4317
cooling	4550	3963	3740
auxiliary equipment	134	85.2	82
no. of heat transfer units	1	1	1
total heat transferred with HEN	387.4	594.9	566.9
heat transferred to ORC	194.4	150.7	141.9
produced power	28	21.7	20.4
Savings (%)			
<i>SYNHEAT model with respect to WEIS</i>			
heating	7.03	11.67	11.72
cooling	0	0	0
auxiliary equipment	55.18	72.31	72.4
<i>HEN-ORC system with respect to WEIS</i>			
heating	6.89	11.55	11.6
cooling	0	0	0
auxiliary equipment	81.28	89.74	89.63

Example 2. The following schemes are considered for this example: conventional separation sequences based on distillation columns (CSS), hybrid configuration based on liquid–liquid

extraction and extractive distillation (OSS), conventional separation sequence for purification of ethanol with mass and energy integration (CSS-EI), and hybrid configuration based on liquid–liquid extraction and extractive distillation with mass and energy integration (OSS-EI). The two last cases use the SYNHEAT model.²⁶ All of the designs are for purification of ethanol, and each ethanol process is applied to the HEN-ORC model. Figure 5 shows the WEIS solution for the sequence CSS, whereas Figure 6 presents the optimal solution using the HEN-ORC model.

For the CSS scheme, the HEN-ORC model yields the following energy savings: 8.29, 14.51, 16.32, and 10.16% for heating and 82.76, 82.93, 80.73, and 84.39% for the auxiliary equipment with respect to sequences I, II, III, and IV, respectively. Moreover, there are reductions by 4.71% for sequence II, 8.92% for sequence III, and 6.38% for sequence IV in cooling utility (considering the cooling water for the ORC). This solution recovers waste heat producing 34, 45, 24.3, and 107.9 kW of electricity for the configurations CSS I, II, III, and IV, respectively. The return on investment for the ORC is 111, 115, 105, and 134% for sequences I, II, III, and IV, respectively. The electric power produced generates profits between U.S. \$18094/year and U.S.\$56148/year, yielding a total annual cost of 8.52% (I), 14.77% (II), 16.28% (III), and 11.05% (IV) lower than the WEIS solution.

For the hybrid configuration (Figure 7) based on liquid–liquid extraction and extractive distillation (OSS), application of the HEN-ORC model (Figure 8) achieves energy savings of 19.28 and 19.7% in the cooling water required for sequences I and II; for the heating utility there are obtained savings of 8.31, 13.15, 4.92, and 4.65% in configurations I, II, III, and IV, respectively. There are energy savings of 84.67% for sequence I, 83.66% for sequence II, 84.64% for sequence III, and 84.33% for sequence IV in the auxiliary equipment. Furthermore, in the solutions for the integrated HEN-ORC there are total areas

Table 4. Associated Cost with and without Energy Integration for DWC, CED, and SVS Sequences

sequence:	DWC			CED			SVS		
type of integration:	WEIS	SYNHEAT	HEN-ORC	WEIS	SYNHEAT	HEN-ORC	WEIS	SYNHEAT	HEN-ORC
area (m ²):	341	369	419	402	421	456	435	452	485
Operating Cost (U.S.\$/year)									
HEN heating	1,079,387	1,003,505	1,004,960	988,910	873,484	874,613	938,196	828,201	829,284
HEN cooling	46704	46704	46704	40403	40403	40403	38130	38130	38130
auxiliary equipment cooling	6983	2956	1050	8472	2346	869	8064	2226	836
ORC cooling			1711			1326			1249
pumping			896			694			654
Capital Cost (U.S.\$/year)									
HEN exchangers		4430	3559		4235	3512		4083	3389
HEN heaters	7903	7625	5987	14165	13742	10450	14972	14569	12169
HEN coolers	15907	15907	15907	14600	14600	14600	13435	13435	13435
auxiliary equipment	5354	4591	4148	5001	3943	3560	4837	3811	3442
ORC cooler			2373			2011			1934
evaporator			4942			3981			3796
condenser									
pump			77			61			58
regenerator			220			186			179
turbine			3321			2674			2541
income from sale of electricity			14561			11285			10630
total operating cost	1,133,075	1,053,166	1,055,323	1,037,785	916,234	917,907	984,391	868,558	870,154
total capital cost	29164	32555	40537	33767	36521	41039	33245	35899	40946
total annual cost	1,162,239	1,085,721	1,081,298	1,071,553	952,755	947,661	1,017,636	904,457	900,470

Figure 5. Conventional separation sequences based on distillation columns (WEIS).

Figure 6. Conventional separation sequences based on distillation columns with energy integration using HEN-ORC model.

Figure 7. Hybrid configuration based on liquid-liquid extraction and extractive distillation (WEIS).

Figure 8. Hybrid configuration based on liquid-liquid extraction and extractive distillation applying the HEN-ORC integration.

61.75, 65.99, 28.77, and 23.97% greater than the one obtained in the WEIS configurations for the different sequences; nevertheless, the waste heat recovered in the auxiliary equipment is used in the ORC (896.7, 427.8, 815.7, and 388 kW) to yield 129.1, 61.6, 117.4, and 55.8 kW of electric power.

Then, the incomes obtained reduce the total annual cost by 10.35, 13.33, 5.41, and 5.01% with respect to the WEIS solution for sequences I, II, III, and IV, respectively. The return on investment for the ORC is 157, 134, 134, and 120% for sequences I, II, III, and IV, respectively. Table 5 presents the

Table 5. Energy Requirements for CSS and OSS with and without Energy Integration

concept/sequence:	CSS				OSS			
	I	II	III	IV	I	II	III	IV
WEIS (kW)								
heating	5270	4540	2150	13000	6180	4320	26300	15200
cooling	4020	3180	1120	4700	5030	3400	18400	9400
auxiliary equipment	820	990	520	2100	520	390	2500	1300
HEN-ORC Model (kW)								
heating	4833	3881	1799	11678	5666.4	3751.6	25004.2	14491.7
cooling	4020	3030	1020	4400	4060	2730	18 400	9400
auxiliary equipment	141.3	168.9	100.2	327.7	79.7	63.7	388.4	203.7
no. of exchangers	1	5	3	4	3	4	1	1
total heat transferred with HEN	437	658.5	350.6	1,322.4	513.5	568.3	1,295.7	708.2
total heat transferred to ORC	241.6	312.5	169	749.8	896.7	427.8	815.7	388
power produced	34	45	24.3	107.9	129.1	61.6	117.4	55.8
Savings (%)								
heating	8.29	14.51	16.32	10.16	8.31	13.15	4.92	4.65
cooling	0	4.71	8.92	6.38	19.28	19.7	0	0
auxiliary equipment	82.76	82.93	80.73	84.39	84.67	83.66	84.64	84.33

Figure 9. Conventional separation sequence with mass and energy integration based on the SYNHEAT model.

energy consumptions with and without energy integration by the HEN-ORC model for sequences CSS and OSS, and Table 6 shows the associated costs for both sequences.

Figures 9 and 11 present the CSS-EI and OSS-EI sequences, respectively, which incorporate mass and energy integration without considering the ORC. These show significant

Table 6. Associated Cost with and without Energy Integration CSS and OSS

sequence: type of integration: area (m ²):	CSS-I			CSS-II			CSS-III			CSS-IV			OSS-I			OSS-II			OSS-III			OSS-IV		
	WEIS	HEN- ORC	HEN- ORC	WEIS	HEN- ORC	HEN- ORC	WEIS	HEN- ORC	HEN- ORC	WEIS	HEN- ORC	HEN- ORC	WEIS	HEN- ORC	HEN- ORC	WEIS	HEN- ORC	HEN- ORC	WEIS	HEN- ORC	HEN- ORC	WEIS	HEN- ORC	HEN- ORC
	256	364	383	222	872,115	745,617	413,006	345,654	2,497,247	433	861	282	737	195	574	1105	1552	595	783					
HEN heating	1,012,345	928,391																						
HEN cooling	40984	40984	30891	32420	30891	11418	10399	44858	51281	41392	813	3976	650	25488	3960	13253	2077							
auxiliary equipment cooling	8360	1440	10093	1722	10093	5301	1022	3341	5301	3341	5301	5301	813	3976	650	25488	3960	13253	2077					
ORC cooling pumping		2126	2750																					
		1113	1440																					
HEN exchanger		3977	5747																					
HEN heater		5671	4953																					
HEN cooler	8511	13561	10958																					
auxiliary equipment	3906	2809	3189	4439	4439	2961	2170	5217	2937	2081	1719	5216	8217	36389	23037	3694								
ORC cooler		2733	3231																					
evaporator		5941	7389																					
condenser																								
pump		94	119																					
regenerator		253	299																					
turbine		3994	4970																					
income from sale of electricity		18094	23401																					
total operating cost	1,061,690	974,056	914,629	782,422	429,726	359,343	2,566,575	2,301,466	1,243,736	1,142,735	868,494	754,889	5,265,204	3,028,947	2,886,930									
total capital cost	25 980	39 037	22 949	40 061	13 464	24 329	35 955	69 567	28 457	64 888	22 498	49 351	69 982	47 028	63 779									
total annual cost	1,087,670	994,999	937,579	799,082	443,191	371,010	2,602,530	2,314,885	1,272,193	1,140,478	890,992	772,205	5,335,187	3,075,976	2,921,651

Figure 10. Conventional separation sequence with mass and energy integration based on the HEN-ORC integration.

Figure 11. Hybrid configuration based on liquid-liquid extraction and extractive distillation with mass and energy integration using SYNHEAT model.

reductions in the associated cost with respect to the WEIS sequences; therefore, the HEN-ORC approach is applied to yield additional energy savings. Figures 10 and 12 show the optimal configuration of the previous optimized designs

(CSS-EI and OSS-EI), where the HEN-ORC model is applied to yield the following additional energy savings. Note that the solution of Figure 10 presents the highest heating utility consumption (0.13% for sequence I, 0.25% for sequence II,

Figure 12. Hybrid configuration based on liquid-liquid extraction and extractive distillation with mass and energy integration applying HEN-ORC model.

Table 7. Energy Requirements for CSS-EI and OSS-EI

concept/sequence:	CSS-EI				OSS-EI			
	I	II	III	IV	I	II	III	IV
SYNHEAT Model (kW)								
heating	5589.3	3859.2	1797.1	11909.1	5603.8	3920.8	20714.6	14514
cooling	4640	3048.2	1034.5	4476.8	4724.1	3000.8	18363	9400
auxiliary equipment	319.3	460.9	252.5	1299.3	249.7	390	1251.6	614
no. of exchangers	1	2	2	2	2	2	1	1
total heat transferred in HEN	380.6	680.7	352.8	1090.8	576.1	399.1	1283.3	785.9
HEN-ORC Model (kW)								
heating	5597.1	3869	1802	11623.2	5666.4	3751.5	20683.9	14534.2
cooling	4640	3030	1020	4400	4060	2730	18363	9400
auxiliary equipment	124.3	167.9	101.8	328.4	79.7	69.915	393.2	220.2
no. of exchangers	1	3	6	5	3	3	1	1
total heat transferred with HEN	372.8	670.9	347.9	1376.6	513.5	568.5	1314	765.7
total heat transferred to ORC	202.8	321	170.1	761.8	896.7	427.5	827.7	414
power produced	29.2	46.2	24.5	109.7	129.1	61.5	119.1	59.6
Savings (%)								
heating	-0.13	-0.25	-0.27	2.4	-1.11	4.31	0.14	-0.13
cooling	0	0.59	1.4	1.71	14.05	9.02	0	0
auxiliary equipment	61.07	63.57	59.68	74.72	68.08	82.07	68.58	64.13

and 0.27% for sequence III) and contains the greatest number of heat exchangers, but this solution has energy savings for cooling utility between 0.59 and 1.71% and for the auxiliary equipment between 59.68 and 74.72%. Moreover, the design obtained produces electric power of 29.2, 46.2, 24.5, and 109.7 kW for CSS-EI I, II, III, and IV, respectively; therefore, the incomes produced are between U.S.\$2964/year and U.S.\$10600/year. The return on investment for the ORC is 108, 117, 105, and 135% for sequences I, II, III, and IV, respectively. The total annual costs obtained are 0.52, 1.30, 1.34, and 6.9% lower than the solutions when the SYNHEAT model is used (Figure 9).

The solutions of Figure 12 show energy savings for heating (4.31% for sequence II and 0.14% for sequences III), cooling (14.05% for sequence I and 9.02% for sequence II), and the auxiliary equipment (68.08% for sequence I, 82.07% for sequence II, 68.58% for sequence III, and 64.13% for sequence IV). The return on investment for the ORC is 157, 134, 134, and 120% for sequences I, II, III, and IV, respectively. The produced electric power is 129.1 kW for sequence I, 61.5 kW for sequence II, 119.1 kW for sequence III, and 59.6 kW for sequence IV. The achieved revenues are between U.S.\$6312/year and U.S.\$12176/year, yielding total annual separation costs 2.98, 7.15, 0.96, and 0.46% lower than the solutions that

Table 8. Associated Cost for Sequences CSS-EI and OSS-EI

sequence:	CSS-EI-I			CSS-EI-II			CSS-EI-III			CSS-EI-IV			OSS-EI-I			OSS-EI-II			OSS-EI-III			OSS-EI-IV			
type of integration:	SYNHEAT	HEN-ORC	375	SYN-HEAT	HEN-ORC	390	SYN-HEAT	HEN-ORC	131	SYN-HEAT	HEN-ORC	176	SYNHEAT	HEN-ORC	877	SYNHEAT	HEN-ORC	580	SYNHEAT	HEN-ORC	1508	SYNHEAT	HEN-ORC	804	
area (m ²):	320																								
HEN heating	1,073,688	1,075,190	741,346	743,231	345,226	346,167	2,287,707	2,232,797	1,076,473	1,088,506	753,183	720,648	3,979,202	3,973,312	2,788,088	2,791,977									
HEN cooling	47305	47305	31077	30891	10547	10399	45642	44858	48163	41392	30594	27832	187214	187214	95834	95834									
auxiliary	3255	1267	4699	1712	2575	1038	13247	3349	2545	813	3976	651	12760	4009	6260	2245									
equipment																									
cooling		1785		2825		1497		6704		7891		3762		7284		3643									
ORC cooling		934		1479		784		3510		4132		1970		3814		1907									
pumping							Annualized Capital Cost (U.S.\$/year)																		
HEN exchanger	4464	3572	8880	6038	5932	4107	15662	10185	21545	13151	23731	15661	10927	7948	7361	5493									
HEN heater	9619	6559	6976	4944	4298	3015	13055	9736	9362	6424	7600	5068	21467	15269	18350	12664									
HEN cooler	15195	15195	10402	10160	5379	5170	20554	13276	14995	12486	11049	9647	36341	36341	23081	23081									
auxiliary	3008	2545	3822	3203	2582	2196		5219	2532	2081	2410	1720	7191	5892	4634	3878									
equipment																									
ORC cooler		2439		3288		2176		5766		6410		3961		6085		3879									
evaporator		5149		7409		4436		14 789		11 255		7034		16 620		9377									
condenser																									
pump		80		122		69		266		308		158		286		153									
regenerator		226		305		201		535		594		367		564		359									
turbine		3442		5086		2964		10600		12176		6488		11375		6312									
income from		15189		24042		12742		57046		67145		32017		61982		31002									
sale of																									
electricity																									
total operating	1,124,249	1,126,483	777,124	780,141	358,349	359,886	2,346,596	2,291,220	1,127,183	1,142,735	787,754	754,865	4,179,177	4,175,635	2,890,183	2,895,609									
cost																									
total capital cost	32288	39213	30081	40558	18193	24339	49272	70377	48436	64888	44791	50107	75927	100,386	53428	65201									
total annual cost	1,156,538	1,150,507	807,205	796,656	376,542	371,483	2,395,869	2,230,550	1,175,619	1,140,478	832,546	772,956	4,255,105	4,214,039	2,943,611	2,929,808									

consider the SYNHEAT model. Table 7 presents the energy consumptions for the sequences CSS-EI and OSS-EI, and Table 8 shows the associated costs for both sequences.

It should be noticed that the areas in the solutions of the HEN-ORC model are greater than the ones of the solutions by the WEIS solution and the one that considers the SYNHEAT model; nevertheless, the solutions by the HEN-ORC model present total annual separation costs lower and this last one generates electric power from the waste heat of the process.

CONCLUSIONS

In this paper has been presented one option to reduce the energy requirements in the bioethanol separation process to yield biogasoline. In this case, the possible energy integration through the simultaneous synthesis of HEN integrated to an ORC has been considered. This integrated scheme improves the energy recovery process because this considers simultaneously the energy integration between process streams, and at the same time this includes the possible recovery of waste heat at low temperature to produce electric power. The proposed integrated scheme was applied to several bioethanol separation processes, and the results have shown that the proposed integrated HEN-ORC scheme produces significant reductions in the required utilities, which improves the overall energy efficiency. Furthermore, the electric power produced from the waste heat recovered is significant, and this reduces significantly the total bioethanol separation cost due to the sale of the electric power produced. Finally, there is required a study for the dynamic behavior of the integrated system to determine the controllability and operability of the system.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by SAGARPA-CONACyT (Grant 174560).

REFERENCES

- (1) Sadhukhan, J.; Ng, K. S. Economic and European Union environmental sustainability criteria assessment of bio-oil-based biofuel systems: refinery integration cases. *Ind. Eng. Chem. Res.* **2011**, *50*, 6794–6808.
- (2) Akgul, O.; Zamboni, A.; Bezzo, F.; Shah, N.; Papageorgiou, L. G. Optimization-based approaches for bioethanol supply chains. *Ind. Eng. Chem. Res.* **2010**, *50*, 4927–4938.
- (3) Solomon, B. D.; Barnes, J. R.; Halvorsen, K. E. Grain and cellulosic ethanol: history, economics, and energy policy. *Biomass Bioenergy* **2007**, *31* (6), 416–425.
- (4) Sosa, M. A.; Chovau, S.; Van der Bruggen, B.; Espinosa, J. Ethanol production from corn contaminated with fumonisins: a preliminary economic analysis including novel processing alternatives. *Ind. Eng. Chem. Res.* **2013**, *52*, 7504–7513.
- (5) Sapp, M. Europe's ethanol affair. *Biofuels, Bioprod. Biorefining* **2007**, *1* (2), 88–91.
- (6) Hoch, P. M.; Espinosa, J. Conceptual design and simulation tools applied to the evolutionary optimization of a bioethanol purification plant. *Ind. Eng. Chem. Res.* **2008**, *47*, 7381–7389.
- (7) Chávez-Islas, L. M.; Vasquez-Medrano, R.; Flores-Tlacuahuac, A. Optimal molecular design of ionic liquids for high-purity bioethanol production. *Ind. Eng. Chem. Res.* **2011**, *50*, 5153–5168.
- (8) Kanchanalai, P.; Lively, R. P.; Realff, M. J.; Kawajiri, Y. Cost and energy savings using an optimal design of reverse osmosis membrane pretreatment for dilute bioethanol purification. *Ind. Eng. Chem. Res.* **2013**, *52*, 11132–11141.
- (9) Errico, M.; Rong, B.-G.; Tola, G.; Spano, M. Optimal synthesis of distillation systems for bioethanol separation. Part 1: Extractive distillation with simple columns. *Ind. Eng. Chem. Res.* **2013**, *52*, 1612–1619.
- (10) Errico, M.; Rong, B.-G.; Tola, G.; Spano, M. Optimal synthesis of distillation systems for bioethanol separation. Part 2: Extractive distillation with complex columns. *Ind. Eng. Chem. Res.* **2013**, *52*, 1620–1626.
- (11) Black, C. Distillation modeling of ethanol recovery and dehydration processes for ethanol and gasohol. *Chem. Eng. Prog.* **1980**, *76* (9), 78–85.
- (12) Barba, D.; Brandani, V.; Di Giacomo, G. Hyperazeotropic ethanol salted-out by extractive distillation. Theoretical evaluation and experimental check. *Chem. Eng. Sci.* **1985**, *40* (12), 2287–2292.
- (13) Iliuta, M. C.; Thyron, F. C. Effect of calcium chloride on the isobaric vapor–liquid equilibrium of 1-propanol + water. *J. Chem. Eng. Data* **1996**, *41* (3), 402–408.
- (14) Sun, T.; Bullock, K. R.; Teja, A. S. Correlation and prediction of salt effects on vapor–liquid equilibrium in alcohol–water–salt systems. *Fluid Phase Equilib.* **2004**, *219* (2), 257–264.
- (15) Further, W. F. Extractive distillation by salt effect. *Chem. Eng. Commun.* **1992**, *116* (1), 35–40.
- (16) Balat, M.; Balat, H. Recent trends in global production and utilization of bio-ethanol fuel. *Appl. Energy* **2009**, *86* (11), 2273–2282.
- (17) Reith, J. H.; Veenkamp, J. M.; van Ree, R. Co-production of bioethanol, electricity and heat from biomass wastes: potential and R&D issues. In *Contribution to the First European Conference on Agriculture and Renewable Energy*; Netherlands Energy Research Foundation ECN: Petten, The Netherlands, 2001.
- (18) Linnhoff, B. A. *User Guide on Process Integration for the Efficient Use of Energy*; Institution of Chemical Engineers: London, UK, 1982.
- (19) Furman, K. C.; Sahinidis, N. V. A critical review and annotated bibliography for heat exchanger network synthesis in the 20th century. *Ind. Eng. Chem. Res.* **2002**, *41* (10), 2335–2370.
- (20) Konukman, A. E. S.; Camurdan, M. C.; Akman, U. Simultaneous flexibility targeting and synthesis of minimum-utility heat-exchanger networks with superstructure-based MILP formulation. *Chem. Eng. Process.: Process Intensification* **2002**, *41* (6), 501–518.
- (21) Mizutani, F. T.; Pessoa, F. L. P.; Queiroz, E. M.; Huan, S.; Grossmann, I. E. Mathematical programming model for heat-exchanger network synthesis including detailed heat exchanger designs. 2. Networks synthesis. *Ind. Eng. Chem. Res.* **2003**, *42* (17), 4019–4027.
- (22) Serna-González, M.; Ponce-Ortega, J. M.; Jiménez-Gutiérrez, A. Two-level optimization algorithm for heat exchanger networks including pressure drop considerations. *Ind. Eng. Chem. Res.* **2004**, *43* (21), 6766–6773.
- (23) Verheyen, W.; Zhang, N. Design of flexible heat exchanger network for multi-period operation. *Chem. Eng. Sci.* **2006**, *61* (23), 7730–7753.
- (24) Jiménez-Gutiérrez, A.; Ponce-Ortega, J. M.; Serna-González, M. Synthesis of heat exchanger networks including pressure drops considerations and detailed design of heat exchangers: a review. *Trends Heat Mass Transfer* **2009**, *11*, 1–16.
- (25) Morar, M.; Agachi, P. S. Review: Important contributions in development and improvement of the heat integration techniques. *Comput. Chem. Eng.* **2010**, *34* (8), 1171–1179.
- (26) Vázquez-Ojeda, M.; Segovia-Hernández, J. G.; Ponce-Ortega, J. M. Incorporation of mass and energy integration in the optimal bioethanol separation process. *Chem. Eng. Technol.* **2013**, *36* (11), 1–10.

- (27) Yee, T. F.; Grossmann, I. E. Simultaneous optimization models for heat integration – II. Heat exchanger network synthesis. *Comput. Chem. Eng.* **1990**, *14* (10), 1165–1184.
- (28) Grossman, I. E. Mixed-integer optimization techniques for algorithmic process synthesis. In *Advances in Chemical Engineering, Process Synthesis*; Anderson, J. L., Ed.; Academic Press: New York, 1996; Vol. 23, pp 171–246.
- (29) Ma, K. L.; Hui, C. W.; Yee, T. F. Constant approach temperature model for HEN retrofit. *Appl. Therm. Eng.* **2000**, *20* (15–16), 1505–1533.
- (30) Ponce-Ortega, J. M.; Jiménez-Gutiérrez, A.; Grossmann, I. E. Simultaneous retrofit and heat integration of chemical processes. *Ind. Eng. Chem. Res.* **2008**, *47* (15), 5512–5528.
- (31) López-Maldonado, L. A.; Ponce-Ortega, J. M.; Segovia-Hernández, J. G. Multiobjective synthesis of heat exchanger networks minimizing the total annual cost and the environmental impact. *Appl. Therm. Eng.* **2011**, *31* (6–7), 1099–1113.
- (32) Lee, K. M.; Kuo, S. F.; Chien, M. L.; Shih, Y. S. Parameters analysis on organic Rankine cycle energy recovery system. *Energy Convers. Manage.* **1988**, *28* (2), 129–136.
- (33) Hung, T. C.; Shai, T. Y.; Wang, S. K. A review of organic Rankine cycles (ORCs) for the recovery of low-grade waste heat. *Energy* **1997**, *22* (7), 661–667.
- (34) Hung, T. C. Waste heat recovery of organic Rankine cycle using dry fluids. *Energy Convers. Manage.* **2001**, *42* (5), 539–553.
- (35) Hettiarachchi, M. H. D.; Golubovic, M.; Worek, W. M.; Ikegami, Y. Optimum design criteria for an organic Rankine cycle using low-temperature geothermal heat sources. *Energy* **2007**, *32* (9), 1698–1706.
- (36) Dai, Y.; Wang, J.; Gao, L. Parametric optimization and comparative study of organic Rankine cycle (ORC) for low grade waste heat recovery. *Energy Convers. Manage.* **2009**, *50* (3), 576–582.
- (37) Desai, N. B.; Bandyopadhyay, S. Process integration of organic Rankine cycle. *Energy* **2009**, *34* (10), 1674–1686.
- (38) Hipólito-Valencia, B. J.; Rubio-Castro, E.; Ponce-Ortega, J. M.; Serna-González, M.; Nápoles-Rivera, F.; El-Halwagi, M. M. Optimal integration of organic Rankine cycle with industrial processes. *Energy Convers. Manage.* **2013**, *73*, 285–302.
- (39) Hipólito-Valencia, B. J.; Rubio-Castro, E.; Ponce-Ortega, J. M.; Serna-González, M.; Nápoles-Rivera, F.; El-Halwagi, M. M. Optimal design of inter-plant waste energy integration. *Appl. Therm. Eng.* **2013**, *62*, 633–652.
- (40) Hipólito-Valencia, B. J.; Lira-Barragán, L. F.; Ponce-Ortega, J. M.; Serna-González, M.; El-Halwagi, M. M. Multiobjective design of interplant trigeneration systems. *AIChE J.* **2014**, *60*, 213–236.
- (41) Vázquez-Ojeda, M.; Segovia-Hernández, J. G.; Hernández, S.; Hernández-Aguirre, A.; Kiss, A. A. Design and optimization of an ethanol dehydration process using stochastic methods. *Sep. Purif. Technol.* **2013**, *105*, 90–97.
- (42) Segovia-Hernandez, J. G.; Vázquez-Ojeda, M.; Gómez-Castro, F. I.; Ramírez-Márquez, C.; Errico, M.; Tronci, S.; Rong, B.-G. Process control analysis for intensified bioethanol separation systems. *Chem. Eng. Process.: Process Intensification* **2014**, *75*, 119–125.
- (43) Brooke, A.; Kendrick, D.; Meeruas, A.; Raman, R. *GAMS – Language Guide*; GAMS Development Corp.: Washington, DC, USA, 2013.