CHEMICAL ENGINEERING TRANSACTIONS

VOL. 39, 2014

A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Peng Yen Liew, Jun Yow Yong

ISBN 978-88-95608-30-3; **ISSN** 2283-9216 DOI:10.3303/CET1439238

Process Integration for Bromine Plant

Stanislav Boldyryev*[a], Petar Sabev Varbanov[b]

[a]Olvia Corporation, Laboratorna Str., 45, 49010 Dnepropetrovsk, Ukraine
[b]Centre for Process Integration and Intensification – CPI[2], Research Institute of Chemical and Process Engineering-MÜKKI, Faculty of Information Technology, University of Pannonia, Egyetem u. 10, H-8200 Veszprém, Hungary
stas.boldyryev@gmail.com

This paper deals with analysis of energy consumption of Ukrainian bromine plant. Process integration allows reducing the energy consumption on 1.5 MW by heat recovery. It is achieved by improvement of recuperative heat exchangers network. Additionally heat recovery may be increased by multistage evaporation of sodium bromide and ferrous chloride. Increase the heat recovery leads utility reduction. This is not only heating and cooling duty but also power pumping and pipe heat losses. The investment for retrofit project is about 757 100 € and payback period about 2 y.

1. Introduction

Bromine industry is an important part of big chemical family. Bromine and bromine compounds have wide application in different fields. Primary using of bromine compounds are in flame retardants, drilling fluids, brominated pesticides (mostly methyl bromide), and water treatment. Bromine is also used in the manufacture of dyes, insect repellents, perfumes, pharmaceuticals, and photographic chemicals. Other bromine compounds are used in a variety of applications, including chemical synthesis, mercury control, and paper manufacturing. The structure of bromine consumption in the world during 2013 is presented in Table 1 (Ober, 2013).

Table 1: World bromine and bromine compounds consumption in 2013

Consumer segment	Consumption, t
Flame retardants	483,000
Drilling fluids	103,500
Organic synthesis	86,300
Pharmaceuticals	77,600
Water treatment	69,000
Agriculture	43,100

The row materials for bromine industry are the sea water brines and underground brines. The bromine available for extraction occurs as bromide in the ocean, in salt lakes and in brine or saline deposits left by evaporation of such waters by solar heat (Harben. 2003). Sea bitterns, the left over concentrated solution after the crystallizing out of salt from the sea water, are very reach of bromine and offers a good raw material for the manufacture of bromine. Crimean bromine industry has 1% of total world production (Ober , 2013). Technology of bromine extraction is based on replacement it by other halogens mostly chlorine (Davenport, R.E. 2003).

The energy consumption of bromine plant is not well highlighted in literature. This paper tries to estimate energy consumption and energy saving potential for bromine plant with technology of bromine extraction via ferric bromide. The plant uses the technology with huge energy consumption which was developed in former Soviet Union and was based on huge and chip resources. In this work the process integration is used as basic instrument for energy efficiency improvement. This methodology showed considerable energy economy in sodium hypophosphite production as reported by Tovazhnyansky et al., 2009, benzene hydrocarbon production (Tovazhnyansky et al., 2011) and other industries (Klemeš et al. 2010)

Please cite this article as: Boldyryev S., Varbanov P.S., 2014, Process integration for bromine plant, Chemical Engineering Transactions, 39, 1423-1428 DOI:10.3303/CET1439238

2. Process analysis

Sea bittern having 0.6-1 g/l bromine is used for manufacture of bromine. The technology for manufacture of bromine has been developed at Crimean Bromine-Iodine Research Institute, Saki, Crimea. The capacity utilization of this plant during the last ten years was noticed to be varying between 30 % to 100 % and their total production always remained far below the demand of bromine in the CIS countries.

2.1 Process description

There are some workshops at the plant, they are: brine pumping, bromine extraction, bromine production, ferrous chloride, wastewater treatment, bromides production, boiler house and cooling water cycle. Analysis of heat energy consumption was made by pinch method with some modifications connected with plant features. Firstly plant has big area which leads to high energy consumption for pumping. Secondly, there are continuous and batch processes connected each other.

Existing process based on bromine extraction from sea brine with use of chlorine. Brine with chlorine is fed to extraction tower where bromine is absorbed by ferric bromide. Ferric bromide further goes to the column. Chlorine is fed to column to and chemical reaction is started. Bromine vapour goes to the top of the column and enters to the condenser where it is condensed by cooling water. Hot mixture of ferric chloride goes out from the bottom of the column and is fed to evaporation unit. Condensed bromine is used as finished product as well as row material for bromides production.

2.2 Estimation of energy saving potential

Stream data of the bromine site is shown on Figures 1, 2.

Name	Inlet T [C]	Outlet T [C]	MCp [W/C]	Enthalpy [kW]	Segm.	HTC [W/m2-C]	Flowrate [kg/h]	Effective Cp [kJ/kg-C]
Ferrous chloride	90,0	40,0	8325	416,3		200,0	1,070e+00	2,800
Bromine condensation	64,0	63,0	1,835e+005	183,4		200,0	---	---
Extra vapour	110,0	109,0	2,660e+005	265,9		200,0	---	---
Condensate of heating steam	120,0	40,0	1307	104,5		200,0	1120	4,200
Condensate of extra vapour	110,0	40,0	486,5	34,06		200,0	417,0	4,200
Water for CaCO3	18,0	55,0	1,746e+004	646,0		200,0	1,500e+00	4,190
Heating of FeCl3	40,0	120,0	544,4	43,56		200,0	700,0	2,800
Evaporation of FeCl3	120,0	121,0	2,611e+005	261,1		200,0	---	---

Figure 1. Stream data of bromine plant

Name	Inlet T [C]	Outlet T [C]	MCp [W/C]	Enthalpy [kW]	Segm.	HTC [W/m2-C]	Flowrate [kg/h]	Effective Cp [kJ/kg-C]
Bromine reactor cooling	60,0	55,0	9312	46,56		200,0	---	---
Correction reactor cooling	90,0	60,0	2682	80,45		200,0	---	---
Extra vapour of 1st evaporation	61,0	60,0	3,964e+005	396,4		200,0	---	---
Extra vapour of 2nd evaporation	75,0	74,0	7,255e+005	725,5		200,0	---	---
Condensate of heating steam	95,0	75,0	2654	53,08		200,0	2275	4,200
1st evaporation	109,0	110,0	3,811e+005	381,1		200,0	---	---
2nd evaporation	114,0	115,0	7,031e+005	703,1		200,0	---	---
Correction reactor heating	55,0	90,0	2682	93,86		200,0	---	---
Preheating of feed	60,0	109,0	2721	133,3		200,0	---	---
Heating system	50,0	80,0	1493	44,80		200,0	---	---
Water to boiler house	20,0	36,0	1,862e+004	298,0		200,0	1,600e+00	4,190
Condensate and treated water	45,0	75,0	1,164e+004	349,2		200,0	1,000e+00	4,190
Water to deaerator	75,0	102,0	5250	141,8		200,0	4500	4,200

Figure 2. Stream data of sodium bromide plant

Based on stream data from Figures 1 and 2 Composite Curves of bromine site were built. There is was Heat Integration at the site. Total energy consumption for heating 3,142 kW and for cooling 2,306 kW. Composite curves of bromine site are presented of Figure 3. There is big distance between the bromine plant and sodium bromide plant. It doesn't allow making heat integration for both processes. Reduction of energy consumption of bromine site will be done by pinch methodology (Smith, 2005). It allow to make the integrated flowsheet for independent processes of the site. Further reduction of energy consumption is possible by application Total Site methodology as reported by Klemeš et al. 1997. It needs to make process integration for independent processes and make an integrated flowsheets. After this it is possible to apply the Total Site methodology.

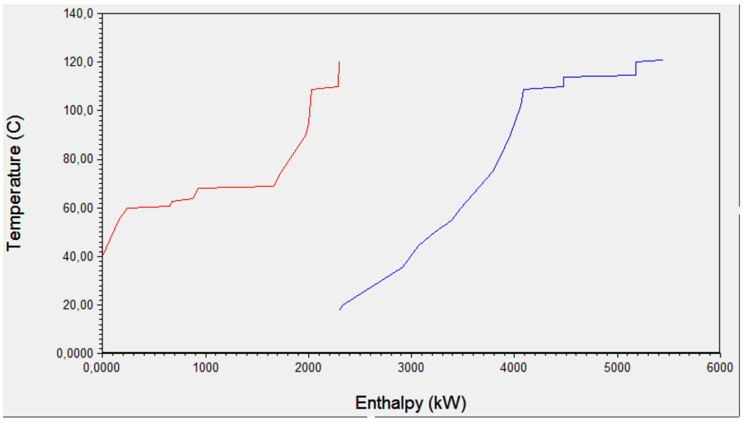

Figure 3. Composite Curves of bromine site

3. Process integration

Economic data for the analysis was used based on plant operation cost, utility and heat transfer area prices. The price of hot utility is 350 €/kWy, cold utility price is 35 Euro/kWy, heat transfer area price is 800 €/m^2, installation cost is 10,000 €/unit, coefficient of nonlinear of heat transfer area cost is 0.8, rate of return 10 % and plant life 5 y.

3.1 Bromine plant

Composite curves of integrated bromine plant are shown on Figure 4. It is typical threshold problem. The minimal temperature difference is 10°C. Hot utility target is 267 kW and cold utility is 320 kW. Heat recovery is increased on 682 kW in comparison of existing process.

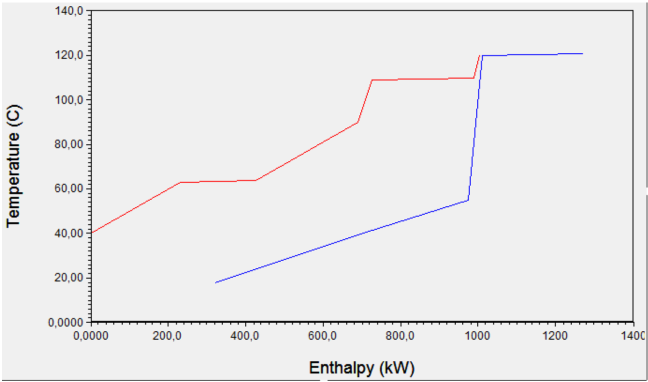

Figure 4. Bromine plant Composite Curves

Heat exchangers network of integrated process is shown on Figure 5. There are 3 recuperative and 6 utility heat exchangers. Total heat transfer area for bromine plant integrated flowsheet is 295 m^2 with shell and tube heat exchangers. Capital cost for heat exchangers network is 222,200 €. Parameters of heat exchangers are presented on Figure 5.

Heat Exchanger	Cold Stream	Cold T in [C]	Tied	Cold Tout [C]	Tied	Hot Stream	Hot T in [C]	Tied	Hot T out [C]	Tied	Load [kW]	Area [m2]	Fouling [C-h-m2/kJ]	dT Min Hot [C]	dT Min Cold [C]
E-101	Water for CaCO3	18,0		55,0		Extra vapour	110,0		109,1	✓	229,3	32,0	0,0000	55,00	91,14
E-110	Cooling Water	20,0		34,5		Condensate of extra vapour	110,0		40,0		34,06	4,9	0,0000	75,51	20,00
E-106	Heating of FeCl3	110,0		120,0		MP Steam	175,0		175,0		5,444	0,5	0,0000	55,00	64,96
E-111	Cooling Water	20,0		34,8		Condensate of heating steam	90,8		40,0		66,42	11,4	0,0000	56,03	20,00
E-109	Cooling Water	20,0		35,1		Bromine condensation	64,0		63,0		183,4	27,3	0,0000	28,94	43,00
E-105	Heating of FeCl3	40,0		110,0		Condensate of heating steam	120,0		90,8		38,11	18,1	0,0000	10,00	50,83
E-100	Water for CaCO3	18,0		55,0		Ferrous chloride	90,0		40,0		416,3	166,5	0,0000	35,03	22,00
E-112	Cooling Water	20,0		35,6		Extra vapour	109,1	✓	109,0		36,63	2,4	0,0000	73,55	89,00
E-107	Evaporation of FeCl3	120,0		121,0		MP Steam	175,0		173,0		261,1	25,2	0,0000	54,00	53,04

Figure 5. Heat exchangers parameters of bromine plant

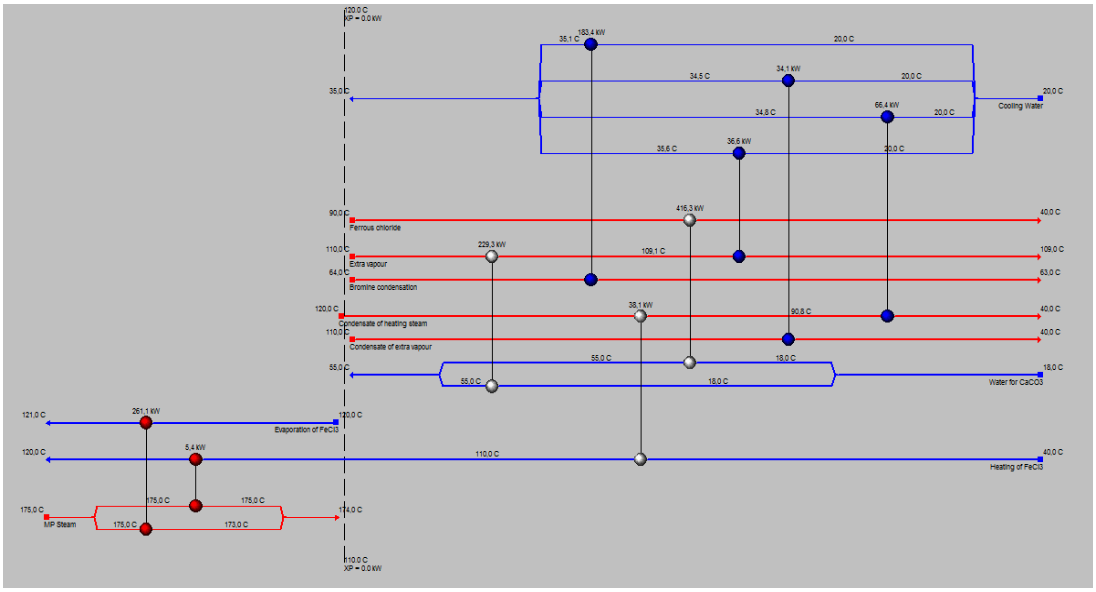

Figure 6. Integrated heat exchangers network of bromine plant

3.2 Sodium bromide plant

Sodium bromide plant has more complicated heat systems and consists from system of brominating reactors, correction reactors, preliminary evaporation station, filtration, main evaporation station, and centrifugation. Sodium bromide plant is the main consumers of steam and cooling water of the site. The energy efficiency of this plant is the main part overall site. Composite curves for optimal ΔT_{min} of sodium bromide plant are presented on Figure 7.

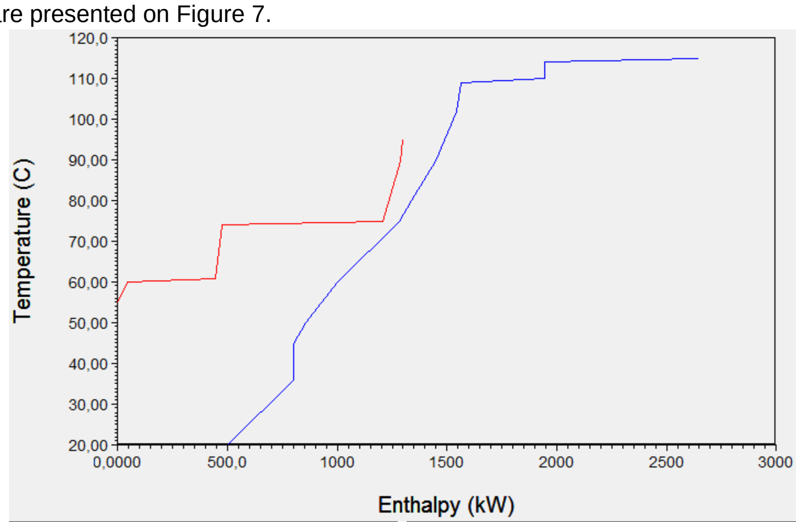

Figure 7. Sodium bromide plant Composite Curves

Optimal minimum temperature difference between hot and cold streams is 3 °C. Hot Pinch temperature is 75 °C; Cold Pinch temperature is 72 °C. Pinch point is localized on main evaporation stage. Hot utility of integrated process is 1,328 kW, cold utility is 486 kW, heat recovery is 817 kW.

Based on composite curves integrated heat exchangers network was built and it is shown on Figure 9. The system includes 16 heat exchangers, 8 of them are recuperative and 8 utility ones. Minimal heat transfer area for shell and tube heat exchanger is 912 m^2. Capital cost targets for heat system is 534,900 €. The characteristics of heat exchangers for sodium bromide plant are presented on Figure 8.

Heat Exchanger		Cold Stream	Cold T in [C]	Tied	Cold Tout [C]	Tied	Hot Stream	Hot T in [C]	Tied	Hot T out [C]	Tied	Load [kW]	Area [m2]		Fouling [C-h-m2/kJ]	dT Min Hot [C]	dT Min Cold [C]
E-126		Preheating of feed	86,8		109,0		MP Steam	175,0		174,8		60,46	4,1		0,0000	66,00	87,99
E-122		Cooling Water	20,0		49,0		Correction reactor cooling	75,0		60,0		40,23	7,0		0,0000	26,03	40,00
E-113		Correction reactor heating	72,0		90,0		MP Steam	175,0		174,6		48,27	2,7		0,0000	85,00	102,6
E-106		Correction reactor heating	55,0		72,0		Extra vapour of 2nd evaporation	75,0		74,4		45,59	53,4		0,0000	3,000	19,37
E-102		Condensate and treated water	45,0		72,0		Extra vapour of 2nd evaporation	75,0		74,1		314,3	273,4		0,0000	3,000	29,13
E-101		Water to boiler house	20,0		36,0		Extra vapour of 1st evaporation	61,0		60,2		298,0	93,0		0,0000	25,00	40,25
E-103		Condensate and treated water	72,0		75,0		Condensate of heating steam	88,2		75,0		34,92	50,8		0,0000	13,16	3,000
E-123		Heating system	50,0		72,0		Extra vapour of 2nd evaporation	75,0		74,5		32,85	32,7		0,0000	3,000	24,55
E-124		Heating system	72,0		80,0		MP Steam	175,0		174,9		11,95	0,6		0,0000	95,00	102,9
E-116		1st evaporation	109,0		110,0		MP Steam	175,0		173,6		381,1	30,4		0,0000	65,00	64,57
E-118		Cooling Water	20,0		53,5		Bromine reactor cooling	60,0		55,0		46,56	16,6		0,0000	6,469	35,00
E-111		Preheating of feed	72,0		86,8		Correction reactor cooling	90,0		75,0		40,23	157,6		0,0000	3,216	3,000
E-104		Preheating of feed	60,0		72,0		Extra vapour of 2nd evaporation	75,0		74,8		32,65	44,3		0,0000	3,000	14,85
E-127		Water to deaerator	75,0		78,5		Condensate of heating steam	95,0		88,2		18,15	12,5		0,0000	16,54	13,16
E-114		Water to deaerator	78,5		102,0		MP Steam	175,0		174,5		123,6	7,6		0,0000	73,00	96,07
E-117		2nd evaporation	114,0		115,0		MP Steam	175,0		169,7		703,1	62,8		0,0000	60,00	55,71

Figure 8. Heat exchangers parameters of sodium bromide plant

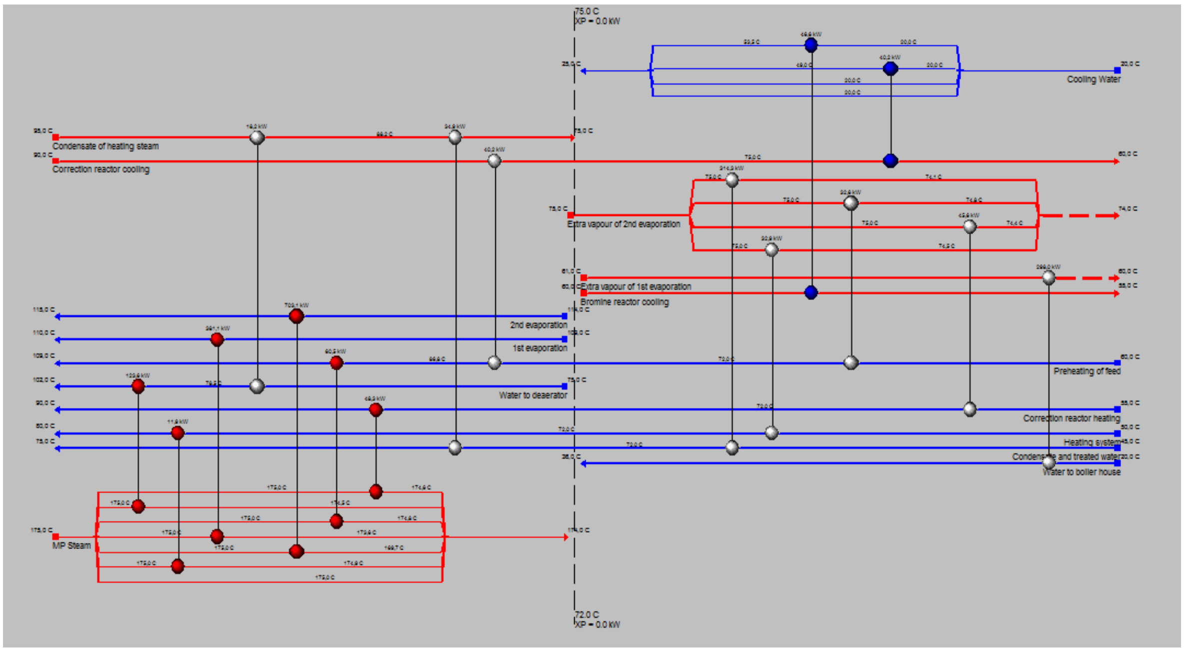

Figure 9. Integrated heat exchangers network of sodium bromide plant

4. Results and discussion

4.1 Bromine plant

Application of pinch design lets to improve heat recovery of bromine plant and reduce the hot and cold utilities on 682 kW. Reduction of energy cost is 265,570 €/y and capital cost for retrofit project is 222 200 Euro. Simple payback period of fund is 10 months.

4.2 Sodium bromide plant

Sodium bromide plant is more complicated for retrofit but it has bigger potential for energy saving. Process integration has shown heat recovery potential 817 kW for hot and cold utilities. It reduces the energy cost on 315,545 €/y, capital investment for heat exchangers network application is 534,900 € and payback period of capital investment at present energy prices is 20.3 months.

4.3 Limitations and future work

Bromine plants have a corrosive media, this point require special materials for heat transfer equipment. Heat transfer area can be reduced by application of high effective heat exchangers as reported by Arsenyeva, et al. 2011. Heat integration of existing plants can be also improved by multi stage evaporation units, especially for ferric chloride and sodium bromide concentration. Additional analysis and deeper research are needed for these stages because of specific media and crystallization features components.

The bromine plants usually are situated on big areas due to huge raw materials volumes. As reported in this paper the plant consists of several units which cannot be integrated due to big distance between them. This problem can be solved by Total Site analysis procedure, which was reported by Klemeš J. et al. 1997. In the last works Boldyryev et al., 2013 proposed extended methodology for Total Site heat recovery. It shown big potential for energy saving and capital cost reduction due to heat transfer area minimisation. Another research of Boldyryev et al., 2013 shows the methodology for capital cost reduction of Site retrofit via power cogeneration procedure. This paper makes a good background for further analysis of bromine plants with use of different instruments of Total Site methodology and heat transfer area minimisation.

5. Conclusion

This paper shows huge potential for energy saving of bromine site by heat recovery improvement with use of process integration methodology. Energy efficiency improvement was performed for two plants of bromine site. The amount of heat recovery for bromine plant is increased on 682 kW, minimum heat transfer area is determined to be 295 m^2, annual economy is 265,570 €/y and payback period 10 months. Heat recovery of sodium bromide plant is increased on 817 kW. Heat transfer for retrofit project is 912 m^2, annual economy 534,900 € and payback period 20.3 months. The minimal temperature difference is 10°C and 3°C for bromine and sodium bromide plant. This work allows making a retrofit of existing bromine site and make general recommendation for further analysis of het recovery and utility systems. The results of this paper will be used for Total Site analysis of bromine plants and selection heat transfer equipment.

6. Acknowledgements

The authors are acknowledge the Centre for Energy Saving Process Integration of National Technical University, Centre for Process Integration and Intensification – CPI^2 of University of Pannonia - the support from the EC project Energy - ENER/FP7/296003/EFENIS and the Hungarian project Tarsadalmi Megujulas Operativ Program - TAMOP – 4.2.2.A-11/1/KONV-2012- 0072, and staff of Public Joint Stock Company "Brom" for support in paper preparation.

References

Arsenyeva O., Tovazhnyansky L. L., Kapustenko P., Khavin G., 2011, Optimal design of plate-and-frame heat exchangers for efficient heat recovery in process industries, Energy, 36, 4588 4598.

Boldyryev S., Varbanov P. S., Nemet A., Kapustenko P., Klemeš J. J., 2013, Targeting Minimum Heat Transfer Area for Heat Recovery on Total Sites. Chemical Engineering Transaction, 35, 79-84.

Boldyryev S., Varbanov P. S., Nemet A., Klemeš J. J., Kapustenko P., 2013, Capital Cost Assessment for Total Site Power Cogeneration. Computer Aided Chemical Engineering, 32, 361-366.

Davenport, R.E. 2003. Bromine: CEH product review. In Chemical Economics Handbook. Menlo Park, CA, USA: SRI Consulting.

Harben, P. 2003. Bromine. Mining Engineering 55(6):18–20.

Klemeš J., Friedler F., Bulatov I., Varbanov, P. 2010, Sustainability in the process industry – Integration and optimization. New York: McGraw-Hill., USA, 362 p.

Klemeš J., Dhole V.R., Raissi K., Perry S.J., Puigjaner L., 1997, Targeting and Design Methodology for Reduction of Fuel, Power and CO2 on Total Sites, Applied Thermal Engineering, 17, (8-10), 993–1003.

Ober J. A., 2013, U.S. Geological Survey, Mineral Commodity Summaries.

Smith R., 2005, Chemical process design and integration, Chichester, UK: Wiley.

Tovazhnyansky L., Kapustenko P, Ulyev L., Boldyryev S., 2011, Heat Integration Improvement for Benzene Hydrocarbons Extraction from Coke-Oven Gas. Chemical Engineering Transaction, 25, 153-158.

Tovazhnyansky L., Kapustenko P, Ulyev L., Boldyryev S., 2009, Synthesis of energy saving integrated flowsheet for sodium hypophosphite production. Chemical Engineering Transactions, 18, p. 93-98.