# Vapour–Liquid Equilibria in the Poly(methyl methacrylate) + + 2-Butanone System Containing Lower Concentrations of Solute at Normal or Reduced Pressures

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Dedicated to Professor Egon Bauman on his 90<sup>th</sup> birthday

Vapour–liquid equilibria (VLE) were determined in the poly(methyl methacrylate) + 2-butanone system under isothermal conditions at 333.15, 343.15, and 353.15 K using an improved allglass micro-ebulliometer with circulation of the liquid phase for the dynamic measurement of total pressure over liquid mixtures. The experimental data were correlated using the UNIQUAC-FV model and the applicability of three known predictive models was tested. It was found that only the UNIFAC-vdw-FV model gives excellent prediction of VLE for the studied system.

Key words:

vapour-liquid equilibrium, experimental data, polymer-solvent system, correlation, ebulliometer

# Introduction

Many industrial processes face a variety of issues related to the thermodynamics of polymer solutions. To evaluate the thermodynamic properties of industrial systems we need experimental data, which are often missing. Alternatively, we can resort to models based on the structure–property relationship to estimate and/or predict the thermodynamic properties, or phase equilibria in particular.

The aim of this study was to provide new – and always welcome – experimental data on vapour-liquid equilibria (VLE) in the poly(methyl methacrylate) [PMMA] + 2-butanone (methyl ethyl ketone) system, determined under isothermal conditions at 333.15, 343.15, and 353.15 K using techniques infrequently exploited for the investigation of polymer solutions. Additionally, three group contribution prediction models developed earlier were tested against the obtained experimental data to see how applicable they may be for practical use.

## Experimental equipment and procedure

Experimental techniques are summarised and discussed in<sup>1</sup>. In our earlier study<sup>2</sup>, we designed a micro-ebulliometer for the quick measurement of the total pressure of systems containing a solvent and a polymer or a non-volatile component, for which only a little amount of material is required. Detailed testing and a discussion about the error

caused by a little hold-up of solvent in the vapour phase part of the equilibrium still was published in the same paper. It was also concluded that the accuracy given in 4 digits in composition was reliable.

For this study however, we improved the original ebulliometer inasmuch as we not only simplified the construction to make operation easier, but also to make it more reliable. The improved ebulliometer is shown in Figure 1. The boiler is now



Fig. 1 – Modified ebulliometer

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Compound	CAS No.	Denotation	Source	Specification
Poly(methyl methacrylate)	9011-14-7	PMMA	Acros Organics	$M_{\rm w}$ = 15 000 g mol <sup>-1</sup> ; M <sub>w</sub> /M <sub>n</sub> = 1.18
2-Butanone, ACS reagent	78-93-3		Sigma-Aldrich	purity >99.0 %

Table 1 – Description of compounds

broader in order to minimise the possibility of caking of the polymer on the boiler finger. The separator of the vapour and liquid phases has been removed, because separation occurs in the whole volume around the thermometer well.

With the improved device, equilibrium data can be collected with only a small amount of polymer available. The experimental uncertainty u in the composition and pressure are estimated as u(w) = 0.0001, and u(P) = 0.001 kPa, respectively, as discussed in<sup>3</sup>.

## Results and data processing

Table 1 shows the quality and the source of the compounds. The PMMA + 2-butanone system was studied at three isotherms: 333.15, 343.15, and 353.15 K. Table 2 summarises the vapour pressure data expressed in terms of 2-butanone activity,  $a_1 = P_1/P_1^{\circ}$ , where  $P_1$  is partial pressure and  $P_1^{\circ}$  is vapour pressure of pure solvent.

The obtained experimental data were correlated using the UNIQUAC-FV model<sup>4</sup>, which includes a contribution for free–volume differences between polymer and solvent molecules, what enables better description of polymer–solvent system. The expression for the activity of a solvent, *i*, in a polymer is used:

$$\ln a_{i} = \ln a_{i}^{C} + \ln a_{i}^{R} + \ln a_{i}^{FV}$$
(1)

where  $a_i$  is the activity of solvent *i* at solution temperature *T*,  $a_i^C$  is the combinatorial contribution to the activity providing the contributions due to differences in molecular size, and  $a_i^R$  is the residual contribution, providing contributions due to molecular interactions to the activity. Both contributions are identical to the original UNIQUAC model described in the DECHEMA Data Collection<sup>1</sup>. The free–volume contribution to the activity,  $a_i^{FV}$ , is calculated by means of the Flory expression:

$$\ln a_i^{FV} = 3c_i \ln \left[ \frac{\tilde{v}_i^{1/3} - 1}{\tilde{v}_M^{1/3} - 1} \right] - c_i \left[ \left( \frac{\tilde{v}_i}{\tilde{v}_M} - 1 \right) \left( 1 - \frac{1}{\tilde{v}_i^{1/3}} \right)^{-1} \right]$$
(2)

where  $c_i$  denotes an external degree of freedom parameter,  $\tilde{v}_i$  is the reduced volume of component *i*, and  $\tilde{v}_M$  is the reduced volume of mixture. Despite the fact that the values of  $c_i$  could be discussed<sup>5</sup> or

Table 2 – Total pressure P and 2-butanone activity  $a_1$  versus mass fraction  $w_1$  in the 2-butanone (1) + PMMA (2) system

w <sub>1</sub>	P (kPa)	<i>a</i> <sub>1</sub>
T =	333.15 K; $P_1^{\circ} = 52.07$	7 kPa
1.0000	52.070	1.0000
0.9524	52.050	0.9996
0.8998	51.997	0.9986
0.8471	51.920	0.9971
0.7995	51.840	0.9956
0.7497	51.706	0.9930
0.6993	51.500	0.9891
T =	343.15 K; $P_1^{\circ} = 74.08$	7 kPa
1.0000	74.087	1
0.9524	74.042	0.9994
0.8998	73.953	0.9982
0.8471	73.842	0.9967
0.7995	73.716	0.9950
0.7497	73.509	0.9922
0.6993	73.190	0.9879
T =	353.15 K; $P_1^{\circ} = 102.9$	6 kPa
1.0000	102.967	1
0.9524	102.895	0.9993
0.8998	102.750	0.9979
0.8471	102.586	0.9963
0.7995	102.380	0.9943
0.7497	102.081	0.9914
0.6993	101.618	0.9869

Standard uncertainties u are u(w) = 0.0001, u(P) = 0.001 kPa

taken as adjustable parameters, in this paper  $c_i = 1.1$  is considered.

The calculation procedure requires the densities of the solvent and of the polymer at the temperature of polymer solution, molecular weight of the repeating unit of component i, van der Waals volume parameters, and the surface area parameters of the repeating unit of component i. The densities are estimated using the DIPPR data bank<sup>6</sup> for the 0.0007

QUAC-FV model for the 2-butanone (1) + PMMz (2) system									
Calculation procedure	T [K]	No. of data points	A <sub>12</sub> [K]	A <sub>21</sub> [K]	$\Delta a$				
Estimation	333.15-353.15	21	-206.65	513.48	0.0005				
Prediction	333.15	7			0.0005				
Prediction	343.15	7			0.0003				

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Table  $3 - A_{12}$  and  $A_{21}$  interaction parameters in the UNI-

 $\Delta a$  = average absolute deviation in calculated activity

353.15

Prediction

solvent and the Tait equation parameters obtained by Rodgers<sup>7</sup> for polymer. The van der Waals volumes and the surface area parameters of the repeating units are calculated using the group contributions values by Bondi<sup>8</sup>, but normalized using the volume and external area of the CH<sub>2</sub> unit in the polyethylene<sup>1</sup>.

The UNIQUAC-FV interaction parameters  $A_{12}$  and  $A_{21}$  have been estimated from the experimental solvent activity data by minimizing the following objective function:

$$O.F. = \frac{1}{n} \sum_{k=1}^{n} \frac{\left| a_{1k}^{calc} - a_{1k}^{exp} \right|}{a_{1k}^{exp}},$$

where *n* is the number of data points,  $a_1^{exp}$  and  $a_1^{calc}$ are the experimental and calculated solvent activities, respectively. Table 3 shows the estimated set of  $A_1$ and  $A_{21}$  interaction parameters in the UNIQUAC-FV model for the temperature range 333.15–353.15 K together with average absolute deviations in calcu-



Fig. 2 – Activity  $a_1$  of 2-butanone in PMMA as a function of 2-butanone mass fraction w, Experimental data at (•) 333.15 K, (**■**) 343.15 K and (**▲**) 353.15 K. Solid line represents predicted activities at 343.15 K using the UNIQUAC-FV parameters estimated using all data within temperature range 333.15–353.15 K.

lated activities. These parameters were used to predict activities at the three particular isotherms. The average absolute deviations in predicted activities are also summarised in Table 3. It can be seen that activities are well predicted using the estimated set of interaction parameters  $A_{12}$  and  $A_{21}$ , and therefore it can be concluded that parameters are practically temperature independent. Figure 2 additionally illustrates successful prediction of data at 343.15 K using the UNIQUAC-FV model.

Note that the simple sorption method, often referred to as total pressure measurement, usually provides data only from the concentration range with a lower solvent content. Such type of data for the PMMA + 2-butanone system are available in literature<sup>9–11</sup> but the dynamic total pressure method for boiling point measurement used in this work can provide data at high solvent concentrations.

For further analyses of the obtained data, we opted for the prediction of phase behaviour using group-contribution predictive models developed earlier: the Entropic-FV model<sup>12</sup>, the GC-Flory EOS model<sup>13</sup>, and the UNIFAC-vdw-FV model<sup>14</sup>. These were used to predict the activities of 2-butanone in mixtures with PMMA, because values for all necessary group parameters for all models have already been published. Models are described in detail in<sup>12-</sup> <sup>14</sup>, where necessary equations, calculation procedure, and parameters are presented.

It was found that the Entropic-FV model overestimates while the GC-Flory EOS model underestimates experimental data; only the UNIFAC-vdw-FV gives excellent prediction of the concentration vs. activity dependence. The reliability of the UNI-FAC-vdw-FV model is illustrated in Figure 3 for 343.15 K.



Fig. 3 – Activity al of 2-butanone in PMMA as a function of 2-butanone mass fraction  $w_{\mu}$ . Experimental data at (•) 343.15 K. Solid line represents predicted activities at 343.15 K using the UNIFAC-vdw-FV model.

## Conclusions

Total pressures over the PMMA + 2-butanone system were determined ebulliometrically in a modified still at three isotherms in the region of diluted concentrations of polymer and expressed in terms of activity. The data obtained were successfully correlated using the UNIQUAC-FV model. Three known predictive models were tested against the obtained experimental data to see how applicable they may be for practical use. It was found that only the UNIFAC-vdw-FV model gives excellent prediction of VLE for the studied system.

## List of symbols

- $a_i \text{activity of component } i$
- $a_i^C$  combinatorial contribution to the activity providing the contributions due to differences in molecular size
- $a_i^R$  residual contribution, providing contributions due to molecular interactions

 $a_i^{FV}$  – free–volume contribution to the activity

- $c_i$  external degree of freedom parameter
- $A_{ii}$  UNIQUAC parameter for interaction i j, K
- *calc* calculated
- exp experimental
- i, j component
- $M_{\rm p}$  number average molar mass, g mol<sup>-1</sup>
- $M_{\rm w}$  weight average molar mass, g mol<sup>-1</sup>
- *n* number of experimental points
- $n_i^{rep}$  number of repeating units of component *i*
- O.F. objective function
- P total pressure, kPa
- $P_i$  pressure of component *i*, kPa
- $P^{o}$  vapour pressure of pure solvent, kPa
- T temperature, K
- *u* uncertainty of measurements
- $w_i$  weight fraction of component *i*
- $\Delta a$  average absolute deviation in activity

#### References

1. *Hao, W., Elbro, H. S., Alessi, P.,* Polymer Solution Data Collection. 1: Vapor–Liquid Equilibrium, Chemistry Data Series XVI, Part 1, DECHEMA: Frankfurt/M., 1992.

- Pavlíček, J., Bogdanić, G., Wichterle, I., Circulation micro-ebulliometer for determination of pressure above mixtures containing solvent and non-volatile component, Fluid Phase Equilib. 297 (2010) 142. http://dx.doi.org/10.1016/j.fluid.2010.05.022
- Bogdanić, G., Wichterle, I., Vapor-liquid equilibrium in diluted polymer + solvent systems, J. Chem. Eng. Data 56 (2011) 1080. http://dx.doi.org/10.1021/je101052a
- 4. Jonquières, A., Perrin, L., Arnold, S., Lochon, P., Comparison of UNIQUAC with related models for modelling vapour sorption in polar materials, J. Membrane Sci. **150** (1998) 125.

http://dx.doi.org/10.1016/S0376-7388(98)00221-X

- Kontogeorgis, G. M., Folas, G. K., Thermodynamic Models for Industrial Applications: From Classical and Advanced Mixing Rules to Association Theories, Wiley, Chichester, 2010. http://dx.doi.org/10.1002/9780470747537
- Daubert, T. E., Danner, R. P., Data Compilation Tables of Properties of Pure Compounds, Design Institute for Physical Property Data, American Institute of Chemical Engineers (DIPPR/AIChE), 1993.
- Rodgers, P. A., Pressure-volume-temperature relationships for polymeric liquids: A review of equations of state and their characteristic parameters for 56 polymers, J. Appl. Polym. Sci. 48 (1993) 1061. http://dx.doi.org/10.1002/app.1993.070480613
- 8. Bondi, A., Physical Properties of Macromolecular Crystals, Liquid and Glasses, Wiley, New York, 1968.
- Tait, P. J. T., Abushihada, A. M., Comparative studies on the use of gas chromatographic and vapour pressure techniques for the determination of the interaction energy parameter, Polymer 18 (1977) 810. http://dx.doi.org/10.1016/0032-3861(77)90186-0
- Wang, K., Xue, Q., Hu, Y., Study on the vapour–liquid equilibria of the mixtures of 2-butanone–PMMA and chloroform–PMMA system, Huadong Ligong Daxue Xuebao (J. East China Univ. Sci. Technol.) 23 (1997) 109. (in Chinese)
- Regener, E., Wohlfarth, Ch., Rätzsch, M. T., Höring, S., Thermodynamik konzentrierter Poly(methylmethacrylat)--Lösungen, Acta Polym. **39** (1988) 618. http://dx.doi.org/10.1002/actp.1988.010391105
- Kontogeorgis, G. M., Fredenslund, A., Tassios, D. P., Simple activity coefficient model for the prediction of solvent activities in polymer solutions, Ind. Eng. Chem. Res. 32 (1993) 362.

http://dx.doi.org/10.1021/ie00014a013

- Bogdanić, G., Fredenslund, A., Simple activity coefficient model for the prediction of solvent activities in polymer solutions, Ind. Eng. Chem. Res. 33 (1994) 1331. http://dx.doi.org/10.1021/ie00029a032
- Kannan, D. C., Duda, J. L., Danner, R. P., Simple activity coefficient model for the prediction of solvent activities in polymer solutions, Fluid Phase Equilib. 228–229 (2005) 321. http://dx.doi.org/10.1016/j.fluid.2004.08.012

# Analysis of Cooling Water Systems in a Petroleum Refinery

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An important area in process integration is the development of methodologies to minimize water and energy use in industry. More than 20 % of the energy consumption in industry is associated with cooling and heating water. This paper presents analysis and optimization of a re-circulating cooling water system, with the aim to satisfy any supply conditions for the cooling tower. The part of the atmospheric crude oil distillation unit was chosen for analysis and synthesis of cooling tower and the cost related to the cooling water system could be reduced by modifying the configuration of the heat exchanger network. In this paper, the KSD methodology for a developed heat exchanger network is expanded with the principle based on the heuristic algorithmic water sources diagram procedure (WSD) to synthesize the mass exchange network.

These procedures are advantageous compared with other methodologies since hand calculation is used, a very useful feature for process engineers. The cooling water network was synthesized, leading to a 40 % reduction in cooling tower load, and consequently, lower operating costs and water consumption.

Key words:

cooling tower, heat exchanger network, cooling water, composite curve

# Introduction

The traditional cooling water system can be regarded as an integrated system consisting of three main components: cooler network, cooling tower, and circulation water pump. The central unit of such system is the cooling tower in which hot water is cooled by air and returned to the process. A simplified diagram of such system is shown in Fig. 1.

Since 2001, there has been intensive research in the area of integrated design of cooling water systems in the chemical and petrochemical industries. For better cooling tower performance and increased cooling tower capacity, modification of the cooling water network is very important<sup>1</sup>. An extensive report on recirculating cooling water systems has already been provided by many authors. Smith et al. developed and described a grass root design method<sup>2</sup> and distributed system for effluent cooling<sup>3</sup>. Optimum design of cooling water systems for energy and water conservation<sup>4,5</sup> was performed for the rejection of waste heat to the environment. Progress in development of cooling water systems has expanded and a comprehensive simulation model of a recirculating cooling system has been devel-



Fig. 1 – Closed loop cooling water system

oped to account for the interaction between the cooling tower performance and the heat-exchanger network configuration<sup>6</sup>. Castro et al. synthesized a cooling water system with multiple cooling towers<sup>8</sup>. The objective was to minimize the total annual cost.

Cooling water requirements of an oil refinery depend on processes in which the water is used for cooling, and on the complexity of the cooling water network configuration. The majority of designs in refineries still employ networks of water coolers that operate in parallel, which implies that heated cooling water is collected to form one or several streams,

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which are sent to the cooling tower regardless of their temperature. Moving from parallel to the series arrangement of cooling water network increases the efficiency of the cooling tower, decreases the temperature differences in the cooling water heat exchangers, and increases the pressure drop through the cooling water network. Water cooling in the processing industry contributes significantly to operating costs, so minimizing external cooling requirements through heat integration is essential for increasing profitability.

#### **Recirculating cooling water systems**

The chemical processing industry, including petroleum refineries, often uses closed-loop cooling water systems to supply the necessary cooling water. Several studies on recirculating cooling water have been reported in the literature varying from insight based on pinch analysis<sup>7,10,16</sup> to mathematical based optimization approaches<sup>15,17,18</sup>. A few authors use mathematical modelling techniques, which involve superstructure optimization in situations where multiple cooling water sources are involved<sup>9,11</sup>. In practice, there are systems with multiple cooling towers. A mathematical optimization technique for debottlenecking cooling water systems characterized by multiple cooling towers with different supply temperature was presented in several previous papers<sup>8,15,17</sup>.

Usually, a closed-loop cooling water system is arranged in a parallel configuration, as presented in Figure 1. In such a configuration, all the hot cooling water, regardless of its temperature, is collected and mixed upon exiting a process. This leads to decreased temperature and increased flow rate of the hot cooling water through the cooling tower, which lowers the heat transfer driving force. Since not all processes require cooling water at the lowest available temperature, as encountered in the cooling-tower's outlet, a cooling water system can possibly be arranged in a serial configuration. Such a configuration enables reuse of the cooling water, leading to lower required flow rate and higher water temperature in the cooling system, providing greater driving forces for heat transfer and lower operating costs.

Figure 2 shows the cooling water system of a typical refinery in a parallel configuration. It can be seen that after it has been used in different refining processes, the cooling water is collected and routed to cooling towers.

Cooling requirements in a refinery depend on the processes using cooling water and on the integration level of the heat exchanger network. In this study, a closed-loop cooling water system of a refinery is analysed to prove that the cooling tower load can be reduced by different configuration of the heat exchanger network using the KSD (*Kim & Smith Design*) graphical method, expanded by the principle based on the



Fig. 2 - Typical flow of cooling water in refineries

water sources diagram (WSD)<sup>13</sup>. The combination of these two methods is advantageous because it is easy to apply in different process features, and all calculations can be done by hand. The method generates flow sheet and information acceptable and understandable for process engineers in practice. Mathematical programming knowledge of applied mathematics as well as the knowledge of how to mathematically describe the process. The mathematical models include a varietv of functions, equations and formulas that are not real-world-engineer-friendly. Kim and Smith have developed and applied a graphical technique for maximization of cooling tower performance through minimization of supply water to the cooling water network. The KSD graphical method<sup>2</sup> utilizes limiting profiles of cooling water flows through heat exchangers to construct the composite curve. By determining pinch temperature and heat load, flow heat capacity (CP) is calculated with minimal water flow-rate through the cooling tower.

The minimal water flow rate through the cooling tower is determined in three steps. The first step is to determine feasible operating envelope of a cooling water system from cooling water composite curve, taking into consideration practical limits of the system. The second step is to explore the feasible operating envelope determined in the first step, to determine the minimal cooling water flow rate. The last step is cooling water network synthesis.

## Cooling water composite curve

Figure 3 shows the feasible region for targeting the water supply of a recirculating cooling system. The cooling water network can be changed within the feasible operating envelope. The feasible area is determined by minimal water flow rate (maximal reuse) and maximal water flow-rate (parallel configuration)<sup>4,5,6</sup>. When determining the feasible area, several practical issues should be considered: the cooling water system cannot

T 1 1 A



Fig. 3 – Composite curve with feasible operating envelope

operate above the temperature of the returning hot water because it might cause fouling problems, corrosion and problems with the cooling tower's packing.

## Case study

The applicability of the proposed methodology for designing a recirculating cooling water network is demonstrated on part of the atmospheric crude oil distillation unit in a local refinery. The analysed parallel cooling water system had eight heat exchangers, with total cooling water flow rate of 311 t h<sup>-1</sup>. The central unit in this system is the cooling tower with a water temperature of 23 °C at the exit. After passing through heat exchangers, it is collected and returned to the cooling tower at about 40 °C.

The current state of the cooling water system is given in Tables 1 and 2. Table 1 shows the flow rates of the recirculating cooling water, together with inlet and outlet temperatures. The temperature, flow rate, and cooling duty are given in Table 2.

Table 1 – Current state of the analyzed system<sup>14</sup>

Heat exchanger	Process stream	Flow rate t h <sup>-1</sup>	Flow rate CW, m <sup>3</sup> h <sup>-1</sup>	$T_{in,CW} $	$T_{out,CW}$ °C
E-1	gas	7.06	7	23	39
E-2	gasoline	75.20	75	23	39
E-3	petroleum	41.90	32	23	39
E-4	light gas oil	107.80	90	23	44
E-5	naphtha	24.10	27	23	39
E-6	LPG	8.60	12	23	34
E-7	top splitter	23.80	37	23	34
E-8	bottom splitter	49.60	32	23	39

Table 2 – Process stream data for this example.								
Heat exchanger	$^{T_{\mathrm{Hin}}}_{\mathrm{\circ C}}$	$\overset{T_{Hout}}{\circ C}$	$^{T_{\text{Cin}}}_{^{\circ}\text{C}}$	$T_{\rm Cout} $ °C	CP, kW °C <sup>-1</sup>	Q, kW		
E-1	70	40	25	55	4.27	128		
E-2	70	40	25	55	46.8	1405		
E-3	64	40	25	49	24.5	587		
E-4	80	45	30	65	62.6	2190		
E-5	75	40	35	70	14.4	504		
E-6	60	35	30	55	6.0	150		
E-7	66	35	30	61	15.2	471		
E-8	60	40	35	55	29.5	590		
						$\Sigma = 6025$		

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The data for cold streams in Table 2 (columns 4 and 5) are estimated with the same temperature difference between the inputs and outputs of hot and cold streams. For maximum reuse at serial configuration,  $T_{\text{Cout}}$  is increased by an average of 15 °C in relation to the data of Table 1 (last column), actual data for a parallel configuration.

### Characteristics of the cooling tower

The inlet temperature of the hot water in the cooling system must be < 70 °C. The wet bulb temperature and the ambient temperature are taken at average values  $T_{\rm wB} = 18$  °C and  $T_{\rm amb} = 25$  °C.

### Construction of composite curve

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The design of cooling water network is based on the cooling water composite curve, which represents overall limiting conditions of the entire network. A composite curve is constructed using data in Tables 1 and 2, with aim of maximal reuse of water (Figure 4 a and b).

The water line began at temperature of 23 °C, and pinch point was found at 55 °C. Targeted minimal cooling water flow capacity is calculated from the heat transferred to the pinch point and the temperature at the pinch point, using the following equation:

$$CP_t = \Delta Q_{pinch} / \Delta T_{pinch}$$
  
 $CP_t = \frac{5093.1}{55 - 23} = 159.16 \text{ kW} \circ \text{C}^{-1}$ 

Required targeted minimum amount of water from the tower is calculated as:

$$F = \frac{159.16 \text{ kW} \circ \text{C}^{-1}}{4.183 \text{ kJ} \text{ kg}^{-1} \circ \text{C}^{-1}} = 38.05 \text{ kg} \text{ s}^{-1} = 136.96 \text{ th}^{-1}$$



Fig. 4 – Cooling water composite curve and targeting for maximum reuse

Since operating costs are proportional to cooling water flow rate, minimal cooling water in this case is optimal.

#### Cooling water network synthesis

The cooling water network was synthesized using target minimum water flow rate of 136.96 t  $h^{-1}$  and flow capacity of 15.16 kW °C<sup>-1</sup>.

Temperature intervals are sorted in order of increasing water temperature. The procedure was developed by combining the KSD methodology and WSD principles.

For synthesis, the following steps are required:

Step 1. Divide the problem into temperature intervals, which are limited by single external cooling



Fig. 5 - Cooling water streams with transferred heat in bracket

water source (cooling tower water at 23 °C) and the internal water sources at various temperatures (Figure 5).

*Step 2.* Represent each operation by an arrow from the respective inlet to outlet temperature. This particular system consists of 7 intervals.

*Step 3.* For each temperature interval, the total number of streams, the number of streams using external cooling water source, and the number of internal water sources must be determined. For every stream in an interval, new flow capacities and transferred heat are calculated by the following equation.

$$CP_{exw/inw} = \Delta Q_{k,j} / \left(T_j - T_{j-1}\right)$$

where  $CP_{exw/imw}$  is flow capacity external water source or internal water sources,  $T_j$  and  $T_{j-1}$  are interval temperature,  $\Delta Q_{kj}$  is transferred heat between intervals for each stream.

The development of a cooling water network is shown in Figures 6–13. Final network diagram with *pinch* point is shown in Figure 11.

By adding the required flow capacities for each stream utilizing an external source, the flow capacity for the cooling tower is obtained at 159.16 kW °C<sup>-1</sup>, corresponding to the targeted water flow rate obtained from the composite curve. *Pinch* point is at 55 °C. The flow capacities of the cooling tower were changed (blue lines in Figure 13) from 159.16 kW °C<sup>-1</sup> to 92.2 kW °C<sup>-1</sup> (62.6 + 14.4 + 15.2). The new network configuration with reduced cooling tower load is shown in Figure 14.





Fig. 12 – Calculation CP for interval 7



Fig. 13 - Final network diagram



Fig. 14 – Cooling water network design with target return temperature of 60.86 °C

#### Operating costs and detailed system analysis

*Operating costs are calculated using the following equation:* 

$$OC = 2.4094 \cdot 10^{-3} (PP) + 44(F_{air}) + + 110(F_{in}) + 2275.132(M) + 1138(B)^4$$

where *PP* is pumping power,  $F_{air}$  is tower air flow rate (t h<sup>-1</sup>), *M* is make-up flow rate (t h<sup>-1</sup>), *B* is blow-down flow rate (t h<sup>-1</sup>) and  $F_{in}$  is cooling cooling tower water flow rate (t h<sup>-1</sup>).

Table 3 – Comparison base case and KSD design methods

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	$\begin{array}{c}F_{2},\\t\ h^{-1}\end{array}$	<i>T</i> ₂, °C	<i>T</i> ₀, °C	E, t h <sup>-1</sup>	B,t h <sup>-1</sup>	M,t h <sup>-1</sup>	OC 10 <sup>3</sup> \$/ year
Base case	305	40	23	7.93	3.97	11.9	151.51
KSD method	136.96	60.9	23	7.93	3.97	11.9	85.02

Cooling tower inlet flow rate of 305 t  $h^{-1}$ , as calculated from heat balance, is by 6 t  $h^{-1}$  lower than cooling water inlet flow rate, due to network losses.

New piping costs should be taken into consideration for a more accurate analysis. By reducing the cooling water flow rate, operating costs were reduced from 151,510 \$/year to 85,020 \$/year. Additional reduction in operating costs could be achieved by implementing air coolers. In this case, two air coolers that provide 260 kW of cooling power were inserted downstream of operation 3. After that modification, an additional internal source became available at 37.5 °C, with flow capacity of 22.58 kW °C<sup>-1</sup>. Cooling water network was then developed using the same procedure, and the solution is given in Figure 15. By implementing air coolers, the total flow capacity was reduced to 144.6 kW  $^{\circ}C^{-1}$ , and with it, the water flow rate to 124.4 t h<sup>-1</sup>. The overall results are given in Table 4.



Fig. 15 – Cooling water network after implementation of air-cooler

	water systems								
	$F_{2}, t h^{-1}$	$^{T_{2}}_{^{2}}$ °C	$^{T_2}_{^{2}}$ °C	E,t h <sup>-1</sup>	B,t h <sup>-1</sup>	M,t h <sup>-1</sup>	OC ·10 <sup>3</sup> \$/year		
Base case	305.00	40	23	7.93	3.97	11.9	151.51		
KSD method	136.96	60.9	23	7.93	3.97	11.9	85.02		
With air coolers	124.40	60.9	23	7.22	3.6	10.8	82,75		

 Table 4 – Comparison of different configurations of cooling water systems

# Conclusion

By implementation of a serial cooling water system configuration, developed by using the KSD method expanded with principles based on the water source diagram, a significant reduction in operating costs has been achieved. This allows better cooling tower performance and increased cooling tower capacity. Additionally, the lower recirculation water flow rate and its higher temperature will benefit the heat transfer process in the cooling tower, further reducing operating costs. By introducing additional air coolers, besides reducing operating costs, fresh water consumption can also be reduced.

## Nomenclature

- CP heat capacity flow rate, kW °C<sup>-1</sup>
- OC operating cost, \$/year
- Q total heat load, kW
- $T_0$  outlet cooling water temperature of cooling tower, °C
- $T_1$  inlet temperature of the heat exchanger network, °C
- $T_2$  outlet temperature of the heat exchanger network, °C
- $T_{\rm amb}$  ambient temperature, °C

#### Abbreviations

- FCC Fluid catalytic cracking
- HEN Heat exchange network
- KSD Kim & Smith Design
- WSD-Water Sources Diagram

#### References

- 1. *Smith, R.*, Chemical Process Design and Integration, John Wiley and Sons Ltd., Chichester, 2005, pp 583-604.
- *Kim, J. K., Smith, R.*, Cooling water system design, Chem. Eng. Sci. **56** (2001) 3641. http://dx.doi.org/10.1016/S0009-2509(01)00091-4

3. *Kim, J. K., Savulescu, L., Smith, R.*, Design of cooling systems for effluent temperature reduction, Chem. Eng. Sci. **56** (2001) 1811.

http://dx.doi.org/10.1016/S0009-2509(00)00541-8

- Panjeshahi, M. H., Ataei, A., Gharaei, M. Parand, R., Optimum design of cooling water systems for energy and water conservation, Chem. Eng. Res. Des. 87 (2009) 200. http://dx.doi.org/10.1016/j.cherd.2008.08.004
- Ataei, A., Panjeshahi, M. H., Parand, R., Tahouni, N., Application of an optimum design of cooling water system by regeneration concept and pinch technology for water and energy conservation, J. Appl. Sci. 9 (2009) 1847. http://dx.doi.org/10.3923/jas.2009.1847.1858
- Panjeshahi, M. H., Ataei, A., Application of an environmentally optimum cooling water system design to water and energy conservation Int. J. Environ. Sci. Tech. 5 (2) (2008) 251. http://dx.doi.org/10.1007/BF03326019
- Linhoff, B., Use Pinch Analysis to Knock Down Capital Costs and Emissions, Chem. Eng. Progr. 90 (1994) 32.
- 8. *Rubio-Castro, E., Serna-Gonzales, M., Ponce-Ortega, J.M., El-Halwagi, M. M.*, Synthesis of cooling water systems with multiple cooling towers, Appl. Therm. Eng. **50** (2013) 957.

http://dx.doi.org/10.1016/j.applthermaleng.2012.06.015

- Majozi, T., Moodley, A., Simultaneous targeting and design for cooling water systems with multiple cooling water supplies, Comput. Chem. Eng. 32 (2008) 540. http://dx.doi.org/10.1016/j.compchemeng.2007.03.016
- Majozi, T., Brouckaert, C. J., Buckley, C. A., A Graphical Technique for Wastewater Minimisation in Batch Processes, J. Environ. Manage. 78 (2006) 317. http://dx.doi.org/10.1016/j.jenvman.2005.04.026
- Majozi, T., Nyathi, On Cooling Water Systems Design for the South African Industry – Two Recent Developments, N., S. Afr. J. Sci. 103 (2007) 239.
- Matijašević, L., Dejanović, I., Spoja, D., A water network optimization using MATLAB- A case study, Res. Con. Res. 54 (2010) 1362. http://dx.doi.org/10.1016/j.resconrec.2010.05.011
- Gomez, J. F. S., Queiroz, E. M., Pessoa, F. L. P., Design procedure for water/wastewater minimization: single contaminant, J. Cle. Pro.15 (2007) 474. http://dx.doi.org/10.1016/j.jclepro.2005.11.018
- 14. http://free-sk.t-com.hr/save of energy in Croatian/
- Gololo, V., Majozi ,T., Zhelev, T., Semkov, K., Guided design of heating and cooling mains for lower water and energy consumption and increased efficiency, Chem. Eng. Trans. 25 (2011) 755.
- Vučković, A., Analysis of cooling water system in oil refining industry, Bachelor's thesis, Faculty of Chemical Engineering and Technology, University of Zagreb, 2009.
- 17. *Gololo, K. V.*, Process integration of complex cooling water systems, Master's thesis, Faculty of Engineering, University of Pretoria, 2011.
- Bošnjaković, F., Knoche, K. F., Pinch analysis for cooling-towers, Energy Convers. Mgmt. **39** (1998) 1745. http://dx.doi.org/10.1016/S0196-8904(98)00073-9
- Bagajewicz, M., A review of recent design procedures for water networks in refineries and process plants, Comput. Chem. Eng. 24 (2000) 2093. http://dx.doi.org/10.1016/S0098-1354(00)00579-2