CHEMICAL ENGINEERING TRANSACTIONS

VOL. 35, 2013

A publication of

AIDIC

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

Guest Editors: Petar Varbanov, Jiří Klemeš, Panos Seferlis, Athanasios I. Papadopoulos, Spyros Voutetakis

ISBN 978-88-95608-26-6; **ISSN** 1974-9791

DOI: 10.3303/CET1335129

Implementation of Heat Integration for Efficient Process Design of Direct Adipic Acid Synthesis in Flow

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Process-design intensification situated under the umbrella of Novel Process Windows heads for integrated and simplified smart-scaled (micro/meso) flow process design in a holistic picture. The example taken here is direct adipic acid synthesis which is an important intermediate for the nylon industry. To investigate its potential for process simplification cost and energy analysis is searched. Process simulation of the flow process with 40 %, 50 % and 98 % conversion is made. An energy efficient process is searched for this novel direct route in particular considering its heat integration for the three conversion cases. For this purpose pinch analysis is employed and a new heat exchanger network (HEN) is designed with minimum total annualized cost. The improvement of the HEN results in 50 - 70 % saving in operating cost which enables to pay back the extra capital cost requirement in less than one year in all cases. The benefit of heat integration is seen to be reduced with increased conversion due to the reduced heat load in the process. Another consideration here is the selection of the heat exchanger type. The pinch analysis is restricted to shell and tube heat exchangers, however by utilization of compact (including microchannel-based) heat exchangers additional benefits in terms of cost and plant complexity can be achieved.

1. Introduction

Process intensification through micro-process technology allows reaching processing through entirely new and innovative equipment in continuous flow mode (Hessel et al., 2009). Transport intensification has been vastly demonstrated (Hessel et al., 2011). Chemical intensification using harsh process conditions to boost microprocessing (high-T, high-p, high-c, safety) is increasingly studied (Hessel et al., 2013). Process-design intensification is a new field in microprocessing and it considers a completely new process design that has a new cost, energy and sustainability structure (Hessel et al., 2012a). The latter two constitute Novel Process Windows. The investigation is started with process simplification at reaction level, which is given by replacing multi-step by direct synthesis. As a demonstration example, the direct oxidation of cyclohexene with hydrogen peroxide for adipic acid synthesis is considered (Hessel et al., 2012b). In previous studies it has been shown that the direct route enables reduction of number of process units considerably which results in the total purchase cost of equipment to be cut approximately in half compared with the two-step industrial route (Vural Gürsel et al., 2012).

In this paper energy analysis is in focus. In the microreactor literature it is common to consider one unit and intensify its operation. However, we consider the chemical process as a whole in a holistic context. To improve energy efficiency of the entire process pinch analysis is taken here. It enables heat integration by maximization of process-to-process heat recovery (Townsend and Linnhoff, 1983). It can be applied with the use of available software programs such as Aspen Energy Analyzer.

In this study the effort of process-design intensification is combined with pinch analysis for designing a heat exchanger network (HEN) that enables energy efficient simplified flow process design. Also it is shown that with the use of compact (including microchannel-based) heat exchangers due to their higher heat transfer coefficient, reduced space requirement and increased safety compared to shell and tube heat exchangers it is possible to gain additional benefits (Reay, 1994).

Please cite this article as: Vural Gursel I., Wang Q., Noel T., Hessel V., 2013, Implementation of heat integration for efficient process design of direct adipic acid synthesis in flow, Chemical Engineering Transactions, 35, 775-780 DOI:10.3303/CET133512

2. Methodology

The adipic acid synthesis by direct oxidation of cyclohexene with 30% hydrogen peroxide and Na_2WO_4 and $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ as a phase-transfer catalyst has been reported by Sato et al. (1998). It has to be noted that the terminology “direct synthesis” is only valid in the strict sense at a lab-scale. On an industrial level, cyclohexene has to be produced from benzene (as cyclohexane) and this constitutes an additional step not considered in this scope. This direct route has been designed and simulated in a previous study in Aspen Plus^{TM} and described extensively with its comparison with the commercial process of two-step air and nitric acid oxidation of cyclohexane including also in terms of cost of equipment (Vural Gürsel et al., 2012).

Since the direct route is not yet commercially applied for adipic acid synthesis, a flow diagram and the process conditions were not available. The reaction characteristics of this process explained by Sato et al. (1998) were considered together with the flow diagram of the commercial nitric acid oxidation process (Oppenheim and Dickerson, 2003) to propose the downstream equipment and their conditions for the direct route. The implementation of microreactor technology was considered since it would enable to overcome limits in interfacial transfer, to safely handle hydrogen peroxide, to explore new, harsher process chemistries, and to test for better selectivity at much reduced reaction times. Accordingly, a microreactor setup is in our group and a yield of adipic acid of about 50 % is currently recorded (Shang et al., 2013). The direct route is simulated with conversion of cyclohexene of 40 % (representing primary result), 50 % (representing current improved result) and 98 % (representing superficial best performance). The capacity selected is 400 kt/y based on average adipic acid production plants. In Figure 1 the flowsheet of this direct flow oxidation process for 50 % conversion is given.

For this process simulation a basic design approach is used and the heating and cooling requirements are satisfied by the use of utilities. However, by employing heat integration, process-to-process heat recovery can be done resulting in reduction of utility loads and consequently operating costs. Pinch analysis is a powerful technique used for this purpose. In pinch analysis a stepwise procedure given in Figure 2 is followed. Aspen Energy Analyzer is used in this study for performing these steps of pinch analysis for direct flow oxidation process. The software programs can recommend several heat exchanger network designs and the design that provides the minimum total annualized cost is selected.

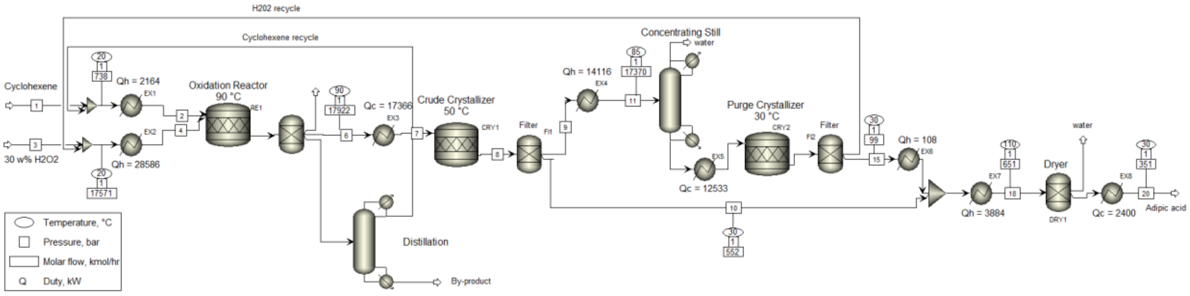

Figure 1: Flowsheet of Aspen Plus^{TM} simulation of adipic acid synthesis by direct oxidation of cyclohexene with hydrogen peroxide (50 % conversion)

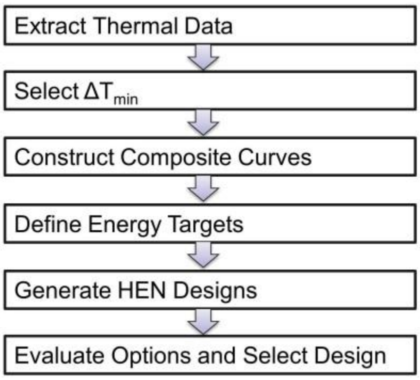

Figure 2: Stepwise procedure of Pinch Analysis

3. Results and Discussion

Pinch analysis starts with extraction of thermal data that are supply temperature, target temperature and heat duty from process heat and material balance. The Aspen Plus^{TM} simulations are used to extract the required data for the direct flow oxidation process. Heating and cooling utilities needs to be specified also. Hot utility of LP steam and cold utility of cooling water is selected that are satisfactory to supply the streams for this process. In order to make cost calculations utility cost and heat exchanger cost is required which are given in Table 1.

The next step is the selection of temperature approach (ΔT_{min}). A rule of thumb value developed from experience with shell and tube heat exchanger at medium temperatures of 10 °C is taken. With this information cold and hot composite curves can be constructed. In Figure 3 this is shown for 50 % conversion case. Composite Curves is used to define energy targets for the process. It is seen that for all three conversion cases the minimum cold utility target is 0. The minimum hot utility target is 17,916 kW, 16,560 kW and 13,492 kW for 40 %, 50 % and 98 %.

Aspen Energy Analyzer is used to generate HEN design options to satisfy most closely the targets for minimum energy consumption. Table 2 gives the total heat exchanger area, capital investment, hot utility duty, cold utility duty and annual operating cost results for the generated best two design options for the three conversion cases.

Table 1: Cost data

LP Steam[a]	Cooling water[a]	Operating time	Heat exchanger cost[b]
11.24 €/GJ	0.28 €/GJ	8,000 h/y	$37{,}614 + 916\ A^{0.81}$

[a] Utility cost modified from Turton et al. (2009) based on current prices.

[b] Coefficients for installed cost of a shell and tube heat exchanger of carbon steel material, updated from Hall et al. (1990) based on Nelson-Farrar cost index for heat exchangers, 1 € = 1.25 $.

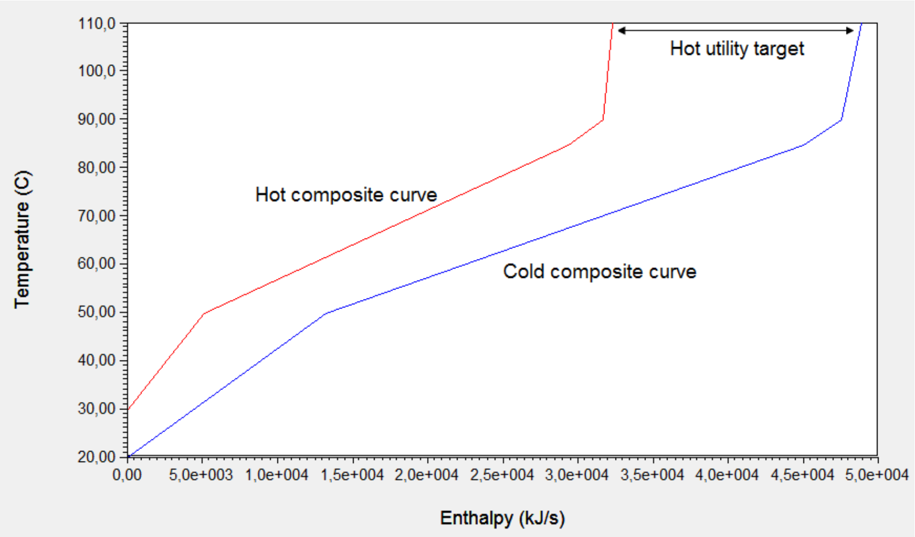

Figure 3: Combined Composite Curves of direct flow oxidation process (50 % conversion)

Table 2: Generated best two HEN design options of direct flow oxidation process for three conversion cases of 40 %, 50 % and 98 %

Design options	Area (m^2)	Capital cost (10^6 €)	Hot utility (kW)	Cold utility (kW)	Operating cost (10^6 €/y)
40 % Design 1	43,515	13.02	18,516	600	6.00
40 % Design 2	48,124	14.26	17,916	0	5.80
50 % Design 1	30,084	9.12	16,560	0	5.36
50 % Design 2	29,315	8.89	16,851	291	5.46
98 % Design 1	9,400	3.24	13,492	0	4.37
98 % Design 2	8,642	3.01	14,150	658	4.59

It is seen that for example for 40 % conversion case, design 2 enables satisfying minimum energy target but at a higher capital cost. In order to be able to select the best design option for each conversion case total annualized cost (TAC) calculation needs to be made. It is the summation of the annualized capital cost and the operating cost. The capital cost is annualized by multiplying with a factor calculated with Eq(1).

$$\frac{r(1+r)^n}{(1+r)^n-1} \tag{1}$$

where r is interest rate and n is the plant life. For a plant life of 10 y and interest rate of 10 % the annualization factor is 0.162745. The calculated TAC of the design options for the three conversion cases is given in Table 3. Design 1 is found to be the best design option for all three conversion cases. A grid diagram is a graphical method for showing coupling of hot and cold streams where the remaining heat is supplied or removed by utilities. In Figure 4 the HEN of design 1 for 50 % conversion case is presented with a grid diagram. The hot streams are seen to run from left to right and cold stream from right to left. For this design there are thirteen heat exchangers. Eight of them achieve process-to-process heat recovery and the rest five is supplied with hot utility of LP steam seen at the bottom of the figure. There is no heat exchanger utilizing cold utility of cooling water seen at the top of the figure.

The generated improved HEN design results are compared with the results of the initial network without heat integration as seen in Table 4. In order to achieve process-to-process heat exchange more heat exchangers are required in the improved HEN resulting in increased capital cost. However, the hot and cold utility requirements are very much reduced indicating a reduced operating cost. The operating cost for 40 %, 50 % and 98 % conversion is calculated to be reduced by 70 %, 68 % and 50 %. With the increase in conversion the heat load in the system is reduced creating less room for improvement. Accordingly, the benefit achieved with heat integration is seen to be reduced.

Pay-back time can be calculated to see how long it takes for the operating cost saving to pay back the extra capital cost requirement. This is given in Table 5. It is seen that with the improvement of the HEN major saving in operating cost is achieved which enables to pay back the extra capital cost requirement in less than one year (4.5 – 8 month) in all cases. These results indicate that that heat integration is a useful technique for efficient design of processes as it results in more sustainable and economical condition.

Table 3: TAC of best two HEN design options of direct flow oxidation process for three conversion cases of 40 %, 50 % and 98 %

	40 % Design 1	40 % Design 2	50 % Design 1	50 % Design 2	98 % Design 1	98% Design 2
TAC, 10^6 €/y	8.117	8.120	6.845	6.904	4.894	5.077

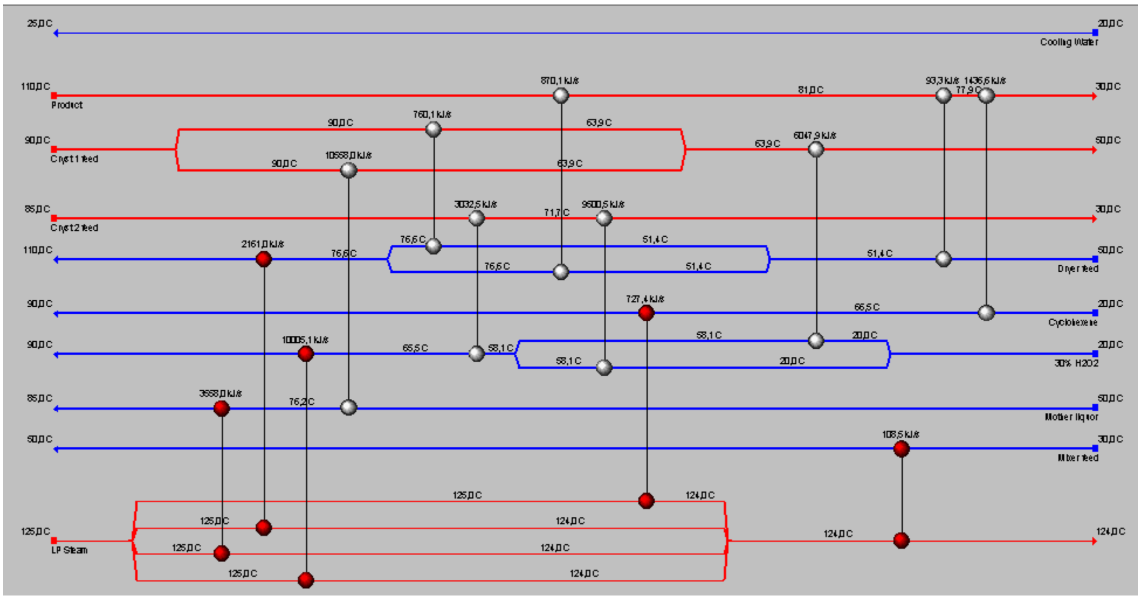

Figure 4: Combined Composite Curves of direct flow oxidation process (50 % conversion)

Table 4: Comparison of improved HEN with initial HEN for three conversion cases of 40 %, 50 % and 98 %

	Area (m^2)	Capital cost (10^6 €)	Hot utility (kW)	Cold utility (kW)	Operating cost (10^6 €/y)
40 % Initial HEN	11,836	3.73	60,105	42,189	19.80
40 % New HEN	43,515	13.02	18,516	600	6.00
50 % Initial HEN	9,257	2.99	48,859	32,299	16.08
50 % New HEN	30,084	9.12	16,560	0	5.36
98 % Initial HEN	4,278	1.60	26,773	13,281	8.77
98 % New HEN	9,400	3.24	13,492	0	4.37

Table 5: Pay-back time for three conversion cases of 40 %, 50 % and 98 %

	Extra Capital cost (10^6 €)	Operating cost saving (10^6 €/y)	Pay-back time (months)
40 %	9.28	13.80	8.1
50 %	6.13	10.72	6.9
98 %	1.64	4.41	4.5

The heat exchanger selection is also very important. Pinch analysis is devised for conventional shell and tube heat exchangers. This is mainly due to lack of readily available data on more advanced compact heat exchangers. However, with the use of compact heat exchangers additional benefits to the heat integration can be achieved. Compact heat exchanger are characterized by having a high area density. Micro heat exchangers being the most compact have an area density greater than 10,000 m^2/m^3 (Polley and Rajiv, 2005) compared to 100 m^2/m^3 of typical shell and tube heat exchanger (Li et al., 2011). A major advantage of compact heat exchangers is their high thermal effectiveness. A higher effectiveness implies a closer temperature approach (Reay, 1994). This means that the hot and cold composite curves can be brought closer to each other increasing the process-to-process heat integration leading to significant energy cost saving with reduced utility loads. In contrast to 6-8 °C or even 10 °C approach of conventional shell and tube heat exchangers, a 1 °C temperature approach is possible (Takats and Nemeth, 2011). Another major advantage of compact heat exchangers is their reduced size and weight for the same heat transfer duty. This makes installation less costly and also for a new plant a reduction in plant size enables reduced investment cost. Some compact heat exchangers also enable multistreaming (Reay, 1994). Most compact heat exchangers allow the application of pure counter current flow. It is most valuable when there is a temperature cross. For shell and tube heat exchangers the solution is to use multiple shells in series whereas in case of compact this can be achieved with single heat exchanger (Haslego and Polley, 2002). For example for the direct flow process example it is seen that (Table 6) three heat exchangers have high number of shells due to presence of temperature cross and they make the major part of the capital cost requirement. By replacing each with single compact heat exchanger it is estimated that the capital cost can be cut at least by half making pay-back time even shorter. All these properties of compact heat exchangers result in reduced plant complexity, increased cost effectiveness and also improved safety.

Table 6: Heat exchangers with temperature cross of direct flow oxidation process of new HEN (50% conv.)

No	Number of shells	Area (m^2)	Capital cost (10^6 €)
2	10	4,627	1.4
4	20	9,375	2.7
11	20	9,177	2.7

4. Conclusions

The investigation of process-design intensification through flow processing is started for the first time by our group. It is exemplified at a currently investigated process example of industrial relevance: direct oxidation of cyclohexene with hydrogen peroxide for adipic acid synthesis. It is demonstrated previously that the direct flow process leads to a more compact plant design owing to the requirement of fewer process apparatus leading to the total purchase cost of equipment to be cut approximately in half. In this study designing of an energy efficient process for this novel direct route is in focus. Pinch analysis is employed for this purpose. By following the stepwise procedure an improved HEN design is achieved for the three conversion cases considered: 40 % (representing primary result), 50 % (representing current improved result) and 98 % (representing superficial best performance). Compared with the initial network where the heating and cooling requirements are all satisfied by utilities, the improved HEN design enables 50 -70 % operating cost saving. It is calculated that this saving pays back the extra capital requirement for the heat exchangers in 4.5 – 8 months. The current use of Pinch Analysis considers only shell and tube heat exchangers due to limited information on compact heat exchanger. However, the utilization of compact heat exchangers (including microchannel-based) can provide additional saving in cost and reduced plant complexity due to more efficient heat transfer. For the case of temperature cross, the additional capital cost can be halved. Using such innovative tools means considering the effect of process intensification also on the utility side aiming at decreasing the size of the plant, thereby rendering a true holistic picture of the intensification. In conclusion, the use of microprocess or other smart-scaled technology can achieve considerable capital cost and energy consumption reduction through process-design intensification lowering the management's main decision barrier towards new technologies. Yet, considerable challenges are expected when releasing the theoretical potential into industrial practice.

Outlook

A detailed study of the heat integration for the direct route and the evaluation of the impact of using compact heat exchangers (including microchannel-based) is a separate paper (Vural Gürsel et al., 2013). Also in our group the environmental impact of the direct route in comparison with the two-step route is analyzed using Life Cycle Assessment. This is given in a paper submitted to Chemical Engineering Journal.

Acknowledgements

Funding by the Advanced European Research Council Grant "Novel Process Windows – Boosted Micro Process Technology" under grant agreement number 267443 is kindly acknowledged.

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