# DIRECT ENTHALPY EXCHANGE BETWEEN PROCESS UTILITIES<sup>†</sup>

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#### Abstract

This paper presents an application of the improved pinch methodology by performing a simplified exergy analysis in a real-size ammonia plant. Besides the well known pinch technics like composite curves and grand composite curve, the improved approach with the extended grand composite curve was implemented. The latter presents the most energy intensive units in the process separated from the process background as well as the direct transfer of enthalpy from hot utilities to cold utilities. Based on this presentation the synthesis of modified heat exchanger network was performed which results in considerable decrease of utilities demand.

#### Introduction

Chemical and other process industries are strongly oriented towards the rationalization of energy consumption. Heat recovery networks have been extensively studied in the last 30 years. In principle, design and synthesis of different process subsystems is based either on a heuristic, thermodynamic or mathematical programming approach.

Thermodynamic pinch analysis<sup>1</sup> was the first tool for optimizing integrated energy systems which offered great insight into the energy sources and sinks in the process as well as into their interactions with other process subsystems. However, the method cannot guarantee optimal solutions due to sequential handling of the interactions among process subsystems. On the other side, in the last two decades a mathematical programming approach to process synthesis and design<sup>2</sup> has been evolving whose advantage is a systematic and simultaneous consideration of interactions between all process factors. Although the great potential of mathematical methods is proven, their main drawback is the limitation on handling small- and medium-size problems while real-size problems have not been successfully solved so far. There have also been attempts to combining both approaches in order to overcome their drawbacks and to

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exploit their advantages.<sup>3,4</sup> Nowadays, it is obvious that sustainable development requires complex integration of processes including heat and mass integration, enthalpy and mass flow optimization and task integration.<sup>5</sup> Nevertheless, pinch methodology will still play an important role by designing new processes and retrofiting the existing ones due to its simplicity and robustness.

This paper presents the application of improved pinch methodology by studying the energetics of a real-size ammonia plant. The methodology was described in our previous papers<sup>6,7</sup> and illustrated by a case study of a formaldehyde process. The method includes integral analysis of heat exchanger network and other energy intensive units in the process, as well as the analysis of individual process subsystems and evaluation of their placement against the pinch temperature in the extended grand composite curve (temperature/enthalpy flow rate).

The paper is organized as follows. First, we introduce a CACHE case study of ammonia synthesis plant.<sup>8</sup> In the next section a computer simulation of process by means of commercial program Design II is described. Further, we present the application of pinch methodology by studying and analyzing the process energetics. An improved concept will be applied which results in considerable savings of utilities.

## Case study of ammonia synthesis plant

The base case was taken from CACHE report where ammonia is produced by means of the Haber-Bosch system. Simplified process flowsheet is shown in Figure 1. The capacity of the plant is 450 000 t/a and the annual time of operation is 330 days.

The synthesis gas mixture of hydrogen and nitrogen in the stoichiometric amount ratio of 3 : 1 is compressed to 70 bar in the compressor Cp1. The outlet stream has the temperature of 266 °C and is used for heating the reboiler of the distillation column (E2) at 147 °C. The gas is then mixed with first recycle stream, which mostly contains unreacted hydrogen, and cooled in heat exchanger C1. The mixture is compressed to 210 bar (Cp2), mixed with the second recycle stream and compressed again to 210 bar (Cp3). It is then heated by the reactor effluent stream to 408 °C in E1 and with the high pressure steam (HPS) in H1 to the temperature of the reaction (430 °C).

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Figure 1: Flowsheet of base case ammonia process

$$3 H_2 + N_2 \rightleftharpoons 2 NH_3$$
  $\Delta_r H = -92 \text{ kJ/mol}$ 

The transformation of synthesis gas to ammonia is highly exothermic. The reaction takes place in the converter with built-in heat exchanger (RB) where the evolved heat is removed by evaporating water in order to maintain isothermal conditions. The reactor effluent stream is cooled by its inlet stream in E1 and by cooling water (CW) in C2 and fed into the absorption column (Ab). Gaseous reactants are cooled in C4 and mostly recycled by the compressor Cp3. 4% of the gaseous reactants stream are fed into the membrane separation unit where hydrogen is separated from unwanted inerts which are exhausted as purge gas in order to avoid their accumulation.

Ammonia is absorbed in water in the absorption column and separated from the solvent in the distillation column (DC) at 4.5 bar. The temperature of the condenser (Cd) is -33 °C and propane is used as a refrigerant. Bottom product of the distillation column contains mostly water, which is recycled to the absorption column after cooling in C3.

# Modelling of case study by commercial computer code

The ammonia process described was designed with the computer simulation program Design II (WinSim Inc.). The compressors were modeled by means of COMPREssor module using an efficiency of 72 %. The reaction between hydrogen and

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nitrogen was modeled in an equilibrium REActor module under isothermal conditions and with 25 % conversion of the reactants. The absorption column was simulated by using rigorous DIStillation column (type ABSorber) with prespecified number of trays, location of feed and Wilson thermodynamics. Distillation column was modeled by means of the rigorous DIStillation module with a total condenser and Wilson thermodynamics.

The results of the simulation were mostly in accordance with those in the CACHE report. The difference has originated from the absorption column where in our case considerable amount of gases ( $H_2$ ,  $N_2$ , Ar,  $CH_4$ ) was absorbed in the water besides ammonia. Those gases were removed before entering the distillation column by using a module COMponent SPLitter.

# Analysis of process energy availability

Given the mass and energy balances, a simplified exergy (energy availability) analysis of the process by using pinch methodology can be performed. To accomplish the task, the composite curves (CCs) and grand composite curve (GCC) have been applied, as well as the improved visualization method, called the extended grand composite curve (EGCC).<sup>7</sup>

The streams of process heat exchanger network system (HEN) and utilities are presented in Table 1. Besides thermal utilities like steam, cooling water and refrigerant, there are usually many other utilities in the process, e.g. chemical utility of the reaction. Such utilities are called energy donors and energy acceptors, while their common name is *energors*. E.g. exothermal reactors, compressors and furnaces are energy donors, while endothermal reactors, boilers and evaporators are energy acceptors. In the ammonia process the reactor (R) and the compressors (Cp1, Cp2, Cp3) are heat donors while the water preheater (PH) and the boiler (B) are heat acceptors.

**Composite curves.** The sum of all the HEN cold streams and the HEN hot streams represent the cold and hot composite curves, CC, respectively, which are shown in a temperature/enthalpy flow rate diagram (Figure 2a). The corresponding pinch temperature,  $T_p = 152$  °C. The upper gap between the curves represents the minimal demand of hot utility (22.42 MW), while the lower gap (58.00 MW) corresponds to the

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minimal demand of cold utility. Both figures are obtained at fixed value of heat recovery
approach temperature ( $\Delta_{\min}T = 10$ K) determined in advance. The actual demands of hot
utility (22.46 MW in H1 and Rb) and cold utility (58.15 MW in C1, C2, C3, C4 and Cd)
indicate that minimum energy target predicted by the method is almost achieved in the
base process flowsheet.

Unit	$T_{\rm s}/^{\rm o}{\rm C}$	$T_{t} / °C$	<i>CF /</i> (kW/K)	$\Delta_{\mathbf{c}}T/\mathbf{K}$	I/kW
HEN hot streams					
E1	430	131	229	5	68 500
E2	251	158	62	5	5 800
C1	158	129	62	20	1 800
C2	131	42	234	8	20 900
C3	151	40	24	6	2 700
C4	92	42	182	8	9 100
Cd	2	-33	679	4	23 800
HEN cold streams					
E1	121	408	239	5	68 500
E2	147	147	5 800	5	5 800
H1	408	430	239	5	5 300
Rb	147	147	17 200	5	17 200
Utilities					
HPS	470	470	5 300	5	5 300
MPS	187	187	17 200	5	17 200
CW	29	41	2 875	3	34 500
Refrigerant	-41	-41	23 700	3	23 700
Other energors					
R	430	430	42 800	20	42 800
PH	27	187	68	3	10 900
В	187	187	31 900	3	31 900
Cp1	128	266	57	20	7 900
Cp2	129	335	64	20	13 200
Cp3	119	121	279	20	558

Table 1: Heat exchanger network, utility and energor streams of ammonia plant

**Grand composite curve.** While composite curves define minimum energy requirements, utility temperature profiles are more clearly presented in a grand composite curve, GCC (Figure 2b). The latter represents the difference between enthalpy flow rates of hot and cold CCs at given temperature. In the GCC the temperatures of hot streams are lowered while the temperatures of cold streams are increased by their contribution temperatures ( $\Delta_c T$ ).



Figure 2: Composite curves a) and grand composite curve b) of HEN in the base flowsheet of ammonia process

High-pressure steam is used in the heater H1 to rise the temperature of the reactor inlet stream. In order to keep the constant temperature in the reactor, water is preheated and evaporated in the built-in heat exchanger, thus, producing the steam at 11.4 bar. The steam produced provides the majority of the reboiler heat flow rate while the remaining heat is provided by the interchange between process streams (shaded area on Fig. 2b). The rest of the steam can be sold on the market. Cooling water is needed in the coolers C1 to C4. Condenser of the distilation column (23.8 MW) is cooled by propane in the refrigeration cycle which was assumed to be provided from an off-site facility and was regarded to be fixed in further analysis. Given the utilities demand and supply, we can review the operating costs of utilities and credit for the steam produced in the base flowsheet (Table 2).

**Extended grand composite curve.** As can be seen from Table 1 the reactor with the built-in boiler is the most energy intensive process unit, yet it is presented neither in the CCs nor in the GCC. In order to properly present and evaluate the interactions

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between the reactor system and other process units, the extended grand composite curve,

EGCC, was constructed  $(T/(I+\Delta I))$ .

Utility	I/MW	$q_{\rm m}$ / (kg/s)	<i>c</i> / (USD/t)	$c_{\rm op}/({\rm MUSD/a})$
Demand				
HPS (100 bar)	5.3	4.12	22	2.58
MPS (11.4 bar)	17.2	8.53	5	1.22
CW	34.5	688	0.0303	0.60
Supply				
MPS (11.4 bar)	25.6	7.5	5	- 1.06
		Net o	perating cost:	3.34

Table 2: Utilities operating cost and credit in the base flowsheet

In the EGCC different energors can be presented aside the GCC as shown in Figure 3 where the reactor system and distillation column are separated from the proces background.



Figure 3: Extended grand composite curve of base process flowsheet Figure 3 clearly shows the cascading of the reaction enthalpy flow rate (*I*<sub>r</sub>) from the reactor (R) to the boiler feedwater which is first preheated from 23 °C to 187 °C (PH) and then evaporated at this temperature (B). A part of the steam produced is used for reboiling the distillation column (17.2 MW) while the rest is exported from the proces. Note that the pinch temperature of the remaining process changes from 152 °C in Figures 2a and 2b to 428 °C in Figure 3. Distillation column is situated across the pinch temperature of 152 °C, its exclusion from the GCC changes the pinch temperature.

## **Integration of base process flowsheet**

By analyzing the energy situation in the base flowsheet we have established almost optimal heat integration among process streams. Anyway, utilities demand can be further reduced through the modification of HEN system which was accomplished by two ideas: first, purge gas has a considerable heating value and could be used as a source of heat and second, boiler feed water could receive the heat from process streams below the pinch temperature instead from hot chemical utility.

**Purge gas**. In the base process flowsheet, 68 mol/s of gases are released from the process. The mixture contains 9.6% of hydrogen, 17.5% of methane and the rest is nitrogen. Its heating value is 163 kJ/mol. The mixture of purge gas and air can be introduced into the furnace in order to burn and produce the hot flue gas with substantial heat flow rate of 11 MW. Figure 4 presents a simplified flowsheet with the modificated HEN system.

The mixture of purge gas and air is preheated to the pinch temperature (152 °C – 10/2 °C = 147 °C) with the hot process stream in heat exchanger C3 before entering the furnace, thus, reducing the cooling water demand for 2.4 MW.

The mixture is then burned in the furnace giving a 600 K rise of temperature. The final temperature of the products of combustion is estimated to be 747 °C (147 °C + 600 °C). The temperature level of the flue gas is suitable to transfer 5.3 MW of heat to the warmest stream in the process, in heat exchanger H1, and rise its temperature from 408 °C to 430 °C, whereas flue gas is cooled down to 450 °C. Note that the high pressure steam is completely replaced by flue gas.



Figure 4: Flowsheet of modified ammonia process

**Boiler feed water**. In the modified flowsheet, water is preheated by hot process streams in C1 and C2 from 27 °C to the pinch temperature, thus reducing the cooling water demand for 9 MW. Feed water is further preheated to 187 °C in the new heat exchanger N1 with the flue gas. The latter cools down from 450 °C to 152 °C and leaves the system at the pinch temperature.

Preheating feed water to the boiling temperature of 187 °C before entering the reactor results in increased production of steam in built-in boiler. The flow rate of the steam produced in the base flowsheet is 16 kg/s (see MPS in Table 2). In the modified flowsheet, water enters the boiler at 187 °C, thus increasing the production of steam to 21.5 kg/s. The extended grand composite curve of the modified flowsheet is shown in Figure 5.

As the inlet mixture to the furnace and feed water to the boiler receive the heat from the process streams below the pinch temperature and flue gas transfers the heat to the process above it, the pinch rules are not violated. We have benefited 11 MW of heat from flue gas and reduced the demand of cooling water for 11.4 MW. Moreover, we have increased the production of steam which can be sold on the market.

Altogether, we have calculated the following potential annual savings:

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- substitution of high presure steam by flue gas in H1 results in saving of 5.3 MW of steam which increases the profit by 2.58 MUSD/a,
- preheating mixture of air and purge gas for the furnace with the proces streams results in saving of 2.4 MW of cooling water (0.04 MUSD/a),
- preheating boiler feed water with the process stream results in saving of 9 MW of cooling water (0.16 MUSD/a),
- additional production of steam in the built-in boiler (21.5 kg/s 16 kg/s = 5.5 kg/s) of the reactor results in additional revenue of 0.79 MUSD/a.



Figure 5: Extended grand composite curve of modified process flowsheet

Table 3 presents the operating costs and credit for the steam produced in the improved ammonia process flowsheet.

The difference between the net operating cost of the base flowsheet (Table 2) and the modified flowsheet (Table 3) is:

$$\Delta c_{\rm op} = 3.34 \text{ MUSD/a} - (-0.23 \text{ MUSD /a}) = 3.57 \text{ MUSD /a}$$
(1)

The net annual effect of the improvements is 3.57 MUSD/a.

Utility	I/MW	$q_{\rm m}$ / (kg/s)	c / (USD/t)	$c_{op}$ / (MUSD/a)	
Demand					
HPS (100 bar)	_	_	_	_	
MPS (9 bar)	17.2	8.53	5	1.22	
CW	23.1	461	0.0303	0.40	
Supply					
MPS (11.4 bar)	25.6	13.0	5	- 1.85 (credit)	
			Net cost:	- 0.23	

Table 3: Utilities operating cost and credit in the modified flowsheet

**Fixed capital analysis of HEN.** In the modified heat-integrated ammonia flowsheet, a part of the utility demand is replaced by heat flow rate exchange between the process streams and two additional streams, flue gas and boiler feed water. Consequently, the area of the modified heat exchangers changes causing the difference in fixed capital of HEN between the base flowsheet and the heat-integrated one (Table 4). The value of the fixed capital of HEN was determined by using the following corellation for unit cost installed<sup>9</sup>:

$$C_{\rm HE} = 700 \cdot A^{0.83} \tag{2}$$

where:

 $C_{\text{HE}}$  fixed capital of heat exchanger, USD, A area of heat exchanger, m<sup>2</sup>.

The difference between fixed capital of HEN in the base flowsheet and in the modified flowsheet is equal to 1.162 MUSD. Given the additional investment ( $\Sigma C_{\text{HE}}$ ) and net saving of utilities ( $\Delta c_{\text{op}}$ ), we can calculate the payback time of the investment as the time to recover the additional value of fixed capital with the savings:

$$t_{\rm PB} = \frac{\Delta (\sum C_{\rm HE})}{\Delta c_{\rm op}} = \frac{1.162 \text{ MUSD}}{3.57 \text{ MUSD/a}} = 0.33 \text{ a} = 4 \text{ months}$$
(3)

Unit	Base flowsheet		Modified flowsheet		
	$A / m^2$	$C_{ m HE}$ / kUSD	$A / m^2$	$C_{ m HE}$ / kUSD	
C1	187	53.8	1313	271.2	
C2	2735	498.6	1909	370.0	
			1146	242.2	
			2407	448.5	
C3	116	36.2	982	213.1	
			96	30.9	
H1	770	174.1	576	136.9	
New (N1)	-		975	211.8	
$\Sigma C_{ m HE}$		762.7		1924.6	

Table 4: Fixed capital of HEN in the base flowsheet and in the modified flowsheet

The result shows that the additional investment could be returned in 4 months by the savings of utilities.

## Conclusions

This paper presents an application of pinch methodology by studying the energetics of a real-size ammonia plant. Utility targets were determined at fixed heat recovery approach temperature by means of hot and cold composite curves. The temperature levels of utilities were shown using the grand composite curve followed by the evaluation of the coresponding operating cost. Extended grand composite curve was constructed which provided deeper insight into the energy flow rates exchange between the streams of HEN and utilities as well as other energy intensive units in the process like reactors, distillation columns etc. The method enables to improve the energy efficiency in the process by applying relatively small modifications of HEN system with low investment cost giving a short payback time period. The advantage of the method presented over more systematic mathematical programming methods is its simplicity, robustness and capability to handle large-size problems with relatively small effort. It shall be used before applying the mathematical programming approach to define the process superstructure.

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## Symbols:

A i	area of heat exchanger,	$m^2$
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- *c* specific cost, USD/t
- *CF* heat capacity flow rate, W/K
- $C_{\rm HE}$  direct fixed capital of heat exchanger, USD
- $c_{\rm op}$  operating cost, USD/a
- *I* enthalpy flow rate, W
- $I_{c,min}$  minimal demand of cold utility, W
- $I_{\rm h,min}$  minimal demand of hot utility, W
- $I_{\rm r}$  reaction enthalpy flowrate, W
- $T_{\rm p}$  pinch temperature, °C
- $T_{\rm s}$  supply temperature, °C
- $T_{\rm t}$  target temperature, °C
- $q_{\rm m}$  mass flow rate, kg/s
- *t*<sub>PB</sub> payback time, a
- $\Delta_{\rm r} H$  reaction enthalpy, kJ/mol
- $\Delta I$  enthalpy flow rate difference, W
- $\Delta_{\rm c}T$  contribution temperature difference, K

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# Povzetek

V članku je opisana uporaba izboljšane metodologije uščipa pri energetski študiji procesa pridobivanja amoniaka. Ob znanih metodah, kot sta metodi sestavljenih krivulj in velike sestavljene krivulje, je uporabljena tudi metoda razširjene velike sestavljene krivulje, ki energijsko intenzivne procesne enote predstavlja ločene od preostalih procesnih tokov in ponazarja tudi neposredni prenos entalpije med vročimi in mrzlimi pogonskimi sredstvi. Na

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osnovi te predstavitve so bile raziskane interakcije reaktorja in destilacijske kolone s preostalim procesom ter predlagane izboljšave procesne sheme, s katerimi je mogoče dosegati znatni prihranek pogonskih sredstev, 3,6 MUSD/a z zelo kratkim vračilnim rokom 4 mesecev.