

Low Temperature Waste Heat in Chemical Industry: Problems and Possible Ways to Recover the Heat of Condensation

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Abstract:

The major large volume inorganic and organic chemicals production processes are energy intensive and consume big quantities of thermal (natural gas, oil fractions and steam) and electrical energy. As the temperatures of the feedstocks used and obtained chemical products are close to the environmental temperature, the high quality energy input in the production unit is used mainly to ensure the driving force of the processes and is finally removed from the process as a low temperature waste heat in water or air coolers and condensers. A significant share of this waste heat is the condensation heat of vapours, mixed with some non-condensable gases. In most cases condensation starts at low temperature and it is difficult to utilize the condensation heat.

In many chemical processes steam is used as a reagent, e.g. in production of hydrogen and synthesis gas by steam reforming of light hydrocarbons or by gasification of coal, heavy hydrocarbons or biomass. In all these processes the steam to hydrocarbon ratio is over the stoichiometric one and after the chemical process is finished, the gaseous mixture is cooled and the surplus steam is condensed at temperatures below 170°C down to ambient temperature. Another example is the ammonia synthesis process, where ammonia is condensed in presence of unreacted hydrogen and nitrogen mixture. The condensation begins at about 60-70°C and the condensation heat is released by cooling water or air. Various thermodynamic cycles and working fluids are proposed to utilize the condensation heat for power generation. However, the low temperatures and the very specific temperature profile of the cooled gaseous-vapour mixtures are the major problems. In this work an attempt is made to estimate (from a Second Law point of view) the recovery and usage potential of the major partial condensation waste heat sources in chemical industry.

Keywords: Chemical processes, Efficiency, Low temperature waste heat, Partial steam condensation

1. Introduction

Chemical industry is an energy intensive sector with 18% of industrial energy use in EU corresponding to about 2000 PJ primary energy demand yearly. The major large-volume inorganic and organic chemicals production processes (incl. oil refining, petrochemicals, rubber and plastics) consume huge quantities of thermal (natural gas, oil fractions and steam) and electrical energy [1].

As the temperatures of the feedstocks used and the obtained chemical products are close to the environmental temperature, the high quality energy input in the production unit is used mainly to ensure the driving force of the processes and finally is removed from the process as a low temperature waste heat in water or air coolers and condensers. The low temperature waste heat in chemical industry is a major source of external exergy losses. A significant share of this waste heat is the condensation heat of vapours, mixed with some non-condensable gases. In most cases condensation begins at low temperature and it is difficult to utilize the condensation heat.

In many chemical processes, steam is used as a reagent, e.g. in production of hydrogen and synthesis gas by steam reforming of light hydrocarbons, by partial oxidation of heavy hydrocarbons or by gasification of coal and biomass [2-4]. In all these moderate pressure (2- 4 MPa) processes, the steam to hydrocarbon ratio is over the stoichiometric one and after the chemical process is finished, the gaseous mixture is cooled and the surplus steam is condensed at temperatures below

170⁰C down to ambient temperature. A part of the condensation heat is utilized to preheat boiler feed water or for other low temperature consuming processes, but most of this heat is removed to the environment. In some very specific processes, e.g., in nitric acid production, the steam is obtained as a by-product of the ammonia oxidation reactions and is condensed and used as a reagent in the NO_x absorption [2].

In other industrial chemical processes vapours of the product have to be condensed in order to separate them from the non-condensable unreacted gases. Examples are the high pressure ammonia and methanol synthesis processes. Ammonia and methanol are condensed at high pressure (ammonia above 10 MPa, methanol at about 6 MPa) in presence of unreacted gaseous mixture. The condensation of ammonia begins at about 50-70⁰C and of methanol at about 60⁰C; the condensation heat is released by cooling water or air [5].

Various thermodynamic cycles and working fluids are proposed to utilize the condensation heat for power generation [1]. However, the low temperatures and the very specific temperature profile of the cooled gaseous-vapour mixtures are the major problems. In this work an attempt is made to estimate from a Second Law point of view the recovery and usage potential of the major waste-heat-from-partial-condensation sources.

2. Partial condensation of steam in chemical production plants

The applicability of some low temperature heat recovery methods to the partial condensation of steam depends on the dew point temperature which is a function of steam partial pressure, i.e., on the flow pressure and steam concentration. It is clear that the steam containing gaseous mixtures at medium and high pressure processes could be of real interest in respect to the condensation heat usage, due to the possible higher dew point temperature (e.g., above 100⁰C).

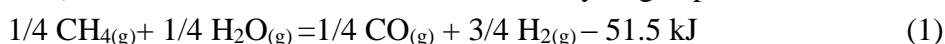
There are many low pressure (atmospheric) industrial processes, where partial condensation of steam exists, but the condensation begins at low temperature (below 100⁰C) and it is difficult to utilize the condensation heat.

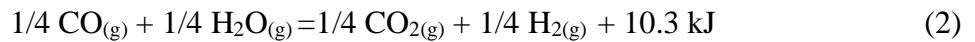
So the most interesting cases are the medium and high pressure industrial chemical processes. Some examples of these processes are analyzed in order to estimate the quantity and quality of the evolved condensation heat. Most cases concern the condensation of water vapours.

2. 1. Partial condensation of steam in hydrogen production by steam reforming

Hydrogen is one of the inorganic chemicals. produced in large volume. An estimation of the world hydrogen production capacity is rather difficult, as also because hydrogen is produced and used in various chemical industry subsectors and no world statistics exists. Moreover, in some cases (catalytic reforming, chlorine-alkaline electrolysis, etc.) hydrogen is generated as a byproduct and consumed in the same site. The capacity estimation values range from 80 to about 120 MM tons yearly [6,7]. From about 80 million metric tons/year in 2011 according to [6], the major part (above 50%) of the generated hydrogen is used in ammonia and methanol production [7], about 38% in oil refineries [6], the balance in other chemical and electrochemical applications. In refining (on-purpose H₂ production) about 96% of hydrogen is produced by steam reforming of natural gas and/or refinery fuel gas, while the remaining 4% is produced by non-catalytic partial oxidation of heavy residues from oil processing [6]. Water is the main hydrogen-containing source and a lot of energy is necessary to split a molecule of water to hydrogen and oxygen. If a part of the produced hydrogen is supplied by another hydrogen-containing feedstock, like hydrocarbons, energy requirements are lower. Thus the most favourable feedstock for hydrogen production is the natural gas (CH₄) because in this case only a half of the hydrogen is obtained from water. However, in refineries some available light hydrocarbons are used in some cases instead of natural gas.

Assuming natural gas (methane) as a feedstock, two basic reactions of hydrogen production are:





Summarizing reactions (1) and (2) the total hydrogen production process could be expressed by the reaction:



The catalytic steam reforming of methane by reaction (1) is an endothermic reaction and to obtain a high degree of conversion of methane, the reaction is performed at temperature above 900°C. The low temperature is favourable for water shift reaction (2), therefore to obtain a highest possible degree of conversion, the reaction is performed in one or two consecutive catalytic stages, at 350-400 (HT shift conversion) and 200°C (LT shift conversion), respectively.

In view of the subsequent hydrogen usage requirements, steam reforming pressure is usually in the range of 2 – 2.5 MPa, despite that low pressure is more favourable for reaction (1).

Steam reforming of methane by reactions (1) and (2) requires some surplus of steam above the stoichiometric ratio in order to obtain higher methane and CO conversion and to prevent carbon formation [3,4]. A 150 to 200% surplus is necessary in one-stage steam reforming of methane, which is commonly used in hydrogen production. As the stoichiometric steam to carbon (steam to methane) ratio in the reaction (3) is 2: 1 mol/mol, in steam reforming for hydrogen production this ratio is 5:1 to 6:1 mol/mol.

After the reactions (1) and (2) are performed, the obtained gaseous mixture is cooled in order to be prepared for the subsequent CO₂ removal by absorption or adsorption processes. Thus the surplus steam is condensed at gradually decreasing temperature. The main feature of this process, known as partial condensation, is the presence of the non-condensable gas, whose concentration determines the mass and heat balance of the condensation and hence the temperature profile of the process. Some major parameters of the partial condensation of the surplus steam in typical hydrogen production plants with steam reforming of methane are shown in Table 1 and Fig. 1.

As it is shown in Table 1, large quantities of surplus steam are condensed when the obtaining gaseous mixture, containing mainly hydrogen and CO₂, is cooled down to the room temperature in order to remove the water and to prepare the flow for the subsequent CO₂ removal by adsorption or absorption process.

Table 1. Surplus steam condensation in hydrogen production by steam reforming of methane

Steam: Carbon ratio inlet reforming, mol/mol	Surplus steam inlet steam reforming %	Steam in wet gas before CO ₂ removal		Steam concentration in wet gas, %	Steam partial pressure in wet gas, bar*	Dew point of steam in wet gas, °C	Condensed steam from dew point to 30°C, t/t H ₂	Heat of condensation from dew point to 30°C, GJ/t H ₂	Exergy of condensation heat from dew point to 30°C, GJ/t H ₂
		mol steam / mol H ₂	t steam / t H ₂						
4:1	100	0.75	4.50	0.2857	5.714	156.8	4.476	11.766	3.304
5:1	150	1.0	6.75	0.3750	7.500	167.8	6.726	17.768	5.232
6:1	200	1.25	9.00	0.4444	8.889	174.9	8.976	23.758	7.197

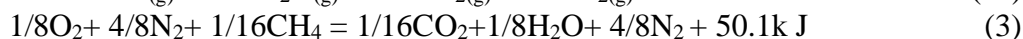
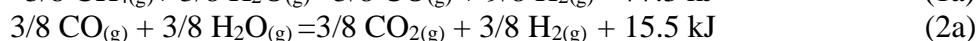
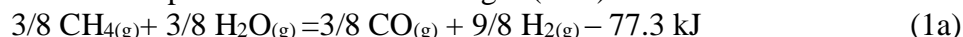
*Total wet gas pressure 20 bar.

If the CO₂ removal is performed by an absorption process, the major part of the condensation heat is consumed in the absorbent regeneration [3,5]. However, in most modern hydrogen production plants, especially in oil refineries, an adsorption process is used with no heat consumption. Thus the only option for the condensation heat usage is the low pressure boiler feed water (BFW) preheating, usually to 105°C. But it is clear that the temperature profile of the partial condensation is very specific and it is not suitable to water preheating. For this reason, the shaft work/electricity generation by an ORC seems the most promising option for this low temperature waste heat recovery. As the capacity of the hydrogen production units in oil refining industry are in the range from 10000 to 100000 t H₂/year (from 1,25 to 12.5 t/h), about 0.6 to 6 MW could be generated in a refinery if a half of the condensation heat exergy could be converted to shaft work by an ORC.

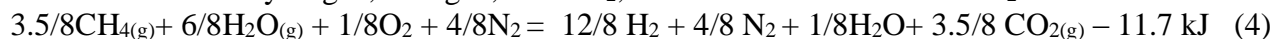
2. 2. Partial steam condensation in ammonia plants

The commercial manufacture of ammonia is based on the catalytic synthesis of ammonia from a highly purified mixture of hydrogen and nitrogen. The combination of both steam reforming and burning processes enables to obtain the hydrogen-nitrogen mixture directly, avoiding the air separation as a preliminary step. Thus the two-step steam and air reforming of hydrocarbons became the best industrial process of the hydrogen-nitrogen mixture preparing for more than 60 years [2,5].

Assuming approximately the oxygen and nitrogen content in air as 20% and 80 % respectively, the following basic reactions of ammonia production from natural gas (CH₄) could be written:



Summarizing reactions (1a), (2a), (3), the obtained gaseous mixture after HT and LT shift conversion contains hydrogen, nitrogen, and CO₂, before to be feed into the CO₂ removal unit:



It is clear that the first two reactions are the same as the reactions (1) and (2) of hydrogen production. But the third reaction in the second reforming (air reforming) changes the share of water in the obtained mixture, adding some more water to the surplus steam input the steam reforming.

The main parameters of the steam reforming in ammonia plants are similar to these in hydrogen plants. However, as in ammonia plants about half of methane is converted in the second reforming stage, the process conditions in the steam reforming can be more unfavourable, the pressure being slightly higher and the temperature - slightly lower. Also the steam surplus is much lower. A 50 to 100% surplus is commonly used with a trend towards the minimum of 50% surplus in the new plants. Some major parameters of the partial condensation of the surplus steam in ammonia production plants with two stage steam and air reforming of methane are shown in Table 2 and Fig. 1. As it is shown in Table 2, the quantities of condensed surplus steam in ammonia plants are lower than in hydrogen plants. Also the heat of condensation, the exergy of heat per ton ammonia and the dew point temperature are lower.

Table 2. Surplus steam condensation in ammonia production by steam reforming of methane

Steam: carbon ratio inlet reforming, mol/mol	Surplus steam inlet reforming, %	Steam in wet gas before CO ₂ removal		Steam concentration in wet gas, %	Steam partial pressure in wet gas, bar*	Dew point of steam in wet gas, °C	Condensed steam from dew point to 30°C, t/t NH ₃	Heat of condensation from dew point to 30°C, GJ/t NH ₃	Exergy of condensation heat from dew point to 30°C, GJ/t NH ₃
		mol steam / mol NH ₃	t steam /t NH ₃						
3:1	50	0.500	0.5294	0.1702	4.255	145.9	0.5250	1.373	0.368
3.5:1	75	0.6875	0.7279	0.2200	5.500	155.5	0.7235	1.901	0.504
4:1	100	0.875	0.9265	0.2641	6.604	162.6	0.9221	2.430	0.703

*Total wet gas pressure 25 bar.

Unlike hydrogen production units, absorption processes in ammonia plants are commonly used in CO₂ removal and in most plants the steam condensation heat is used mainly to ensure the absorbent regeneration [5]. The low temperature part of the condensation heat is used for BFW preheating, but it is not sufficient, because much more HP steam is generated in ammonia plants than in hydrogen production. Condensation heat is used only for BFW preheating only in some ammonia plants where a physical CO₂ absorbent is used and no heat is necessary for the regeneration. For this kind of ammonia plants, shaft work/electricity generation by an ORC, using condensation heat, could be an interesting option, having in mind the higher power consumption in these plants for the CO₂ solvent regeneration.

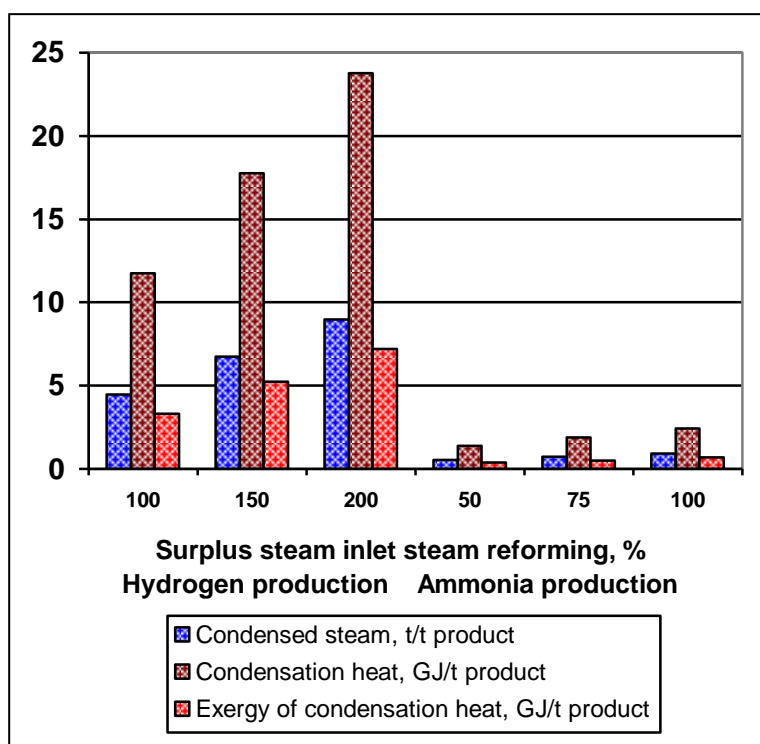


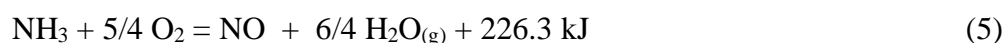
Fig. 1. Partial condensation of steam from synthesis gas, obtained by steam reforming of methane in hydrogen and ammonia production processes. (Data from Tables 1 and 2).

An ORC could be also an promising option for the surplus condensation heat, which occurs when a CO₂ removal unit using a high heat consuming chemical absorbent is converted to a modern low heat consuming solvent [5]. As the capacity of modern ammonia plants is in the range from 600 to 1800 t NH₃ /day (25-75 t/h) and steam: carbon ratio inlet steam reforming is 3:1, about 1 to 3 MW could be generated if a half of the condensation heat exergy could be converted to shaft work by an ORC.

2. 3. Partial steam condensation in nitric acid plants

Nitric acid is one of the basic industrial chemicals with annual world production of about 50 million metric ton/year (100% basis). Around 80% of nitric acid is produced as “weak acid” (50-69%) and is used in fertilizers production. The weak nitric acid production is based on three main chemical processes: catalytic oxidation of ammonia in air to nitric oxide, homogeneous oxidation of NO to NO₂ and absorption of NO₂ in water.

Catalytic oxidation of ammonia in air to nitric oxide (NO) and water is carried out on Pt/Rh alloy catalyst gauzes at 800-950^oC :



As ammonia oxidation is carried out with oxygen from air, ammonia concentration in the reaction mixture has to be less than 10-11%, in order to ensure some oxygen excess, needed predominantly for running of the reaction (5). As a consequence of this, the obtained hot gaseous mixture, referred to as “nitrous gas” contains no more than 10 % NO, about 15% water, 5-6 % O₂; the balance is nitrogen. The nitrous gas is cooled in a series of heat exchangers and the heat is used in a steam Rankine cycle to generate shaft work for compressor(s) driving. In the last stage of cooling to room temperature or lower, the water vapours condensed and some quantity of diluted nitric acid is obtained. The dew point temperature depends on the process pressure.

The oxidation of ammonia by air by the reaction (5) is favoured by lower pressures, but the higher pressure is more favourable for the next two processes. Thus, there are two kinds of nitric acid

production plants: single (or mono-) pressure plants, where all processes are carried out at the same pressure (0.8-1/0 MPa is commonly used) and dual pressure plants, where the ammonia oxidation is carried out at a lower pressure (usually about 0.4 MPa), but NO oxidation and NO₂ absorption – at a higher pressure (about 0.8-1.2 MPa). Thus in the single pressure plants the dew point is in the range of 100 - 105°C [17], and in dual pressure plants – about 85 - 90°C [8,9]. The major parameters of the steam partial condensation in both kind of nitric acid plants are shown in Table 3.

Table 3. Partial steam condensation in nitric acid production

Ammonia oxidation pressure, MPa	Steam in wet nitrous gas		Steam concentration in wet nitrous gas, %	Steam partial pressure in wet nitrous gas, MPa	Dew point of steam in wet nitrous gas, °C	Condensed steam from dew point to 30°C, t/t HNO ₃	Heat of condensation from dew point to 30°C, GJ/t HNO ₃	Exergy of condensation heat from dew point to 30°C, GJ/t HNO ₃
	mol steam / mol HNO ₃	t steam /t HNO ₃						
0.40	1.5	0.428	14.6	0.0584	85	0.402	1.015	0.214
0.80	1.5	0.428	14.6	0.1168	103	0.415	1.060	0.260

As the condensed liquid is really weak nitric acid with about 30-35% HNO₃, the effective values of heat and exergy are about 30% higher than the values in Table 3.

The capacity of modern nitric acid plants is in the range from 40 to 80 t HNO₃/h (HNO₃ as 100%), so about 1 to 2.3 MW could be generated if a half of the condensation heat exergy could be converted to shaft work by an ORC.

2. 4. Partial ammonia condensation in ammonia synthesis

Ammonia synthesis from hydrogen and nitrogen by reaction:



is restricted by the unfavourable position of the chemical equilibrium and by the relatively low activity of the promoted iron catalysts. Even at high pressures from about 8 up to 30 MPa, only 15–25% of the synthesis gas is converted to ammonia per pass. After the removal of ammonia by its condensation at low temperatures, the unreacted hydrogen–nitrogen mixture is returned to the reactor. Therefore, industrial ammonia synthesis is a recycle process. Thus, to produce 1 kg ammonia, 4–6 kg synthesis gas must be recycled through the reactor and the condensation system.

The outlet reactor ammonia concentration is in the range 12 - 20%, depending on the process pressure and the reactor design. As the synthesis loop pressure is between 8 and 30 MPa, the partial pressure of ammonia is rather high and theoretically should be from 1.2 to 6 MPa, ammonia dew point should be between 30 and 100°C and at pressures above 13 MPa, ammonia could be condensed by water or air cooling only. However, the VLE position of ammonia in the presence of non-condensable gases is very unfavourable. The real vapour pressure of ammonia in this system is up to twice as high as the equilibrium pressure of pure ammonia at the same temperature. Thus the partial condensation of ammonia from the gas mixture, containing maximum possible value 20% of ammonia at maximum process pressure 30 MPa, begins at relatively low temperature (65–70°C) and the ammonia content at temperatures 25–30°C is still high (7–8%). Therefore, the condensation is implemented in two stages: the first stage down to the room temperature [5, 10], the second stage down to the -20°C. As it is shown in Table 4, if the process pressure is 30 MPa, the dew point is in the range 53-66°C and most of produced ammonia is condensed in the first condensation stage - above the 30°. At lower process pressure, e.g. 20 MPa, the dew point drops down to 42°C and the share of ammonia condensed in the first stage decreases. As is shown in Table 4, the utilization of the heat of partial ammonia condensation is possible really only if the process pressure is not lower than 30 MPa. However, the optimal process pressure in modern low-energy ammonia plants is in the range from 15 to 20 MPa, so the ORC application for the ammonia condensation heat is not applicable.

Table 4. Partial ammonia condensation in ammonia synthesis

Ammonia synthesis pressure, MPa	Ammonia in recycle gas, %			Ammonia partial pressure in recycle gas, MPa	Dew point of ammonia in recycle gas, °C	Condensed ammonia from dew point to 30°C, t/t NH ₃	Heat of condensation from dew point to 30°C, GJ/t NH ₃	Exergy of condensation heat from dew point to 30°C, GJ/t NH ₃
	Inlet reactor	Outlet reactor	Outlet first condenser at 30°C					
30	8.0	20	8.0	6.0	66	1.00	1.144	0.134
30	2.0	20	8.0	6.0	66	0.739	0.845	0.099
30	6.0	18	8.0	5.4	61	0.959	1.100	0.125
30	4.0	16	8.0	4.8	56	0.752	0.861	0.079
30	2.0	14	8.0	4.2	53	0.552	0.634	0.048
20	6.0	18	10.2	3.6	48	0.821	0.943	0.082
20	4.0	16	10.2	3.2	43	0.613	0.709	0.052
20	2.0	14	10.2	2.8	42	0.413	0.474	0.027
15	4.0	16	11.2	2.4	37	0.471	0.541	0.031

2. 5. Overall estimation of the partial condensation potential for power generation by ORC

An overall estimation of the partial condensation potential of the above 4 processes for shaft work generation by ORC is shown in Table 5. To obtain a plausible estimation, some basic parameters are assumed for all cases: only a half of the heat exergy is available for usage; the exergy efficiency of the ORC is 0.8; thus the exergy efficiency of the overall system may be estimated as 0.4. This approach is not quite precise, as the analysed heat sources have different dew point temperatures and the temperature intervals of the condensation heat are very different.

Table 5. Partial vapour condensation potential for power generation by ORC

Process	Hydrogen production by steam reforming	Synthesis gas production in ammonia plants	Nitric acid production	Ammonia synthesis
Process pressure, MPa	2.0	2.5	0.4 and 0.8	10 - 30
Dew point, °C	157-175	146-163	85-103	42-66
Condensed steam from dew point to 30°C, t/t product	4.5 – 9.0	0.52 – 0.92	0.40-0.42	0.55-1.0
Heat of condensation from dew point to 30°C, GJ/ t product	12 - 24	1.4-2.4	1.0- 1.1	0.6-1.1
Exergy of condensation heat from dew point to 30°C, GJ/ t product	3.3 – 7.2	0.37-0.70	0.21-0.26	0.05-0.13
Available exergy of condensation heat, GJ/t product	1.6 – 3.6	0.19-0.35	0.11 - 0.13	0.024-0.07
Power generation in ORC: - GJ/ t product - MWh/t product	1.3 – 2.9 0.4 – 0.8	0.16 – 0.28 0.044-0.078	0.89 – 0.10 0.025-0.029	0.019–0.056 0.005-0.016
Product capacity in a single plant t/h	2 - 10	25 - 75	40 - 80	25 - 75
Power generation capacity in a single plant, MW	0.8 – 8.0	1.1 - 5.8	1.0 - 2.3	0.12 - 1.12
World production, MM t/year	30 [6]	160 [11]	60 [11]	160 [11]
World maximum power generation capacity by partial condensation heat utilization, MW	1500 - 3000	880 - 1560	190-220	100-300

At 50% availability assumed, this means that the bottom source temperature would also be different, e.g., in hydrogen and ammonia production by steam reforming about 90-100°C, in nitric acid production 55-60°C, in ammonia synthesis – 40-50°C. It is clear that in the first two cases the availability interval and the exergy efficiency of the system could be increased above 40%, whereas in the last case the temperature interval is too narrow and the exergy efficiency would be lower.

The results in Table 5 show that the hydrogen and synthesis gas production by steam reforming of hydrocarbons have a maximum shaft work generation potential of the partial steam condensation due to the relatively high dew point temperatures and the large volume of production. However, it should be kept in mind that in most ammonia production plants this heat is currently used in the regeneration of the CO₂ removal solvent. In hydrogen plants the condensation heat is used only partially and so an ORC implementation seems appropriate. The condensation heat in nitric acid process could also be a promising option, especially in mono high pressure nitric acid plants.

In most ORC system the generated shaft work is transformed to electricity by a generator coupled directly or by a gear to the turbine shaft. But in some cases various options to cogeneration exists, e.g. in ammonia and nitric acid plants it can be more efficient to use the generated shaft work to drive the compressor in a refrigeration cycle, as in these plants the cold is necessary for some processes (second stage ammonia condensation, nitric oxides absorption) [9, 10].

3. Partial condensation of steam and ORC temperature profiles

The temperature profile of the partial steam condensation is very specific. Unlike the temperature profile of the sensible heat sources, the major part of the partial steam condensation heat is evolved at the temperatures near to the dew point. The dependence of the condensation heat on the temperature is an exponential function, no matter whether the condensation is going in the presence of the non-condensing gas or not (Fig. 2 - Top). At temperatures close to the dew point, the condensation heat is much more than the sensible heat of the noncondensing gas, so the temperature of the source decreases slowly and it is appropriate that the available heat is utilized to evaporate the working fluid in an ORC (Fig. 2 - Bottom). After the major part of the condensation heat is evolved, the temperature decreases more steeply and it is suitable to use the rest of the heat to preheat the working fluid. It is clear from a thermodynamic point of view that the temperature profile of the working fluid should be similar to the heat source profile in order to reduce the exergy losses due to the irreversible heat exchange. Hence, the right working fluid selection is the crucial step in an ORC design.

Since the first attempts to use ORC for power generation based on some low temperature heat sources (geothermal, ocean, etc.) more than 50 years ago [12], hundreds of research results have been published, and various ORC designs have been implemented in practice [13-15]. The working fluid selection is the main subject of the intensive research on the ORC application and the conclusion is that no global solution exists, but each particular case has a specific optimum working fluid and operating parameters.

Two examples of the temperature profiles of heat absorption by the working fluid in an wet and a dry (or isentropic) ORC are shown in Fig. 2- Bottom and in Table 6. The major parameters of both cycles are the same, excluding the vapour superheating in the “wet” cycle. The 1 and 2 versions of each ORC example refer to two working fluids which have different evaporation heat to C_p ratio ($\Delta H_{\text{evap}}/ C_p$). It is clear that the temperature profile of the working fluid depends mainly on this ratio. As it could be seen in Fig. 2, bottom, the temperature profile of the working fluid is the more similar to the profile of the heat source the lower this ratio is. Hence, in case the partial steam condensation is the heat source, the evaporation heat to C_p ratio ($\Delta H_{\text{evap}}/ C_p$) could be used as one of the criteria used in the working fluid selection. After the most appropriate working fluid is selected, the right evaporation heat to C_p ratio could be fitted by some variation of the evaporation pressure and related temperature. It is clear from figure that the temperature profile of the partial steam condensation as a heat source is more favourable for power generation by ORC, than the most frequent case when the low temperature source heat is the only sensible heat of the cooled fluid.

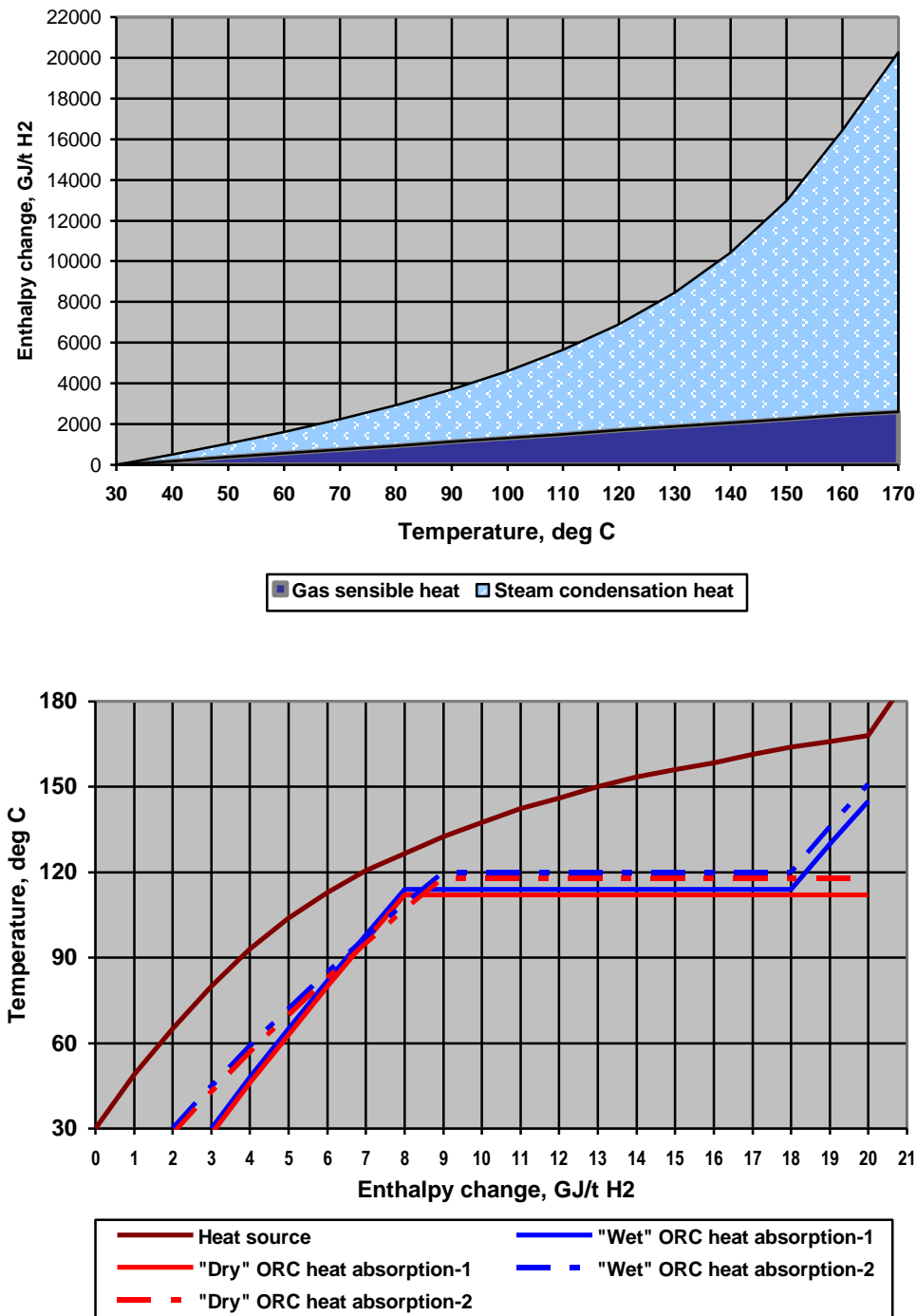


Fig. 2. Partial condensation of steam from synthesis gas, obtained by steam reforming of methane in hydrogen production process and heat absorption by ORC working fluids. (Data from Table 1, Steam to carbon ratio inlet reforming 5:1 mol/mol).

Top: Source heat distribution. Bottom: Temperature profile of heat exchange in ORC.

4. Exergy indices of the steam partial condensation heat recovery by ORC

The total available heat exergy, evolved by the steam and gas hot flow, is calculated as a sum of the exergies of the condensation heat and sensible heat of the non-condensed steam, obtained water and non-condensable gas [16]:

Table 6. Power generation efficiency of the partial steam condensation heat utilization by ORC
(Data from Fig. 2)

ORC in hydrogen production by steam reforming Steam to carbon ratio inlet reforming 5:1 mol/mol	Example 1		Example 2	
	“Wet” ORC-1	“Dry” ORC-1	“Wet” ORC-2	“Dry” ORC-2
Total heat of steam condensation and sensible heat from dew point to 30°C, GJ/ t H ₂	20.260		20.260	
Hot source dew point temperature, T _{dew} °C	168		168	
Exergy of total source heat from dew point to 30°C, GJ/t H ₂	5.0285		5.0285	
Source temperature output preheater, °C	80	80	65	65
Exergy of source heat from dew point to temperature output preheater, GJ/t H ₂	4.9259		4.9781	
Temperatures in ORC, °C				
- Evaporation, T _{evap}	114	114	120	120
- Condensation, T _{cond}	30	30	30	30
- Superheating, T _{sup}	145	-	151	-
Pinch point temperature approach, ΔT _{min} °C	12.5	12.5	12.5	12.5
Evaporation heat to Cp ratio (ΔH _{evap} / C _p)	172	206	116	141
Absorbed heat from ORC working fluid, GJ/t H ₂ :				
- Preheating	5.0	5.0	7.0	7.0
- Evaporation	10.0	12.0	9.0	11.0
- Superheating	2.0	-	2.0	-
- Total absorbed heat	17.0	17.0	18.0	18.0
Exergy of heat input ORC, total, GJ/ t H ₂ , incl.:	3.4746	3.4165	3.6859	3.6256
- Preheating	0.6579	0.6579	0.9716	0.9716
- Evaporation	2.2989	2.7586	2.1747	2.6580
- Superheating	0.5178	-	0.5396	-
Power generated in ORC, GJ/ t H ₂	2.5553	2.5088	2.7112	2.6662
Thermal efficiency of the ORC	0.1503	0.1476	0.1506	0.1481
Thermal efficiency of the overall heat utilization system	0.1261	0.1238	0.1338	0.1316
Exergy losses total, GJ/ t H ₂ , incl.:	2.4732	2.5197	2.3173	2.3623
- internal losses in heat exchangers	1.4513	1.5094	1.2922	1.3485
- internal losses in ORC	0.6388	0.6272	0.6778	0.6665
- external losses from ORC condensation	0.2805	0.2805	0.2969	0.2969
- external losses from non-utilized heat	0.1026	0.1026	0.0504	0.0504
Exergy efficiency of ORC turbine and pump	0.80	0.80	0.80	0.80
Exergy efficiency of the absorbed heat utilization	0.5187	0.5093	0.5446	0.5356
Exergy efficiency of the available heat utilization	0.5082	0.4989	0.5392	0.5294

$$E_{Qsource} = \int_{T_{out}}^{T_{in}} [dH_{cond} + (1-x)dH_{steam} + x.dH_{water} + dH_{gas}] - T_0 \cdot [dS_{cond} + (1-x).dS_{steam} + dS_{water} + dS_{gas}] \quad (1)$$

where x is the share of the condensed steam, T_{in} = T_{dew} is the dew point temperature and T_{out} = 30°C is the temperature of the hot source output the system.

The real used part of heat exergy of the steam and gas hot flow, is calculated by the same equation, but the lower limit is the temperature of the hot flow output the preheater (80 and 65°C in examples 1 and 2, respectively).

The exergy of heat absorbed by the hypothetical working fluid, is calculated as a sum from the working fluid exergy increasing in preheater, evaporator and superheater:

$$E_{Qworkingfluid} = \int_{T_{evap}}^{T_{in}} dH_{preh} + \int_{T_{evap}}^{T_{evap}} dH_{evap} + \int_{T_{sup}}^{T_{evap}} dH_{sup} \quad (2)$$

assuming C_p of the liquid and gaseous working fluid as constants. $T_{in} = 30^{\circ}\text{C}$ is the working fluid temperature input the preheater, T_{evap} is the working fluid evaporation temperature and T_{sup} is the temperature of the working fluid output the superheater.

The exergy efficiency and the exergy losses distribution of two examples of the partial steam condensation heat utilization by ORC in hydrogen production by steam reforming of methane are shown in Table 6 and in Figure 3.

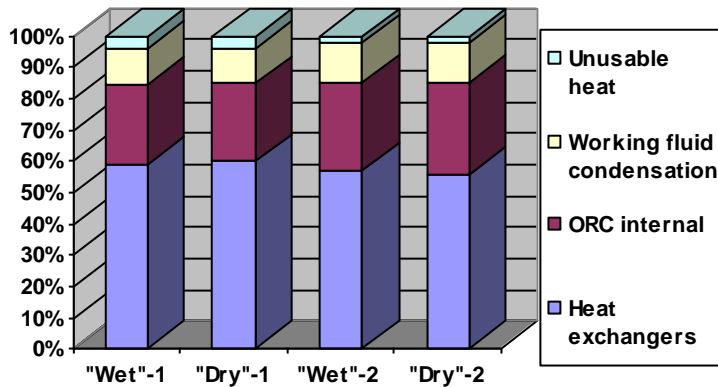


Fig. 3. Exergy losses distribution in the partial steam condensation heat utilization by ORC. Examples data from Table 6.

The major exergy losses (above 50% of the total losses) are due to the irreversibility of the heat exchange from heat source to the working fluid. Thus, the main potential to increase the exergy efficiency of the system is to optimized the approach of the working fluid temperature profile to the heat source temperature profile. As the working fluid temperature profile in the partial steam condensation heat recovery is more favourable than in other waste heat recovery cases, it is possible to optimize the selection and parameters of the working fluid in such kind of systems in order to decrease the heat exchanger losses significantly.

5. CONCLUSIONS

The potential of the partial vapours condensation heat recovery for shaft work generation is analyzed in detail. Hydrogen, ammonia and nitric acid industrial production plants are found to have significant potential to generate shaft work which can be transformed to electricity or cold. Hydrogen production by steam reforming of hydrocarbons in oil refineries is the most promising process with world potential power generation capacity estimated up to about 3000 MW.

The features and advantages of the partial steam condensation as a heat source for power generation by ORC are analyzed and some recommendations about working fluids selections and ORC parameters optimization are made. The temperature profile of the partial steam condensation as a heat source is found to be more favourable to heat recovery by ORC than the most abundant waste heat sources, evolving the sensible heat only. The exergy efficiency of the heat recovery system and exergy losses distribution depend mainly on the similarity and approach of the temperature profiles of the heat source and the working fluid temperature profiles.

Nomenclature

<i>BFW</i>	Boiler Feed Water
<i>D</i>	Exergy Losses
<i>E</i>	Exergy
<i>H</i>	Enthalpy
<i>HP</i>	High Pressure, MPa
<i>LP</i>	Low Pressure, MPa

<i>LT</i>	Low Temperature, °C
<i>MP</i>	Middle Pressure, MPa
<i>ORC</i>	Organic Rankine Cycle
<i>Q</i>	Heat
<i>T</i>	Temperature
η_e	Exergy Efficiency

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