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Process Integration Analysis of an Industrial Hydrogen Production Process

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Abstract

The energy efficiency of an industrial hydrogen production process using steam methane reforming (SMR) combined with the water gas shift reaction (WGS) is analyzed using process integration techniques based on heat cascade calculation and pinch analysis with the aim of identifying potential measures to enhance the process performance. The challenge is to satisfy the high temperature heat demand of the SMR reaction by minimizing the consumption of natural gas to feed the combustion and to exploit at maximum the heat excess at low temperature by producing valuable steam or electricity or by performing cogeneration. By applying a systematic methodology based on energy-flow models, process integration techniques and a multi-objective optimization procedure, the process performances defined by the specific natural gas consumption and the specific steam or electricity production is optimized and analyzed for different operating conditions (i.e. air preheating, pre-reforming/reforming, WGS temperature) and process modification options like pre-reformer integration. Identified measures are to increase the production of exportable steam by consuming the entire waste heat and optimizing the steam production pressure level, and to reduce the natural gas consumption by adjusting process parameters. By these measures the performance can be varied between 0.53-0.59 kmol natural gas/kmol H_2 for the specific total natural gas consumption and 1.8-3.7 kmol steam/kmol H_2 for the specific steam production.

Keywords: Hydrogen, Steam methane reforming, Multi-objective optimization, Process integration, Thermo-economic modeling

1 Introduction

In order to satisfy the worldwide hydrogen demand, hydrogen has to be produced industrially. On an industrial scale hydrogen is synthesized mainly by chemical conversion of hydrocarbons. Due to economic reasons only a small percentage is produced by electrochemical processes being more energy-intensive. Thermal, thermochemical, biochemical and photochemical processes have so far not found many industrial applications [2]. In this study an industrial hydrogen process generating H_2 by steam methane reforming (SMR) combined with water gas shift reaction (WGS) and H_2 purification is analyzed with regard to the energy efficiency. In terms of energy performance, the challenge consists in satisfying the heat demand from the reforming reaction at high temperature and valorizing at maximum the heat excess at lower temperature. The objective of this study is to analyze the energy efficiency of the present configuration and to identify potential measures to enhance the process performance. Different process layouts with different operating conditions are evaluated, compared and optimized systematically by applying a consistent methodology based on process flowsheeting, energy integration techniques and multi-objective optimization [1, 5, 6].

2 Process Description

The process energy flow diagram described in Figure 1 represents the process unit operations that are relevant for the energy analysis. Natural gas and steam are heated up to produce syngas ($CO+H_2$) according to the endothermic SMR reaction Eq.1. To increase the chemical conversion and accordingly the energy efficiency, the reaction is performed at different temperatures in a pre-reformer (T_{preref}) and reformer (T_{ref}) unit. After the reforming two different H_2 purification routes are followed. In the first route, the process gas is cooled down before entering the water-gas-shift reactor where the CO is converted into CO_2 and additional H_2 according to the exothermic WGS reaction Eq.2. After pressure swing absorption (PSA) highly pure H_2 (99.99%) is released. In the other route, the process gas is cooled down, separated and purified resulting in several pure streams; CO_2 stream after chemical absorption with amines (MDEA), CO stream, water stream and enriched H_2 stream (98%). Table 2 reports common operating ranges.

SMR: $CH_4 + H_2O \xleftrightarrow{\Delta h_r^0 = \frac{206 kJ}{mol}} CO + 3H_2$ Eq. 1

WGS: $CO + H_2O \xleftrightarrow{\Delta h_r^0 = -\frac{41 kJ}{mol}} CO_2 + H_2$ Eq.2

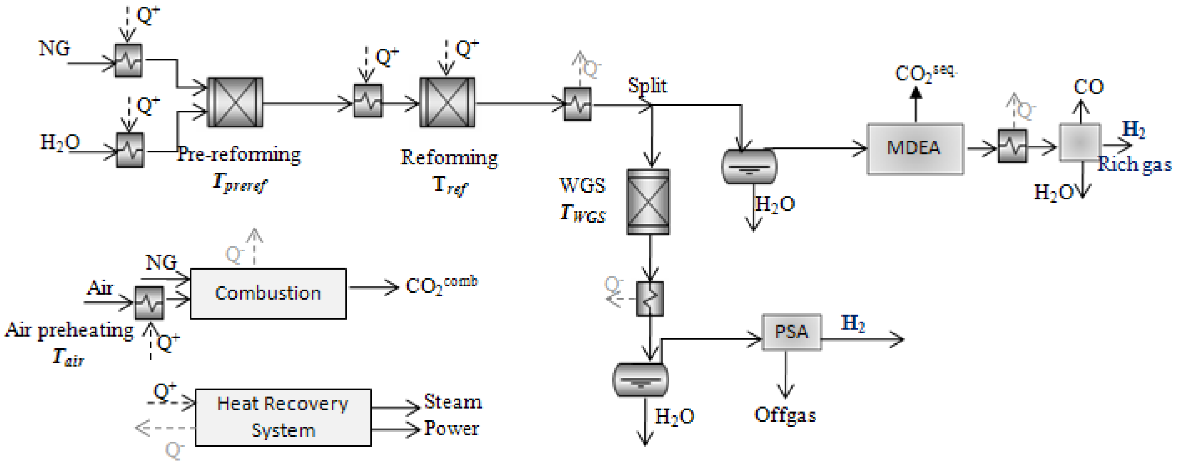

Figure 1: Process energy flow diagram.

3 Process Modeling

3.1 Method

The process is optimized by using simultaneously an energy-flow model and a separate energy integration model as described in [1]. Using a multi-objective framework, the process operating conditions are defined in order to minimize the specific natural gas consumption and to maximize the specific steam production.

3.2 Thermodynamic model

The energy-flow model represented in Figure 1 computes the chemical and physical transformations and the associated heat transfer requirements using the commercial flowsheeting software Belsim-Vali [1]. The model being a representation of the current industrial process is developed based on the industrial process operating conditions.

3.3 Energy-integration model

The energy-integration model determines the optimal heat recovery and computes the combined heat and power production using heat cascade constraints and a linear programming model. The energy consumption of the process is minimized by calculating thermodynamically feasible energy targets and achieving them by optimizing heat recovery systems, energy supply methods and operating conditions. The energy integration model is based on the definition and identification of the hot and cold streams and their minimum approach temperature ΔT_{min} to allow heat transfer and the calculation of the heat cascade as explained in [1, 3]. A $\Delta T_{min}/2$ contribution of 4 is assumed for the gas streams.

The hot and cold composite curves illustrated in Figure 2 represent the heat needs of the process. Outside the shaded area representing the potential heat recovery, the process needs have to be satisfied by a hot utility delivering heat to the process at higher temperatures and by a cold utility dissipating heat from the process at lower temperatures.

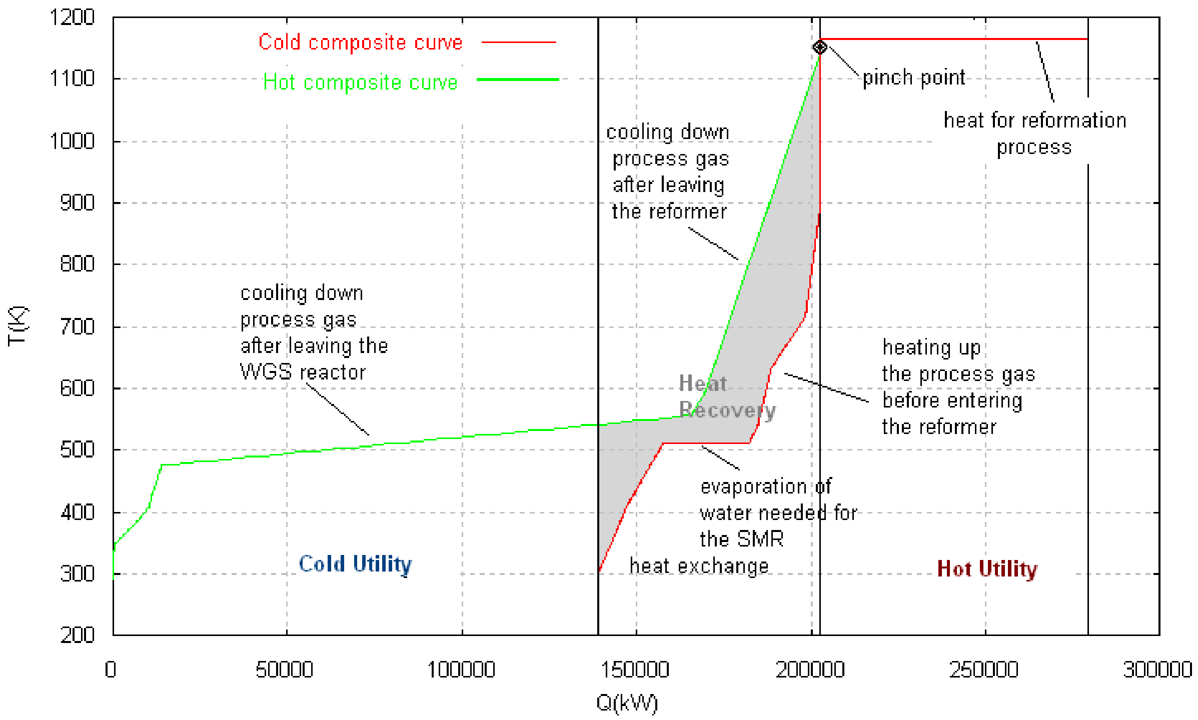

Figure 2: Hot and cold composite curves of the industrial hydrogen process.

The grand composite curve with the integrated utilities represented in Figure 3 visualizes the process energy integration.

Above the pinch point the heat required by the endothermic reforming process is satisfied by the combustion of natural gas and optionally depleted hydrogen streams (hot utility). The applied combustion model considers radiative and convective heat transfer of the flue gas, as well as the preheating of the air feeding the combustion. Below the pinch point the process is a heat source and heat has to be dissipated from the process. A stream of cooling water (cold utility) can satisfy these process demands as illustrated by the case without steam exportation on Figure 3.

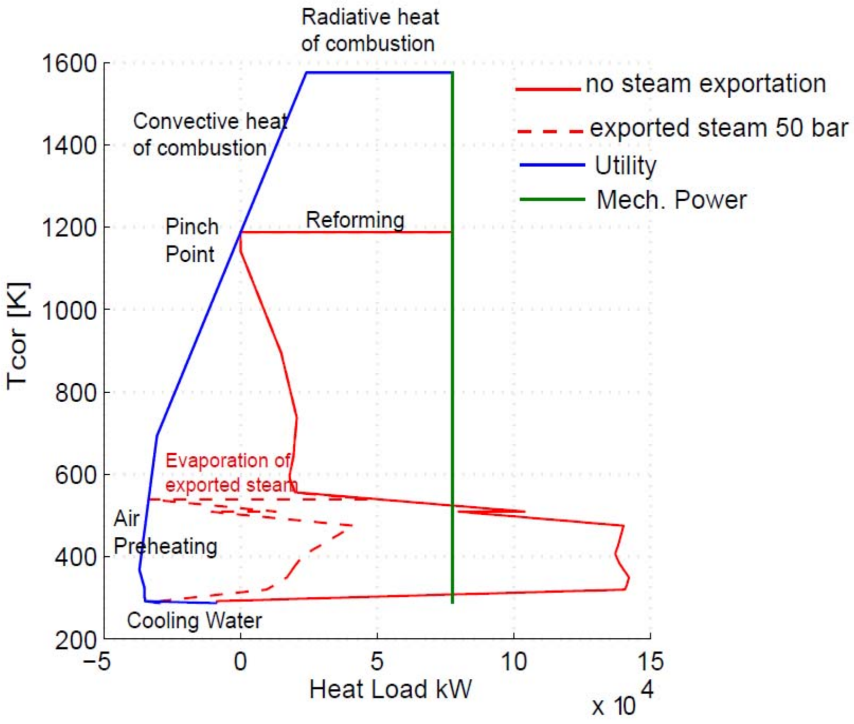

Figure 3: Grand composite curve of the process with integrated utilities.

However different possibilities to exploit the exergy value of the heat excess at low temperature can be considered in order to improve the performance of the examined process. These measures are steam export or combined electricity production that are introduced as utilities in the energy integration model. The influence on the energy integration is illustrated for the production of exportable steam at a pressure of 50 bar and a temperature of 550 K on Figure 3.

4 Process Performance

4.1 Performance indicators

In order to compare the influence of the different measures a set of performance indicators is defined:

- Specific total natural gas consumption:

$$C_{natgastot}^{specific} = \frac{total\ natural\ gas\ consumption\ \left[\frac{kmol}{s}\right]}{H_2\ production\ \left[\frac{kmol}{s}\right]}$$

The total consumption of natural gas is referring to the part of the natural gas which is used to feed the combustion and to the part consumed for the hydrogen production itself.

- Specific steam production:

$$P_{steam}^{specific} = \frac{exportable\ steam\ production\ \left[\frac{kmol}{s}\right]}{H_2\ production\ \left[\frac{kmol}{s}\right]}$$

$$P_{steam}^{specific} = \frac{exportable\ steam\ production\ \left[\frac{kmol}{s}\right]}{H_2\ production\ \left[\frac{kmol}{s}\right]}$$

- Specific exergy of produced steam:

$$B_{steam}^{specific} = \frac{exportable\ steam\ exergy\ [MW]}{H_2\ production\ \left[\frac{kmol}{s}\right]}$$

- Specific electricity production:

$$P_{electricity}^{specific} = B_{electricity}^{specific} = \frac{electricity\ production\ [MW]}{H_2\ production\ \left[\frac{kmol}{s}\right]}$$

The specific production of electricity is based on the assumption that the turbines feature a mechanical efficiency of 99% and an isentropic efficiency of 70%. The specific exergy of the electricity production equals the specific electricity production, since electric power is pure exergy.

4.2 Performance improvement

To improve the process performance several measures aiming at maximizing the exploitation of excess heat below the pinch point and minimizing natural gas consumption for the combustion are analyzed.

Measures to exploit the heat excess

For the exploitation of the excess heat below the pinch the influence of different parameters on the process performance is analyzed by a sensitivity analyses under the constraint that $C_{natgastot}^{specific}$ remains constant. Table 1 summarizes the different results. The variation of the steam pressure level (i.e. evaporation temperature) shows that the maximal flowrate of exportable steam at 550 K is reached for a steam pressure of 38.6 bar. Instead of exporting steam, electricity can be generated by a steam network valorizing the heat excess. A steam network consisting of three headers (850 K / 150 bar, 503 K / 27 bar and 293 K / 0.02 bar) and two turbines features the best performance. However, compared to the production of exportable steam, the generation of electricity results in a lower specific exergy export. Another interesting alternative is the cogeneration of steam and electricity. The idea is to define a steam network generating electricity and performing the evaporation and the condensation at a temperature level that is settled above the production of the exported steam. By changing the condensation level pressure a trade-off is observed between the electricity and the steam production competing for a limited amount of waste heat.

Table 1: Performance indicators for different process configurations.

Configuration	$C_{natgastot}^{specific}$ $\frac{kmol\ natural\ ga}{kmol\ H_2}$	$P_{steam}^{specific}$ $\frac{kmol\ steam}{kmol\ H_2}$	$E_{steam}^{specific}$ $\frac{MW}{\frac{kmol}{s}H_2}$	$E_{electricity}^{specific}$ $\frac{MW}{\frac{kmol}{s}H_2}$
No steam exportation	0.59	-	-	-
Exported steam @50 bar	0.59	3.1	58	-
Exported steam @38.6 bar	0.59	3.8	70	-
Electricity generation	0.59	-	-	45
Cogeneration P_{cond}=37 bar	0.59	1.82	33.6	9.1
Cogeneration P_{cond}=45 bar	0.59	1.85	34.2	8.0

Multi-objective optimization

The influence of the operating parameters on the process performance is analyzed in a multi-objective optimization [6]. The fixed objectives are to minimize the natural gas consumption for the combustion and to maximize simultaneously the steam production by varying appropriate decision variables. Table 2 presents the chosen process parameters; T_{air}, T_{preref}, T_{ref} and T_{WGS} and their respective variation range. The steam for export is generated at the optimal conditions of 550K and 38.6bar and no additional natural gas consumption just to satisfy the heat demand of the steam production is accepted.

The generated Pareto plot in Figure 4 represents the optimal trade-off between the objectives in the case of the maximum steam export production. An increased specific steam production goes in pair with an increase of the specific natural gas consumption. Using the full range of the process parameters the performance can be varied between 0.53-0.59 kmol natural gas/kmol H_2 for the specific total natural gas consumption and 1.8-3.7 kmol steam/kmol H_2 for the specific steam production. Table 3 summarizes the influence of the different operating parameters on the objectives. Relative to these results there are opportunities to enhance the current process performance.

Table 2: Decision variables for the multi-objective optimization.

Parameter	Abbreviation	Variation Range
Pre-Reforming T	T_{preref}	439-650°C
Reforming T	T_{ref}	581-700°C
WGS T	T_{WGS}	206-227°C
Air preheating T	T_{air}	400-627°C

Table 3: Influence on process performance.

$T_{air} \nearrow$ $T_{preref} \nearrow$ $T_{ref} \nearrow$	$C^{specific}_{natgastot} \searrow$	$P^{specific}_{steam} \searrow$
$T_{WGS} \nearrow$	$C^{specific}_{natgastot} \nearrow$	$P^{specific}_{steam} \nearrow$

Compared to a ordinary steam generator with a boiler efficiency of $\eta=0.95$ and producing steam with a steam to natural gas ratio of 14.9 $\mathrm{kmol_{steam}/kmol_{naturalgas}}$, the supplementary production of steam within this industrial process is a favorable option. As illustrated in Figure 4, between point 6 and point 4 the curve has a slope of

$$\frac{\Delta P^{specific}_{steam}}{\Delta C^{specific}_{natgastot}} = 63.5 \frac{kmol\ steam}{kmol\ natural\ gas}$$

and between point 4 and point 5 of

$$15.4 \frac{kmol\ steam}{kmol\ natural\ gas}.$$

Above point 4 there is a need to buy an additional amount of natural gas to satisfy the demands and export additional steam, while from point 6 to 4 the steam production is based on excess heat. Similar optimizations with and without a pre-reforming step and including the variation of the steam to carbon ratio allow to study the benefit for steam export and the trade-off between steam and electricity production.

5 Conclusion

The energy analysis based on process integration techniques identified several measures to enhance the performance of an industrial hydrogen process. Measures identified are to use the maximal amount of available heat excess by increasing the production of steam for export by adjusting the pressure and temperature levels according to the peculiarities of the process, and to reduce the natural gas consumption for combustion without interfering with the specific steam production by adjusting the process parameters. The assessed efficiency of the steam production within this process reaching 64 or 15.4 $\mathrm{kmol_{steam}/kmol_{naturalgas}}$ depending on the process configuration is higher than the one of an ordinary steam generation unit (14.9 $\mathrm{kmol_{steam}/kmol_{naturalgas}}$). This study is the basis for a future thermo-economic analysis designing the process to perform with the highest energy and economic performance.

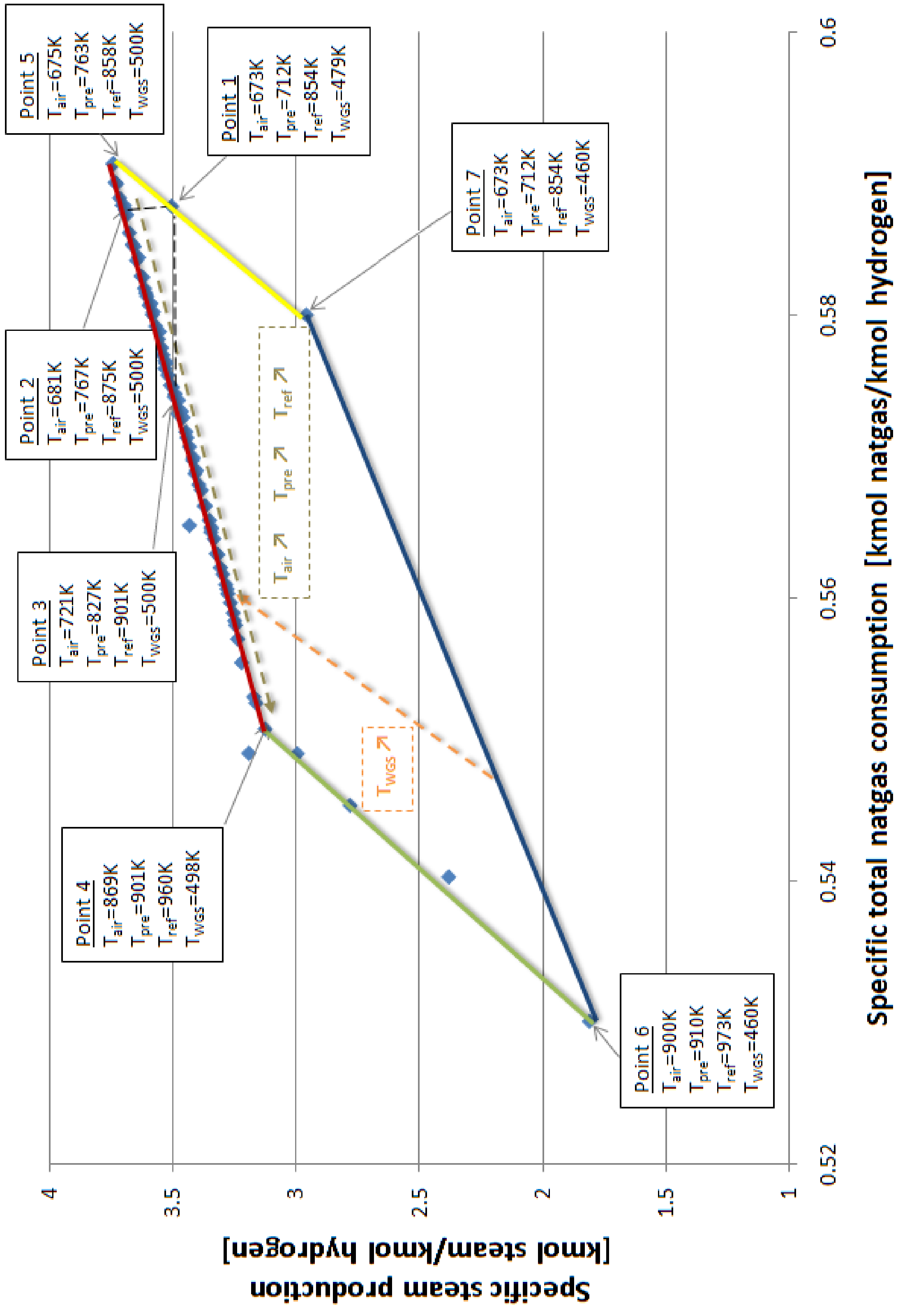

Figure 4: **Optimal solutions in the Pareto domain for variation of the process parameters.**

Acknowledgments

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