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# UTILISATION OF FLUIDS WITH LOW GLOBAL WARMING POTENTIAL IN SUPERCRITICAL ORGANIC RANKINE CYCLE

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## ABSTRACT
Organic Rankine cycle is simple and convenient technology for power and electricity production that can successfully exploit low temperature heat sources by the use of a refrigerant as a working fluid. However, as high GWP refrigerants are being phased out, the pursuit for the suitable low GWP working fluid continues. We have compared the performance of several wet, dry and isentropic fluids in a supercritical Rankine cycle. Thermal efficiency and net work produced were the primary parameters for comparison of high GWP R134a with its suggested low GWP replacements, namely R1234yf and R152a. Exergy analysis shows superior exergetic efficiency of R134a at high evaporator pressures. Nevertheless, R152a is a promising working fluid for a supercritical cycle, achieving larger net work and good thermal efficiency, albeit demanding a higher heat input.

## NOMENCLATURE

| | |
|---|---|
| $ex$ | specific exergy (kJ/kg) |
| $h$ | specific enthalpy (kJ/kg) |
| $i$ | specific irreversibility (kJ/kg) |
| $M$ | molecular mass (kg/kmol) |
| $p$ | pressure (MPa) |
| $q$ | specific heat (kJ/kg) |
| $s$ | specific entropy (kJ/kgK) |
| $T$ | temperature (K) |
| $w$ | specific work (kJ/kg) |
| $\eta$ | efficiency (%) |

Subscripts

| | |
|---|---|
| *0* | reference state |
| *1, 2, etc.* | states of the cycle |
| *b* | normal boiling point |
| *c* | critical |
| *C* | condenser |
| *E* | evaporator |
| *ex* | exergetic |
| *H* | heat source |
| *P* | pump |
| *T* | turbine |
| *th* | thermal |

## INTRODUCTION
Over the last few decades Organic Rankine Cycle (ORC) has been in the focus of energy engineering research. Unlike the conventional steam cycle ORC employs organic working fluids, typically refrigerants or hydrocarbons. Use of an organic fluid has a number of advantages: the fluid with higher molecular mass than water evaporates at lower temperatures; thus the cycle can be powered by a lower temperature heat source than the conventional water cycle (Chen et al., 2010). Utilised heat sources include waste heat (Long et al., Wang et al., 2013, Wang et al., 2011), biomass (Al-Sulaiman et al., 2011, Tańczuk and Ulbrich, 2013), geothermal (El-Emam and Dincer, 2013, Cammarata et al., 2014) and solar energy (Wang et al., 2014), to name a few. However, depending on the cycle design and its operating parameters, in order to ensure efficient operation of the system, the appropriate selection of the working fluid is the key issue. Hence, the quest for the favourable working fluid in

an ORC has been ongoing for decades ((Bao and Zhao, 2013) and references therein).

A suitable fluid for an ORC has to fulfil a number of requirements. Desirable properties include low specific volumes, high efficiency, moderate pressures, low cost, low toxicity, low ozone depletion potential (ODP) and low global warming potential (GWP) (Tchanche et al., 2009). The latter is particularly important as with continuous efforts to reduce greenhouse gas emissions many high GWP fluids are being banned and phased out. Since the Kyoto protocol R22 has been replaced by other pure fluids of fluid mixtures, amongst others R134a, R407C, and R410A, whose GWP is still rather high. Furthermore, R134a is being phased out in Europe and in developed countries the initiative to completely ban most uses of hydrofluorocarbons (HFC) is well under way. Low GWP refrigerants have to be developed to replace the current generation of HFCs. The most promising replacement is hydrofluoroolefin (HFO) family, with R1234yf as the best candidate. Hence, low GWP working fluids in ORC are in the spotlight on current scientific research (Molés et al., McLinden et al., 2014).

While most commercial ORC plants exhibit a simple architecture: sub-critical working conditions, single-component working fluids, single evaporation pressure, and possible use of a recuperator heat exchanger (Quoilin et al., 2013), the use of fluids with low critical temperatures, even when low temperature sources are employed, offers the possibility for the cycle to operate at supercritical conditions. Schuster et al. (Schuster et al., 2010) reported improved exergetic efficiency of the supercritical Rankine cycle (SRC). SRC operation bypasses the liquid-vapour boundary which results in an improved thermal match between the source and the fluid, which allows for more effective heat utilization. Thus, irreversibilities are lower and exergy destruction is reduced.

In this paper, we have compared the performance of several historically popular and heavily utilised refrigerants with their suggested replacements as potential working fluids in a SRC. A range of pressures and temperatures have been investigated in order to identify the optimal set of operational parameters for each refrigerant that ensures satisfactory energetic and exergetic performance. Prospective low GWP replacements for R134a were of particular interest.

## METHODOLOGY

ORC consists of four basic transformation of the working fluid; the standard cycle configuration is shown in Figure 1. All processes are considered to be steady-state and adiabatic. All potential and kinetic energy losses are neglected. Fluid properties at specific points of the cycle were determined using REFPROP 9.1. Isentropic efficiencies of the pump and the turbine were fixed at 80%. Heat rejection was assumed to take place at ambient conditions. Therefore, condensing temperature was estimated to be 298K, and condensation pressure for each fluid was determined. High cycle pressure was modelled in 3-10 MPa range and the maximum temperature, at the turbine inlet, was varied 400 K - 470 K. Energy and exergy efficiencies, as well as the net work produced, required heat input and the extent of exergy destruction in individual cycle components were calculated using the equations below:

$$w_P = h_2 - h_1 \tag{1}$$

$$w_T = h_3 - h_4 \tag{2}$$

$$w_{net} = w_T - w_P \tag{3}$$

$$\eta_{th} = \frac{w_{net}}{q_H} \tag{4}$$

$$\eta_{ex} = \frac{w_{net}}{ex_H} \tag{5}$$

$$i_{total} = i_P + i_E + i_T + i_C \tag{6}$$

derived from the energy balance for the cycle and the exergy balance for individual processes:

$$w_P + q_H = w_T + q_C \tag{5}$$

$$ex_{in} + q\left(1 - \frac{T_0}{T}\right) = ex_{out} + w + i \tag{6}$$

where $ex_{in}$, $ex_{out}$ and $ex_H$ are specific exergies at the inlet, outlet and heat source conditions, respectively.

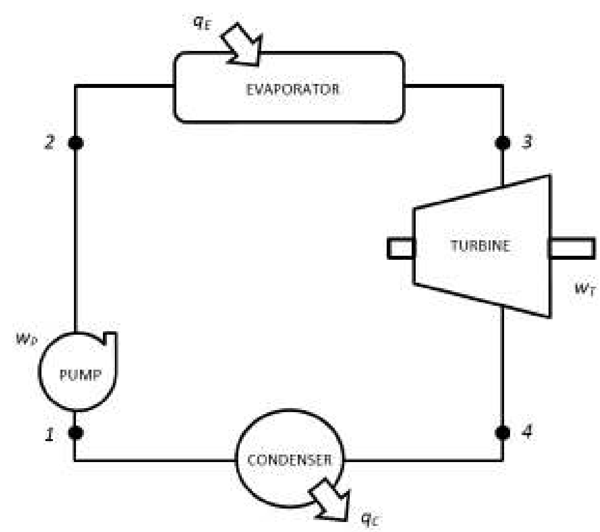


Figure 1. Schematic of a simple ORC operating at supercritical conditions.

Six working fluids, presented in Table 1, were selected for the study: R124, R134a, R143a, R152a, R1234yf and RC318. Chosen fluids present a good mix of wet, dry and isentropic varieties, as seen in Figure 2. It is worth noting remarkable similarity of $ds/dT < 0$ slopes for R124 and R1234yf, as well as for R134a and R143a fluid pairs at the vapour boundary, with R124 and R134a having somewhat higher critical points. R124 and R1234yf also have virtually identical *h-p* profile. Additionally, specific volume of the fluid at the turbine inlet, which affects the size, and therefore the cost of the systems, and condensing and evaporating temperatures were taken in account. Since the cycle is to operate at supercritical conditions, critical point parameters were essential. Please note that the lowest investigated pressures are below the critical pressure for R134a and R1234yf. Additionally, properties of R1234yf at temperatures above 410 K and that of R134a above 455 K are estimates.

Other important properties of suitable working fluids for an ORC are high vapour density, low viscosity and high thermal conductivity. Low density fluids require higher flow rates, which increases the size of the system, and therefore the cost alike. Low viscosity both in liquid and vapour phase is desirable to reduce the frictional losses in heat exchangers and pipes. Comparison of saturated vapour properties at 298K and those of supercritical vapour at 10 MPa of the selected fluids are given in Table 2. VFR is the isentropic volume flow ratio: the specific volume variation across the turbine for an isentropic process (Bao and Zhao, 2013). RC318 and R124a have both high vapour density and VFR, yet their viscosities are high as well. R143a and R152a have low viscosities and high thermal conductivity, but also the lowest supercritical vapour density.

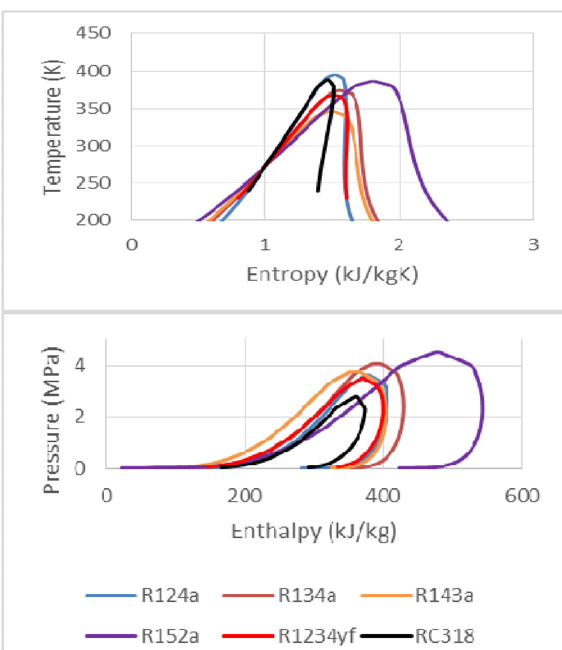


Figure 2. (a) *T-s* and (b) *p-h* diagrams for six working fluids.

Besides thermodynamic and transport characteristics, GWP was the crucial factor. Selected fluids cover GWP values over several orders of magnitude (Table 1). RC318, R134a and R143a, which all have very high GWP, have been originally suggested as suitable replacements for R22. High GWP of R134a presents a problem for modern protocols and increasingly stricter limits on refrigerant properties. R1234yf and R152a are considered here as promising substitutes. While all fluids are in lower toxicity category, low GWP fluids fall into lower flammability group (unlike high GWP which do not exhibit flame propagation). All fluids, apart from R124, have zero ODP.

## RESULTS AND DISCUISSION

Energetic and exegetic analysis of the performance of the six selected working fluids was carried out. Fundamental evaluation of the suitability of the fluid to be employed in a SRC was based on the maximum achievable thermal efficiency and net power produced, as well as on the maximum exergy efficiency and extent of the exergy destruction. Maximum thermal efficiency in all cases was found for the highest temperature at the turbine inlet, which was 470 K in our model. However, variation of the high cycle pressure affected the optimal thermal performance differently, as shown in Figure 3. While the efficiency peaked at the maximum pressure of 10 MPa for most fluids, the best performance was found at 9 MPa for R152a (17.5%) and 8 MPa for R124a (16.5%). As the pressure of evaporator increases larger pump work is required and the heat input in the evaporator decreases. It is worth mentioning that R134a at 10 MPa reached the maximum efficiency of 17.2%. However, R1234yf did not perform nearly as well with the highest thermal efficiency of 15%.

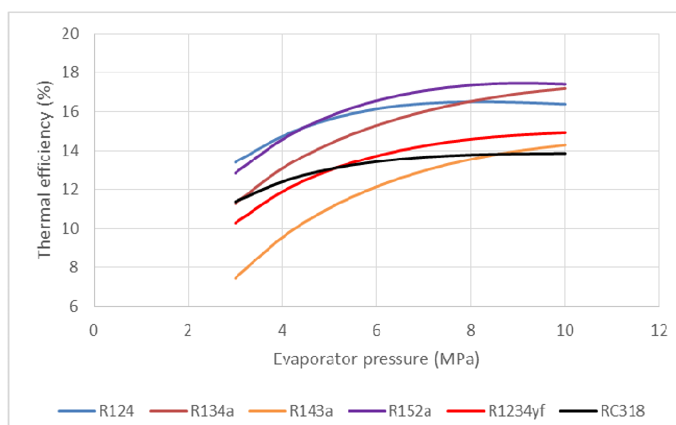


Figure 3. Thermal efficiency of the SRC depending on high cycle pressure for turbine inlet temperature of 470K.

Maximum net work was also found for 470 K as the highest investigated temperature and, like in the case of thermal efficiency, different fluids exhibited optimal performance at dissimilar pressure levels, as shown in Figure 4.

Table 1. Supercritical ORC selected fluid properties

| Fluid | $M$ (kg/kmol) | $T_b$ (K) | $T_c$ (K) | $p_c$ (MPa) | ODP* | GWP** | ASHRAE Class*** | $p_C$ (MPa) |
|---|---|---|---|---|---|---|---|---|
| R124 | 136.48 | 261.19 | 395.43 | 3.6243 | 0.022 | 620 | A1 | 0.3809 |
| R134a | 102.03 | 247.08 | 374.21 | 4.0593 | 0 | 1300 | A1 | 0.6624 |
| R143a | 84.041 | 225.91 | 345.86 | 3.7610 | 0 | 4300 | A2 | 1.2566 |
| R152a | 66.051 | 249.13 | 386.41 | 4.5168 | 0 | 120 | A2 | 0.5938 |
| R1234yf | 114.04 | 243.7 | 367.85 | 3.3822 | 0 | 4 | A2L | 0.6797 |
| RC318 | 200.03 | 267.18 | 388.38 | 2.7775 | 0 | 10250 | A1 | 0.3117 |

* ODP: Ozone depletion potential, relative to R11;
** GWP: Global warming potential, relative to $CO_2$;
*** ASHRAE Standard 34 – Refrigerant safety group classification. 1: No flame propagation; 2: Lower flammability; 3: Higher Flammability; A: Lower Toxicity; B: Higher Toxicity.

Table 2. Density, viscosity and thermal conductivity of saturated and supercritical refrigerant vapour.

| State | Property | |
|---|---|---|
| Saturated vapour at 298 K | $\mu$ (μPa·s) | RC318 > R124a > R134a > R152a > R1234yf > R143a |
| | $k$ (mW/mK) | R152a > R134a > R143a > R124a > RC318 > R1234yf |
| Supercritical vapour at 10 MPa | $\rho$ (kg/m$^3$) | RC318 > R124a > R1234yf > R134a > R143a > R152a |
| | $\mu$ (μPa·s) | RC318 > R124a > R1234yf > R134a > R143a > R152a |
| | $k$ (mW/mK) | R152a > R143a > R1234yf ≈ RC318 ≈ R124a > R134a |
| | $VFR$ | RC318 > R124a > R152a > R1234yf ≈ R134a > R143a |

Preference of R124 for lower pressures was notable as the maximum work of 40.8 kJ/kg was found for 5MPa; same pressure suited RC318 resulting in its net work maximum of 30.2 kJ/kg. Similarly, R1234yf achieved moderate 40.5 kJ/kg at 7 MPa. Inclination towards higher pressures was observed for R143a – 43 kJ/kg at 9 MPa, and R134a – 50 kJ/kg at 8 MPa. Nevertheless, nearly 50% higher net work of 72.6 kJ/kg was found for R152a at 6 MPa, which combined with the highest thermal efficiency, makes this fluid the obvious frontrunner. While similarly high efficiency was found for R134a, the work it produced was more modest; R124 achieves comparable efficiencies at lower pressures, yet the net work is substantially lower.

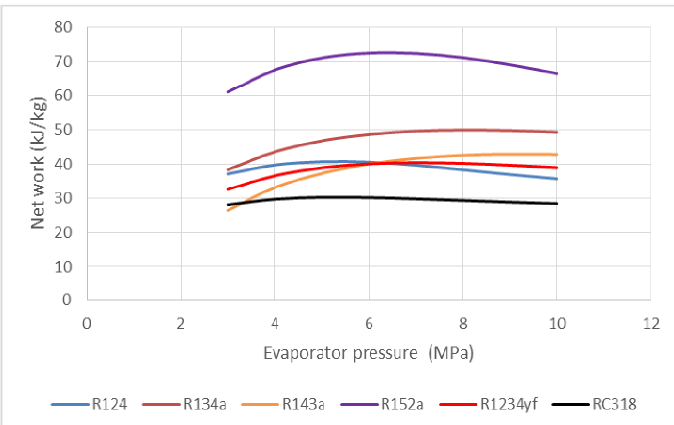


Figure 4. Cycle net work as the function of high cycle pressure (turbine inlet temperature = 470K).

Results indicate that the selection of the high operational pressure can be a complex task if the compromise between lower thermal efficiency and higher work produced needs to be made. At 6 MPa R152a cycle had thermal efficiency of 16.6%, while at the maximum efficiency parameters the total work decreases to 69.2 kJ/kg. The described performance requires heat input of 438 and 396 kJ/kg of heat, respectively. Naturally, higher heat input is required for lower evaporator pressures, presented in Figure 5. While the same trend is obvious for all fluids, it is clear that R152a is significantly more heat-demanding than the other selected fluids. Like in previous graphs, trends for R134a and R143a are almost identical, with other fluids requiring lower heat inputs. Choice of the working fluid may be dictated by the amount of heat available.

The exergy analysis was performed at the operational parameters at which our SRC achieved the best energy conversion performance. The trends are identical to those presented in Figure 3, again proving R152a to be the dominant choice. The exergy efficiency was found to be 56.1 % for the optimal thermal efficiency performance and 54.7 % for maximal net work. However, R134a reached the maximum exergy efficiency, equal to that of R152a, at its highest thermal efficiency settings. The net work produced at these conditions was 49.3 kJ/kg, requiring merely 297 kJ/kg of heat.

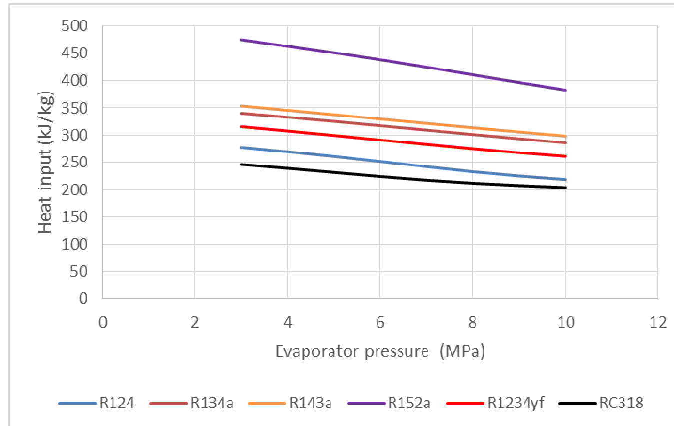


Figure 5. Magnitude of heat input required 470K of temperature to be reached at the turbine inlet as the function of high cycle pressure.

Better exergetic performance was found at lower temperatures and exergy efficiency variation with cycle high pressure, for the minimum investigated temperature at the turbine inlet of 400 K, is presented in Figure 6. Exergy efficiency curves of most fluids exhibited a characteristic peak at relatively low pressures; further increase of the high operation pressure leads to an increase in exergy destruction. Conversely, R124 and RC318 showed dissimilar trend as their exergy efficiency continuously decreased with increasing pressure. The highest exergetic efficiency of 62% was reached by R124 at 3 MPa, yet this is below the critical pressure for the given fluid, indicating that a subcritical cycle is in the case a better choice. However, in a supercritical scenario, at 4 MPa and 410 K, R124 achieved 60.5%. Comparably high exergy efficiencies were found for R134a and R152a. While exergy efficiency of R152a drops rapidly at pressures above 5 MPa, R134a exhibits a plateau at ~57%, which was the maximum one for R1234yf.

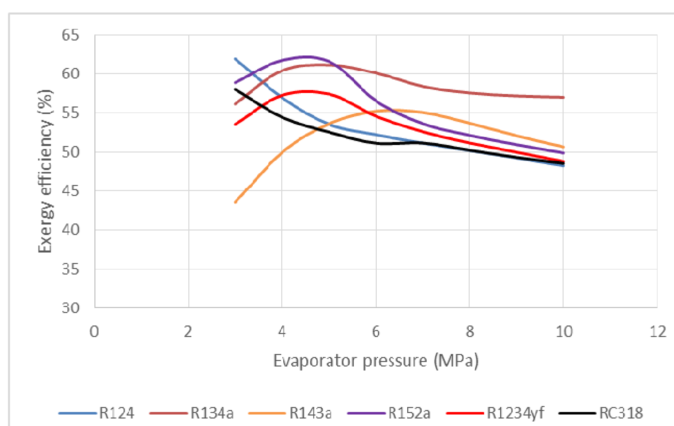


Figure 6. Exergetic efficiency of the SRC depending on high cycle pressure for turbine inlet temperature of 400 K.

In order to gain deeper insight in exergy destruction, separate SRC elements were examined. Irreversibilities of individual transformations, and the overall cycle, are presented in Figure 7, for the best exergetic performance of the given fluid. Heat rejection (condenser) and pressure increase (pump) steps did not significantly contribute towards exergy loss. As expected, the main source of exergy destruction was the evaporator, typically around 70% of the overall exergy destroyed. Due to the better thermal match between the working fluid and the heat source in supercritical conditions, exergy destruction is lower than in subcritical case. Thus, the expansion becomes an influential source of irreversibilities.

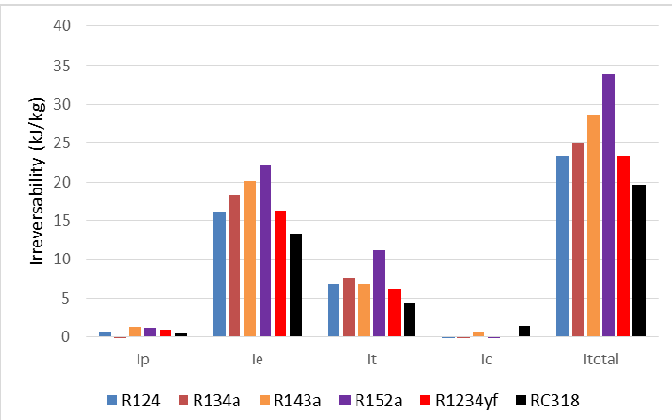


Figure 7. Irreversabilities in individual cycle elements for the maximum exergetic efficiency scenario.

The extent of exergy destruction in the evaporator and the turbine appears to be consistent with the general fluid performance. Exergy loss of R1234yf is lower than that of R134a; unfortunately, both the thermal performance and the work produced are also lower. Total irreversabilities in R152a cycle are ~36% higher than those of R134a cycle for the same maximum exegetic efficiency. However, this is due to substantially larger exergy destruction in the expander, compared to all other fluids. The presented values are for 61% exergy efficiency for both fluids, and equivalent thermal performance of 13.8% and 13.4% for R152a and R134a, respectively. The former, however, at the same operational pressure of 5 MPa, has the capacity of 50 kJ/kg net work output, compared to 29.4 kJ/kg for the latter. Despite the greater exergy loss in the turbine, R152a has proportionally lower exergy destruction contribution from the evaporator stage, proving it is a favourable thermal match at to the heat source at supercritical conditions.

Calculated thermal and exergy efficiencies are the theoretical maximums for the given cycle, since any heat, potential and kinetic energy losses were ignored. More accurate results can be obtained by using isentropic efficiencies of the pump and the turbine for the specific pressure ratio for the given fluid (Sauret and Rowlands, 2011). Our future work will incorporate heat exchanger design and the associated cost of cycle operation at supercritical conditions.

## CONCLUSIONS

We have investigated suitability of wet, dry and isentropic fluids with dissimilar GWP to be employed in a supercritical Rankine cycle. High cycle temperature and pressure were varied in the range of 400-470 K and 4-10 MPa, respectively. Results showed R1234yf, a suggested replacement for R134a, could not reach the same thermal efficiency or the new work produced. On the other hand, R152a achieved higher thermal efficiency across the whole investigated pressure range. R152a produced remarkably higher net work, but also required substantially larger heat input than other investigated fluids. Exergetic performance of R134a at moderate pressures and lower temperatures was comparable to that of R152a. At higher pressures exergy efficiencies of R152a and R1234yf were similar and low. In spite of the greater extent of the exergy loss, R152a imposes itself as a promising low GWP working fluid for a supercritical ORC.

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