

1 **Effect of working fluids on the performance of a novel direct** 2 **vapor generation solar organic Rankine cycle system**

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10 **Abstract:** A novel solar organic Rankine cycle (ORC) system with direct vapor generation
11 (DVG) is proposed. A heat storage unit is embedded in the ORC to guarantee the stability of
12 power generation. Compared with conventional solar ORCs, the proposed system avoids the
13 secondary heat transfer intermediate and shows good reaction to the fluctuation of solar
14 radiation. The technical feasibility of the system is discussed. Performance is analyzed by using
15 17 dry and isentropic working fluids. Fluid effects on the efficiencies of ORC, collectors and the
16 whole system are studied. The results indicate that the collector efficiency generally decreases
17 while the ORC and system efficiencies increase with the increment in fluid critical temperature.
18 At evaporation temperature of 120°C and solar radiation of 800 Wm⁻², the ORC, collector and
19 overall thermal efficiencies of R236fa are 10.59, 56.14 and 5.08% while their values for Benzene
20 are 12.5, 52.58 and 6.57 % respectively. The difference between collector efficiencies using
21 R236fa and Benzene gets larger at lower solar radiation. The heat collection is strongly

22 correlated with latent and sensible heat of the working fluid. Among the fluids, R123 exhibits the
23 highest overall performance and seems to be suitable for the proposed system in the short term.

24 **Keywords:** *solar thermal power generation, organic Rankine cycle, direct vapor generation,*
25 *working fluid, critical temperature*

26 **1. Introduction**

27 Solar energy is one of the potential heat source for organic Rankine cycle (ORC). Solar radiation
28 has the maximum capacity and the minimum replenishment time among all of available
29 sustainable energies [1]. By using the ORC, low-medium temperature solar thermal power
30 system can be an attractive option. A temperature of about 100°C or slightly higher is sufficient
31 to drive the ORC and evacuated/double glazing flat plate collectors (FPC), evacuated tube
32 collectors (ETC), compound parabolic concentrators (CPC), and parabolic trough collectors
33 (PTC) with small concentration ratio can be competent in solar energy collection for the ORC.
34 Such solar ORC systems are capable to efficiently harness solar energy in temperature ranges
35 from 100 to 200°C. They have advantages including the ability to scale down to small unit sizes,
36 cogeneration near the point of usage, relatively low technical requirement in heat storage and
37 good applicability in regions without rich direct solar radiation resource.

38 At present, most of the solar ORCs under investigation use heat transfer fluid (HTF) to carry
39 away energy in the collectors and then release it to the organic fluid [2-11]. The heat transfer
40 irreversibility in the evaporator is very large as shown in Fig. 1. The vertical axis is the
41 temperature and the horizontal is the heat transferred from HTF to the organic fluid. Adverse
42 current heat exchanger is exemplified. The inlet temperature of the organic fluid is close to the
43 environment temperature. Given the pinch point temperature (ΔT_{pp}) and the ORC operating
44 condition, a low mass flow rate of HTF results in a high HTF inlet temperature while a high one

45 is accompanied with a high HTF outlet temperature. Therefore, it is difficult to lower the HTF
46 average temperature. This is disadvantageous because solar energy collection is less efficient at
47 high operating temperature. Moreover, the use of HTF increases the investment. Additional
48 power is needed for the pumping of HTF, which can significantly reduce the system net power
49 output especially for small-scale solar ORCs.

50 The above mentioned problems can be solved by using direct vapor generation (DVG)
51 technology. The DVG technology with water as the working fluid (known as direct steam
52 generation, DSG) has been widely investigated [12-16]. In a DSG system, steam is directly
53 generated in the solar field, hence eliminating the boiler in the power section. The power
54 consumption by the solar field recirculating pump is also reduced. The collectors benefit from
55 the constant temperature and high coefficient of heat transfer in the evaporation region of water.
56 The feasibility of the DSG technology has been demonstrated within the DISS (Direct Solar
57 Steam) project [17, 18]. During the 1500 hours operation no problem in the solar specific
58 components like the absorber tubes or the ball joints has occurred. A demonstration plant of 8
59 MWht has also been built by Abengoa Solar [19]. The plant has been operated and evaluated for
60 one year. In this period, an innovative control strategy system that guarantees the stability of the
61 plant even under transient conditions has been validated. The first commercial solar thermal
62 parabolic trough power plant with DSG technology in the world has been producing electricity
63 since 2011 [20]. The 5 MWe solar thermal power plant uses a new generation of parabolic
64 trough made of composite material combined with an efficient thin-glass mirror which reflects
65 more than 95% of the sun radiation. After two years of successful operation, the power plant has
66 shown practical applicability of the DSG technology.

67 Though the DVG technology using the organic fluid for the purpose of power conversion has
68 not yet attracted much attention, it seems to be a perfect match to the ORC. The reasons are
69 given as follows.

70 Firstly, it can react to the fluctuation in solar radiation in a simple way. In the conventional
71 DSG power generation system, in order to prevent the droplets from hitting the blades and
72 causing damage, the water (a typical wet fluid) entering the expander must be superheated. This
73 leads to great difficulty in controlling the system under variable solar radiation. The superheated
74 steam is also accompanied by low coefficient of heat transfer in the receiver, and thus the
75 collector efficiency is decreased. Through the replacement of water by a dry or isentropic
76 organic fluid, these problems can be overcome. There is no need to guarantee the superheat state
77 when the fluid leaves the solar field. The fluid from the collectors can be even at liquid or binary
78 phase state with a specially designed heat storage unit. The power generation is steady over a
79 wide range of solar radiation, which is certainly a big advantage of this kind of system.

80 Secondly, the technical issues associated with the pressure are less critical. In the
81 conventional DSG system, the maximum operation pressure is generally above 10 MPa, and the
82 technical requirement on the receiver is high. While in a DVG-ORC system the pressure can be
83 significantly reduced by choosing appropriate fluids. For example, the saturation pressure of
84 R245fa at 100 °C is 1.3MPa, and it is 1.3 MPa for R123 at 125 °C, 1.1 MPa for Acetone at 150
85 °C, 1.6 MPa for PF5056 (Perfluorohexane) at 175 °C, 1.3 MPa for Cyclohexane at 200 °C. These
86 fluids can be considered for different operating temperatures. The technical requirement in the
87 DVG system gets much lower than that in the DSG system. Moreover, the operating pressure in
88 the DVG system may be even lower than that of HTF in a commercial solar thermal power plant.
89 The mixture of two aromatic hydrocarbons (diphenyl and diphenyl ether, THERMINOL® VP-1)

90 is suitable fluid to transport heat in the solar field [21, 22]. The saturation pressure of this HTF at
91 400°C is about 1.2 MPa. The design pressure at the solar field inlet has been set at 2.5 MPa to
92 avoid evaporation at the outlet of the solar field. The technical issues associated with the HTF
93 pressure in the receiver, storage tank, etc. are similar with those in the DVG system. Since the
94 HTF technology has been well proven, the DVG technology is expected to be feasible.

95 Thirdly, there have been many successful applications of DVG technology using
96 refrigerant. One application is the solar assisted heat pump (SAHP) systems [23-26]. CPC, FPC
97 and evacuated heat pipe collectors can be employed. The solar collectors and the heat pump
98 evaporator are integrated into a single unit to transfer solar heat to the refrigerant. The direct
99 expansion SAHP systems are widely used for domestic heating and bathing. Long-term
100 performance (>5years) has been investigated and demonstrated [27]. There are products
101 available in the market [28, 29]. R134a is a commonly used fluid in SAHP systems, in which the
102 operating pressure may range from 0.4 to 1.6 MPa (the saturation pressure at 10 and 60 °C
103 respectively). The DVG technology with low boiling point refrigerant has reached a considerable
104 degree of maturity.

105 The solar ORC system with DVG is promising. However, study on this kind of system is
106 limited. A close view to its performance is required. In particular, as vapor is generated directly
107 in the collectors, the working fluid influences not only the heat to power conversion but also the
108 solar energy collection. Among the properties of the working fluid, the critical temperature
109 seems to be most relevant to the thermodynamic performance. The effects of fluid critical
110 temperature on the efficiencies of isolated ORC [30-32], geothermal power generation [33],
111 waste heat recovery [31, 34, 35] and solar power system [3] have been estimated by lots of

112 researchers. A general conclusion has been made: higher system efficiency can be achieved by
113 using fluid of higher critical temperature.

114 Notably, the influence of working fluids on the solar energy collection is rarely investigated.
115 In the proposed solar ORC system, an inner-type heat storage unit is employed, which enables
116 the system to work steadily. Seventeen fluids have been selected as listed in Table 1. These
117 working fluids have also been examined in many previous studies [3, 7, 31, 32, 36]. The working
118 fluids are vaporized directly in the collectors. Due this innovative design the effect of working
119 fluids is different from that on a solo ORC or conventional solar ORC system with HTF. In this
120 paper, influence of working fluids on the collectors, ORC, and the whole system is investigated
121 with respect to their critical temperatures. Suitable fluids are suggested with comprehensive
122 consideration of the thermodynamic efficiency, technical and environmental aspects.

123 **2. System configuration**

124 The configuration of the proposed system is shown in Fig. 2. The system consists of solar
125 collectors, pumps (P) and a fluid storage tank with phase change material (PCM), expander,
126 generator (G) and condenser. The collectors serve as the direct vapor generator. In contrast to the
127 traditional solar Rankine system, an organic fluid storage tank with PCM is embedded into the
128 system. Owing to this inner-type heat storage unit, the system can work smoothly without any
129 complicated control strategy.

130 In practical operation, there can be three modes:

131 I) The system needs to generate electricity and solar radiation is available. In this mode, valves
132 1, 2 and 3 are open and pump 1 is running. The organic fluid is heated and vaporized through the
133 collectors under high pressure. The vapor flows into the expander, exporting power in the
134 process due to the pressure drop. The outlet vapor is cooled down and condensed to a liquid state

135 in the condenser. The liquid is pressurized by pump 1. The organic fluid is then sent back to the
136 collectors for recirculation. In case solar radiation is too strong (higher than the design value),
137 valve 4 can be open and pump 2 can run to prevent the organic fluid from being superheated in
138 the collectors and to efficiently utilize solar energy. Part of the solar heat is stored. If solar
139 radiation is lower than the design value, some liquid can be vaporized by the PCM. The fluid
140 leaving the collectors can be at vapor phase, binary phase or liquid phase, and the ORC is able to
141 work steadily over a wide range of solar radiation.

142 II) The system does not need to generate electricity but solar radiation is strong. Valves 3 and 4
143 are open. Pump 2 is running. In this mode, solar heat is transferred to the PCM by the organic
144 fluid. Heat is stored.

145 III) The system needs to generate electricity but solar radiation is very weak or unavailable.
146 Valves 1, 2 and 5 are open and pump 1 is running. Heat is released from the PCM and converted
147 into power by the ORC.

148 Mode I presents the simultaneous processes of heat collection and power generation while
149 Mode II or Mode III is the independent process of heat collection or power conversion.

150 **3. Thermodynamic modelling**

151 The power generated by the expander and that consumed by the pump are calculated by Eq. (1)
152 and Eq. (2), respectively.

$$153 \quad W_t = m(h_{t,i} - h_{t,o}) \quad (1)$$

$$154 \quad W_p = m(h_{p,o} - h_{p,i}) \quad (2)$$

155 The isentropic efficiency for the expander and the pump is defined by Eq. (3) and Eq. (4),

$$156 \quad \varepsilon_t = \frac{h_{t,i} - h_{t,o}}{h_{t,i} - h_{t,os}} \quad (3)$$

157
$$\varepsilon_p = \frac{h_{p,os} - h_{p,i}}{h_{p,o} - h_{p,i}} \quad (4)$$

158 where *os* represents the ideal thermodynamic process. The energy required in the heating process
 159 of the ORC is calculated by the enthalpy increment of the organic fluid from the pump to the
 160 expander.

161
$$Q = m(h_{t,i} - h_{p,o}) \quad (5)$$

162 The ORC efficiency is defined by the ratio of the net power output to the heat supplied,

163
$$\eta_{ORC} = \frac{W_t \cdot \varepsilon_g - W_p}{Q} \quad (6)$$

164 For the solar ORC system with DVG, the thermal efficiency of a solar collector is generally
 165 expressed by

166
$$\eta_{cl}(T) = \eta_{cl,0} - \frac{A}{G}(T - T_a) - \frac{B}{G}(T - T_a)^2 \quad (7)$$

167 The solar collector modules available on the market have effective area between 1.0 m² and 2.0 m²
 168 . Their thermal efficiency can be calculated by Eq. (7). In a solar ORC system tens or hundreds
 169 square meters of collectors are usually required, the temperature difference between neighboring
 170 collectors is supposed to be small. To calculate the overall collector efficiency it is reasonable to
 171 make the assumption that the average operating temperature of the collector changes
 172 continuously from one module to another. The working fluid in the collector is mostly at liquid-
 173 phase and binary phase. For the binary phase region, the temperature is constant and it is easy to
 174 calculate the collector efficiency. For the liquid phase region, in order to reach an outlet
 175 temperature T_o of the fluid with an inlet temperature T_i , the required collector area is obtained by

176
$$S_l = \int_{T_i}^{T_o} \frac{mC_p(T)}{\eta_{cl}(T)G} dT \quad (8)$$

177 The heat capacity of a fluid at liquid state can be expressed by a first order approximation

$$178 \quad C_p(T) = C_{p,0} + \alpha(T - T_0) \quad (9)$$

179 With $c_1 = A/G$, $c_2 = B/G$, the collector area according to Eqs. (7), (8) and (9) is calculated by

$$180 \quad S_l = \frac{m}{c_2 G (\theta_2 - \theta_1)} \left[(C_{p,a} + \alpha \theta_1) \ln \frac{T_o - T_a - \theta_1}{T_i - T_a - \theta_1} + (C_{p,a} + \alpha \theta_2) \ln \frac{\theta_2 - T_i + T_a}{\theta_2 - T_o + T_a} \right] \quad (10)$$

181 θ_1 and θ_2 are the arithmetical solutions of Eq. (11) ($\theta_1 < 0$, $\theta_2 > 0$).

$$182 \quad \eta_{cl,o} - c_1 \theta - c_2 \theta^2 = 0 \quad (11)$$

$$183 \quad C_{p,a} = C_{p,0} + \alpha(T_a - T_0) \quad (12)$$

184 The thermal efficiency of the collectors with liquid is calculated by

$$185 \quad \eta_{cl,l} = \frac{m(h_{l,o} - h_{l,i})}{GS_l} \quad (13)$$

186 The thermal efficiency of the collectors with working fluid in the binary-phase and the overall
187 collector system are calculated by Eq. (14) and Eq. (15), respectively,

$$188 \quad \eta_{cl,b} = \frac{m(h_{b,o} - h_{b,i})}{GS_b} \quad (14)$$

$$189 \quad \eta_{cl} = \frac{m(h_{b,o} - h_{l,i})}{G(S_l + S_b)} \quad (15)$$

190 The overall electricity efficiency of the solar ORC is expressed by

$$191 \quad \eta_{sys} = \eta_{ORC} \cdot \eta_{cl} \quad (16)$$

192 The relative increment in overall electricity efficiency of solar ORC with DVG over that with
193 HTF is expressed by

$$194 \quad \Delta \eta_{sys} = \frac{\eta_{sys,DVG} - \eta_{sys,HTF}}{\eta_{sys,HTF}} \quad (17)$$

195 **4. Results and discussion**

196 In this section the influence of working fluid on the system performance is evaluated with
197 respect to the critical temperature. The effects of fluid critical temperature on the ORC efficiency
198 at given evaporation temperature, on optimum evaporation temperature and maximum system
199 efficiency at given solar radiation, on solar energy collection efficiency at given evaporation
200 temperature and solar radiation, and on overall system efficiency at given evaporation
201 temperature and solar radiation, are investigated successively. An efficiency comparison between
202 the solar ORCs with DVG and HTF is conducted.

203 Some assumptions are made in the simulation: Evaporation and condensation processes are
204 isobaric while expansion and pressurization processes are adiabatic. Pump, expander and
205 generator efficiencies are 0.65, 0.75 and 0.85 respectively. The first heat loss coefficient A of
206 solar collectors is $0.82 \text{ Wm}^{-2}\text{C}^{-1}$, the second heat loss coefficient B is $0.0064\text{Wm}^{-2}\text{C}^{-2}$, and the
207 optical efficiency is 0.661. These are common values for commercial medium temperature
208 collectors [37].

209 **4.1. Effect of critical temperature on ORC efficiency at given evaporation temperature**

210 The ORC efficiency variation with the critical temperature of 17 different working fluids is
211 shown in Fig. 3. At a given evaporation temperature, the ORC efficiency generally increases
212 with increment in the critical temperature which is consistent with the previous results by Liu et
213 al. [34] and Aljundi et al. [30]. As this study is limited to subcritical cycle, some fluids of
214 relative low critical temperatures are excluded at higher evaporation temperature (120 and 150
215 °C).

216 It is observed that by increasing evaporation temperature, fluids of higher critical temperature
217 result in more significant increment in ORC efficiency as compared to the lower critical
218 temperature fluids. Therefore, the efficiency difference among the fluids is increased with the

219 increment in evaporation temperature. For instance, the ORC efficiency using benzene
220 overcomes that using butane by 14.36 % at evaporation temperature of 100°C, while the value is
221 31.82 % at the evaporation temperature of 150°C.

222 **4.2. Effect of critical temperature on optimum evaporation temperature and maximum** 223 **thermal efficiency at given solar radiation**

224 Optimum evaporation temperature is a useful parameter in system design. At a given solar
225 radiation, optimum evaporation temperature is the temperature at which maximum solar thermal
226 power efficiency is achieved. For each fluid, the optimum evaporation temperature is a
227 compromise between the efficiencies of solar energy collection and power conversion. The
228 increment in the evaporation temperature will lead to higher power conversion efficiency but
229 lower collector efficiency. Effect of critical temperature on optimum evaporation temperature at
230 four consecutive levels of radiation (400, 600, 800 and 1000Wm⁻²) of 17 working fluids is shown
231 in Fig. 4.

232 At stronger solar radiation, the optimum evaporation temperature increases with the
233 increment in critical temperature for most working fluids but in case of weaker solar radiation it
234 becomes constant and even a decreasing trend can be found. The reason behind this phenomena
235 is that when the solar radiation decreases, fluids having higher critical temperature show very
236 large decrement in their optimum evaporation temperature as compared to fluids having lower
237 critical temperature. For example, if solar radiation decreases from 1000 to 400 Wm⁻², optimum
238 evaporation temperature of benzene is decreased by 57°C while for R227ea it is decreased by
239 merely 2°C. Notably, when the evaporation temperature gets close to the critical temperature of
240 a fluid, the ORC efficiency may increase very slowly or even decrease with increasing

241 evaporation temperature. This leads to a relatively constant optimum evaporation temperature
242 which is near the critical temperature of the fluid.

243 At solar radiation of 1000 Wm^{-2} , isopentane and R236ea have not shown optimum
244 evaporation temperatures within their critical temperature.

245 The maximum solar thermal power efficiencies of the 17 working fluids are shown in Fig. 5.
246 In general, maximum thermal efficiency at given solar radiation acts as an increasing function of
247 critical temperature.

248 The difference of maximum thermal power efficiency among the working fluids decreases
249 with the decrement in solar radiation. For instance, at 1000 Wm^{-2} relative increment in maximum
250 thermal efficiency of benzene over R227ea is 63.87 %, while the value decreases to 33.55 % at
251 solar radiation of 400 Wm^{-2} . The reason is as the solar radiation gets weaker, fluids having
252 higher critical temperature show larger decrement in maximum thermal power efficiency in
253 comparison with fluids having lower critical temperature.

254 The variation in maximum thermal efficiency has not shown same trend as shown by ORC
255 efficiency. At the solar radiation of 400 Wm^{-2} , the optimum evaporation temperatures of all
256 fluids under consideration are around $105 \text{ }^\circ\text{C}$. At this evaporation temperature, the relative
257 increment in maximum solar thermal power efficiency of benzene over RC318 is 27.69%, while
258 the relative increment in ORC efficiency of benzene over RC318 is 40.53%. The inconsistent
259 variations of maximum solar thermal power efficiency and ORC efficiency indicate that the
260 influence of working fluids on collector efficiency cannot be neglected.

261 **4.3. Effect of critical temperature on collector efficiency at given evaporation temperature**
262 **and solar radiation**

263 In a conventional solar ORC system with HTF, the collector efficiency depends on the heat
264 transfer from the HTF to the organic fluid. For most collectors the efficiency drops faster at
265 higher operation temperature. A large mass flow rate of HTF is generally preferable to reduce the
266 peak temperature in the collectors and to achieve a high overall heat collection efficiency [22].
267 Given information on the heat transfer (e.g. the pinch point temperature of 10°C, ratio of mass
268 flow rates of HTF and organic fluid of 10), the effect of working fluid on collector efficiency
269 will be not significant as shown in Fig. 6. The difference of collector efficiencies among the
270 working fluids is very small. However, in the solar ORC system with DVG, effect of critical
271 temperature on collector efficiency is much more appreciable. Some results are shown in Figs. 7,
272 8 and 9. Collector efficiency is calculated at three levels of evaporation temperature as well as on
273 four stages of solar radiation. On the whole, at given evaporation temperature and solar radiation,
274 collector efficiency is a decreasing function of critical temperature. It is concluded that in case of
275 DVG system, critical temperature strongly affects collector efficiency which will further affect
276 the electricity efficiency of the system.

277 Behind this phenomenon, it is found that fluids of higher critical temperature have usually
278 higher value of enthalpy ratio (ratio of the latent of vaporization to the sensible heat) as shown in
279 Fig. 10. The sensible heat is the amount of heat required to raise the temperature of working fluid
280 from subcooled liquid to saturated liquid state, while latent heat of vaporization is the heat
281 required to change phase of the fluid from saturated liquid to saturated vapor phase. Higher
282 enthalpy ratio elevates the average operating temperature of the collectors which results in
283 decrement in collector efficiency.

284 At a given evaporation temperature, difference of collector efficiencies among the working
285 fluids increases with the decrement in solar radiation. This is because fluids having higher

286 critical temperature show larger decrement in their collector efficiency. For example, at
287 evaporation temperature of 100°C when solar radiation changes from 1000 to 400Wm⁻², the
288 collector efficiency using benzene is decreased by 12.17 % while for R227ea it is decreased by
289 9.1%. So, the influence of critical temperature on collector efficiency becomes more significant
290 at weaker solar radiation.

291 Furthermore, the influence of critical temperature on collector efficiency becomes more
292 evident at higher evaporation temperature. At the evaporation temperature of 150°C, when the
293 solar radiation changes from 1000 to 400 Wm⁻², the collector efficiency using benzene is
294 decreased by 27.18 %.

295 **4.4. Effect of critical temperature on thermal efficiency of the system at given evaporation** 296 **temperature and solar radiation**

297 Effect of critical temperature on solar thermal power efficiency is shown in Figs. 11, 12 and 13.
298 In general, thermal efficiency of the system is observed to be an increasing function of critical
299 temperature. However, it becomes constant and even a decreasing trend could be found at weak
300 solar radiation and high evaporation temperature. As shown in Fig. 13, the system thermal
301 efficiency is decreased with the increment in critical temperature at evaporation temperature of
302 150°C and solar radiation of 400 Wm⁻². At weaker solar radiation and higher evaporation
303 temperature effect of critical temperature on collector efficiency gets more evident. Therefore,
304 system thermal efficiency starts decreasing with the critical temperature on these conditions.

305 At a given evaporation temperature, difference of system thermal efficiencies among the
306 working fluids decreases with the decrement in solar radiation. That is because fluids having
307 higher critical temperature show larger decrement in the system thermal efficiency as compared
308 to lower critical temperature fluids. At evaporation temperature of 100°C, decrement in system

309 thermal efficiency of benzene is 1.86% if solar radiation decreases from 1000 to 400 Wm⁻²,
310 while for R227ea it is only 1.22%.

311 **4.5. Efficiency comparison between solar ORCs with DVG and HTF**

312 The proposed system is simpler than conventional solar ORCs due to the elimination of HTF.
313 The irreversibility in the collectors can be reduced by the high coefficient of phase-change heat
314 transfer. Besides, the solar ORC with DVG is more advantageous in terms of overall electricity
315 efficiency, as shown in Table 2. The evaporation temperature is 120 °C. The solar radiation
316 ranges from 400 to 1000 W/m². The pinch point temperature difference between HTF and
317 organic fluid is 10 °C. The efficiency superiority of solar ORC with DVG is highly appreciable
318 under low solar radiation. The relative increment in efficiency ($\Delta\eta_{sys}$) varies from about 8% to
319 50%, and fluids of lower critical temperature generally offer larger $\Delta\eta_{sys}$.

320 **4.6 Suitable working fluids for the solar ORC with DVG**

321 Thermodynamic efficiency is just one aspect of fluid for the solar ORC application. It is
322 necessary to take into account other issues including toxicity, flammability, cost, availability,
323 ODP and GWP [2]. The selection of working fluid in the proposed system is more crucial than
324 that for solar ORCs with HTF. In light of the system characteristics, there are some criteria the
325 working fluid should meet.

326 (1) Dry or isentropic fluid. At the present of a dry or isentropic fluid, optimum ORC
327 performance can be achieved when fluid operates along the saturation vapor curve without being
328 superheated [38-43]. On the other hand, wet fluids are not favorable in the ORCs. They are not
329 desirable for the solar ORC system with DVG owing to the need of superheat at the inlet of the
330 turbine to avoid droplets during expansion process [44]. This will lead to inefficient solar energy
331 collection regarding the low conductivity of superheated vapor. For example, the conductivity of

332 R134a at 150 °C and 2.0MPa (superheat) is only $0.025\text{Wm}^{-1}\text{K}^{-1}$. Moreover, it is not easy to
333 guarantee a superheat state of fluid under fluctuating solar radiation. The fluid storage tank with
334 PCM is unable to function as a superheater. The system control strategy is complicated in order
335 to prevent part load operation of the turbine.

336 (2) Moderate operation pressure. Compared with ORCs for utilization of industrial waste
337 heat, geothermal energy and biomass energy, solar ORC with DVG is more susceptible to the
338 operating pressure. The collectors and storage unit are expected to play a prominent role in the
339 cost-effectiveness of the system. According to Fig.2, higher operating pressure leads to stricter
340 technical requirement in the collectors and storage tank. Thicker pipe and tank are needed and
341 the cost is increased. For the sake of low cost, fluids having operating pressure less than 2 MPa
342 are preferred. 2 MPa is a pressure that many commercial solar collectors can tolerate [45].

343 (3) Proper critical temperature. Supercritical cycle is not suitable for the solar ORC system
344 with DVG because, in practical operation, it is difficult to control the pressure and temperature
345 of fluid leaving the collectors. The expander can also suffer from off-design operation.
346 Conversely, subcritical cycle can offer constant temperature and pressure in the vaporization
347 process. By employing an inner-type heat storage unit it is much easier to maintain a steady state
348 of fluid at the inlet of the expander, as illustrated in Section 2. To obtain an acceptable power
349 conversion efficiency, the hot side temperature of the solar ORC system is usually higher than
350 100°C . Therefore, a critical temperature higher than 100°C is required for the fluid.

351 The fluid selection is a cumbersome process since it is difficult for one fluid to meet all the
352 criteria. Among the various fluids, R245fa is commonly investigated and numerous works on its
353 performance can be found in the literature. This fluid has zero ODP and low GWP, and thus is
354 considered to be a promising replacement for chlorine-containing compounds. It is also favorable

355 and recommended in commercial ORC plants [46-48]. However, R123 may be a more suitable
356 fluid than R245fa for the proposed system in the short term regarding its lower operating
357 pressure as well as higher efficiency. For example, the saturation pressure of R123 at 30 °C and
358 120 °C is 0.11 MPa and 1.20 MPa, while it 0.17 MPa and 1.93 MPa for R245fa. R123 is also
359 more beneficial than benzene and cyclohexane in the temperature range below 120 °C, because it
360 is not flammable and avoids inward leakage of air through the collectors more easily when solar
361 radiation is unavailable. The saturation pressure of benzene and cyclohexane at 30 °C is only
362 15.9 kPa and 16.2kPa, and high vacuum can be facilitated especially in cold environment.

363 Under current legislation, R123 will be phased out by 2030 due to an ODP of 0.02.
364 Fortunately, new fluids which exhibit similar thermodynamic performance as R123 but have
365 more environmentally friendly properties, are being developed. HFO1336mzz(Z) (cis-
366 $\text{CF}_3\text{CH}=\text{CHCF}_3$) is a representative. It is a dry fluid, and has zero ODP, very low GWP of 9 and
367 extremely good thermal stability at temperature up to 250°C [49]. Its boiling point is 33.4 °C and
368 the saturation pressure at 120 °C is about 1.1 MPa [50]. It is deemed as drop-in replacement of
369 R245fa and R123, and can be used in ORCs, high temperature heat pumps as well as air
370 conditioning chillers [51]. So far studies on the performance of HFO1336mzz(Z) as an ORC
371 fluid have been based on experimental data from DuPont. Comprehensive information about this
372 fluid is unavailable on the database like REPROP and CoolProp, and its latent heat of
373 vaporization has been predicted by molecular simulations [52]. In view of the operating pressure,
374 toxicity, flammability, ODP and reported power efficiency [50], HFO1336mzz(Z) might be an
375 alternative working fluid for the solar ORC with DVG in the long term.

376 **5. Conclusions**

377 The solar ORC system with DVG is feasible. It has much lower operating temperature and
378 pressure than solar thermal power generation system with DSG. Depending on the working fluid,
379 its operating pressure can be even lower than that of HTF in recent commercial solar thermal
380 power plants. The commercialization of DVG technology in the SAHP application highlights the
381 potential of the proposed system. With the inner-type heat storage unit, the system can generate
382 power smoothly. Compared to conventional solar ORC systems, the proposed system excludes a
383 secondary heat transfer circuit, and the heat transfer irreversibility and negative power for pumps
384 are reduced. The efficiency increment of solar ORC with DVG over that with HTF is very
385 significant. All these advantages make the proposed system suitable for distributed power
386 generation.

387 The effect of working fluids on the system performance is analyzed. Isentropic and dry fluids
388 of moderate critical pressure and proper critical temperature are good match to the DVG.
389 According to the simulation results, the working fluid of solar ORC system with DVG affects
390 significantly the heat collection efficiency. In contrast to the ORC efficiency, the collector
391 efficiency generally decreases with the increment in the fluid critical temperature. At lower solar
392 radiation, the effect of fluid critical temperature on the collector efficiency is more significant
393 while the effect on optimum evaporation temperature is less appreciable.

394 Working fluid selection is crucial to the solar ORC with DVG. The system cost is supposed
395 to be strongly related to the operating pressure. R123 seems preferable to R245fa in light of
396 operating pressure and the efficiency, and can be employed for the DVG system in the short term.
397 The former has an overall electricity efficiency of about 6.1% on the condition of evaporation
398 temperature of 120 °C and solar radiation of 800W/m².

399

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400
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531

532 **Figure Captions**

533 Fig.1. The temperature - heat ($T-Q$) curve for the evaporator

534 Fig. 2. Configuration of the proposed solar ORC system

535 Fig. 3. Influence of critical temperature of working fluid on ORC efficiency

536 Fig. 4. Influence of critical temperature of working fluid on optimum evaporation temperature

537 Fig. 5. Influence of critical temperature of working fluid on maximum thermal efficiency

538 Fig. 6. Influence of critical temperature of working fluid on collector efficiency at evaporation

539 temperature of 120 °C for solar ORC system with HTF

540 Fig. 7. Influence of critical temperature of working fluid on on collector efficiency at evaporation

541 temperature of 100 °C

542 Fig. 8. Influence of critical temperature of working fluid on collector efficiency at evaporation

543 temperture of 120°C

544 Fig. 9. Influence of critical temperature of working fluid on collector efficiency at evaporation

545 temperture of 150°C

546 Fig.10. Influence of critical temperature of working fluid on enthalpy ratio at evaporation

547 temperture of 100,120 and 150°C

548 Fig. 11. Influence of critical temperature of working fluid on system thermal efficiency at

549 evaporation temperature of 100°C

550 Fig. 12. Influence of critical temperature of working fluid on system thermal efficiency at

551 evaporation temperature of 120°C

552 Fig. 13. Influence of critical temperature of working fluid on system thermal efficiency at

553 evaporation temperature of 150°C

554 **Table caption**

555 Table 1 Working fluid properties

556 Table 2 Relative increment in overall electricity efficiency of solar ORC with DVG

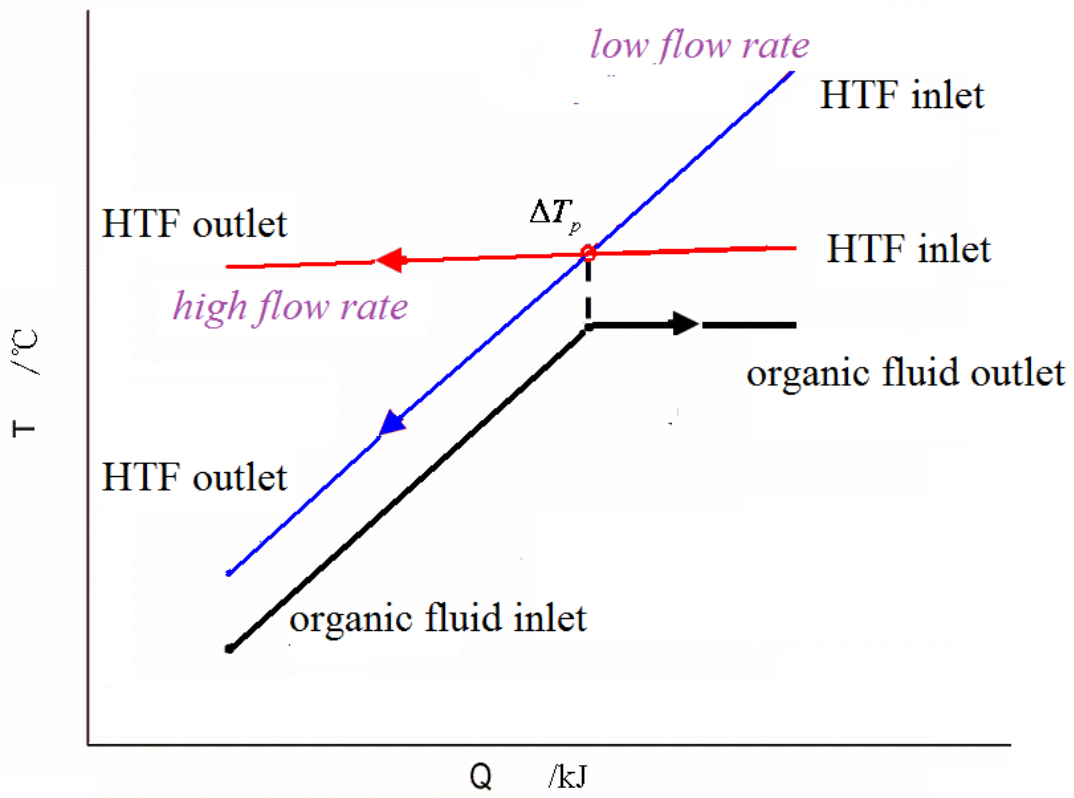
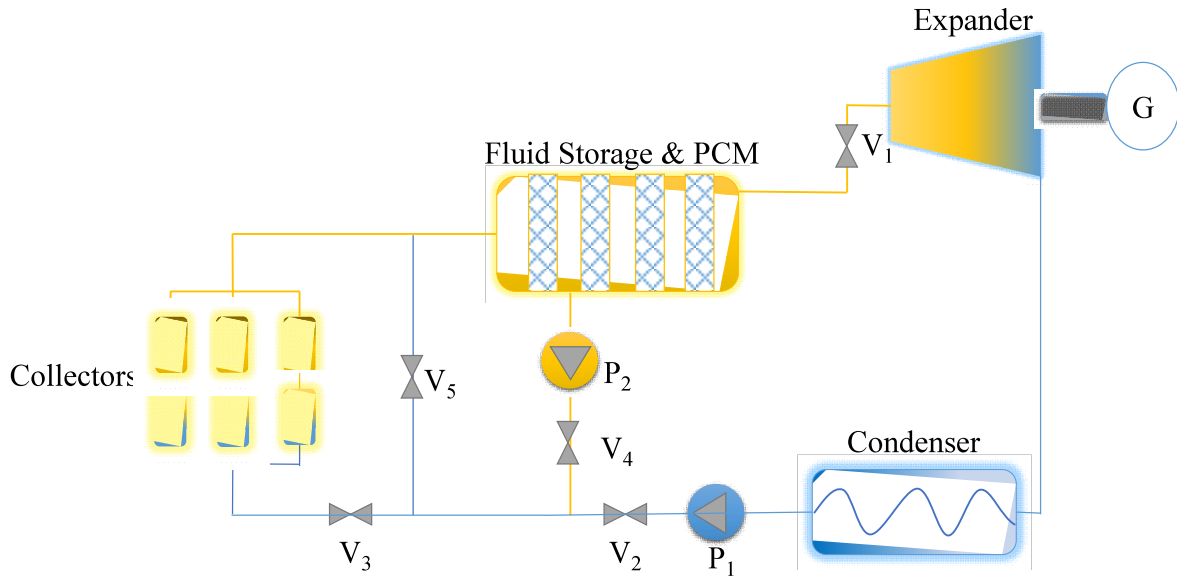
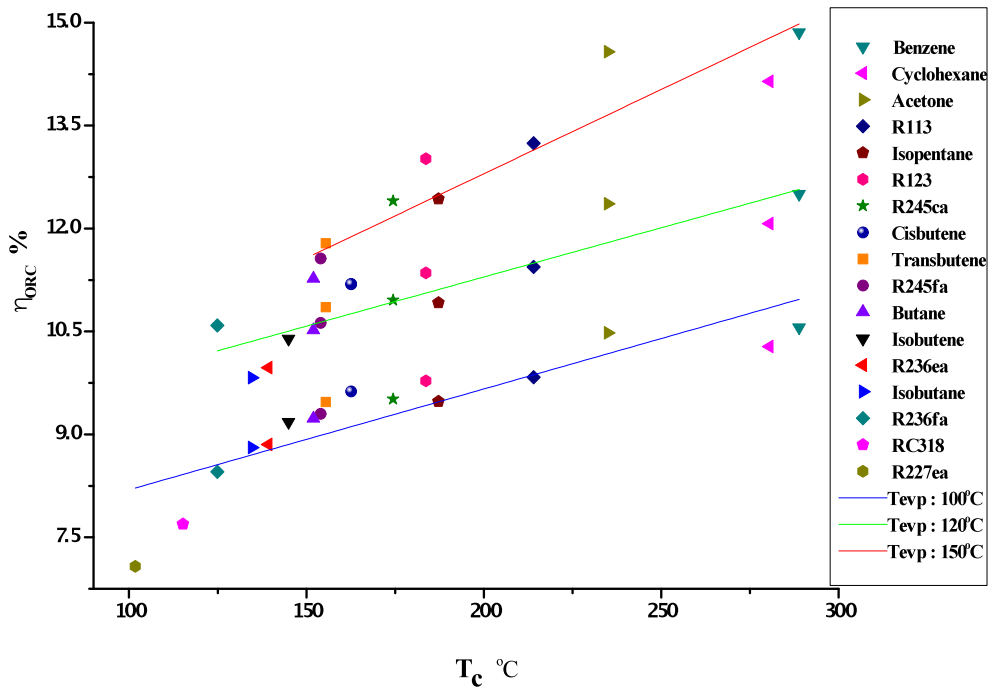


Fig.1. The temperature - heat ($T-Q$) curve for the evaporator [22]



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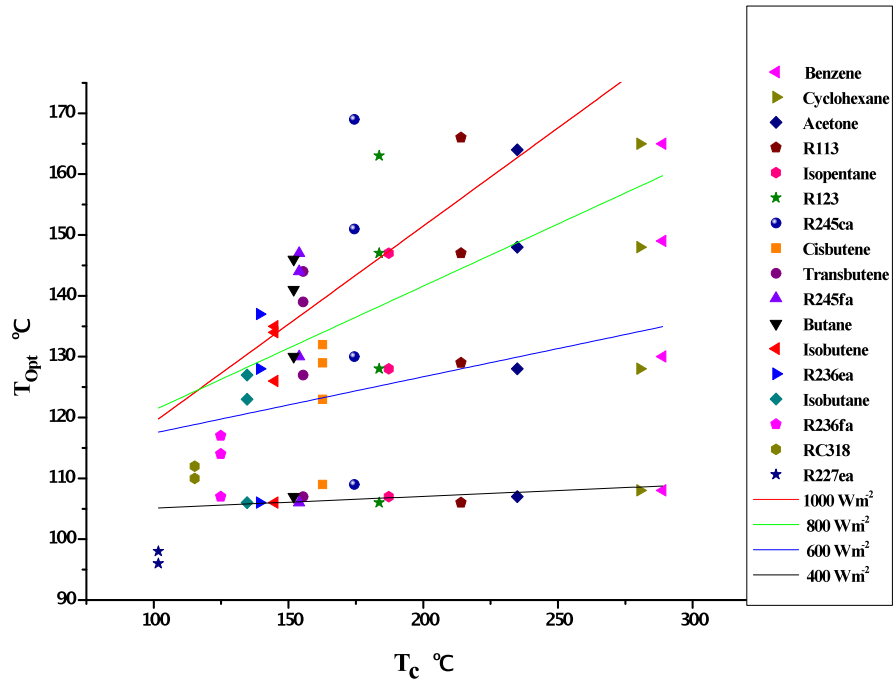
Fig. 2. Configuration of the proposed solar ORC system



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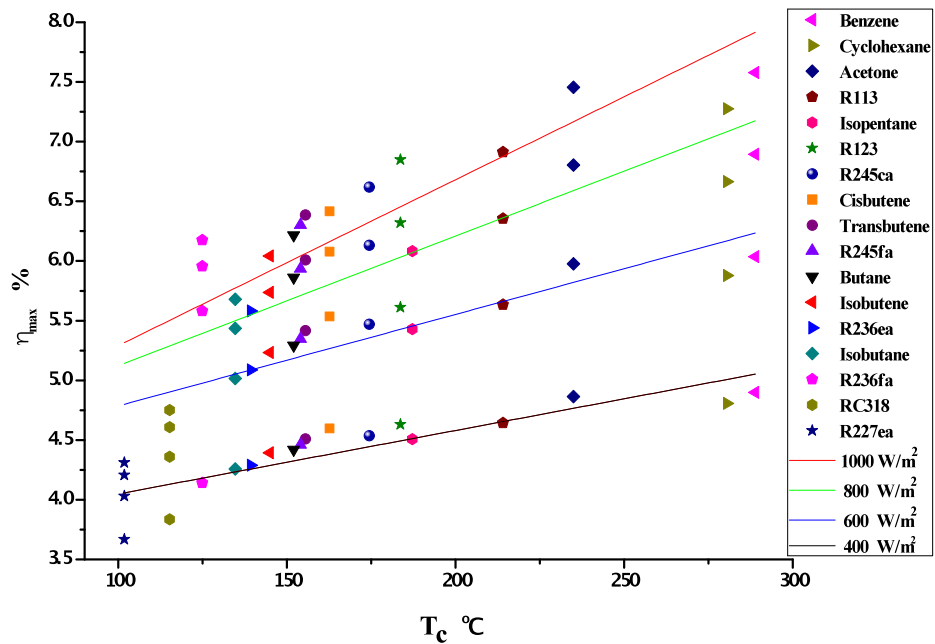
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Fig. 3. Influence of critical temperature of working fluid on ORC efficiency



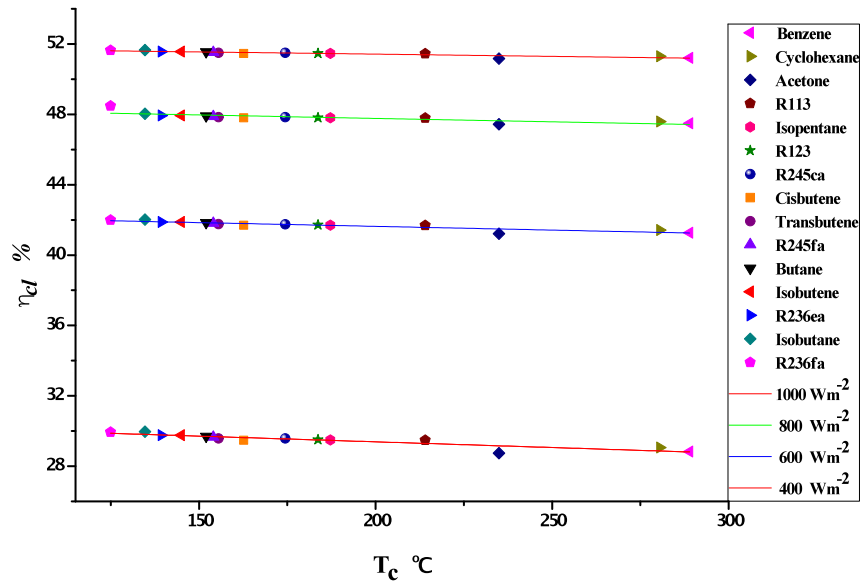
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565 Fig. 4. Influence of critical temperature of working fluid on optimum evaporation temperature



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567 Fig. 5. Influence of critical temperature of working fluid on maximum thermal efficiency

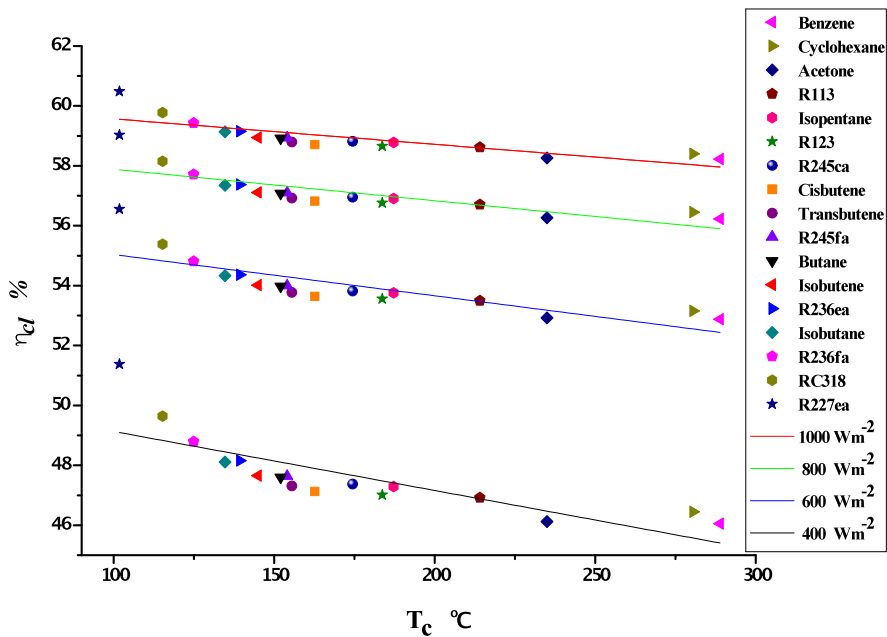


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569 Fig. 6. Influence of critical temperature of working fluid on collector efficiency at evaporation

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temperature of 120°C for solar ORC system with HTF

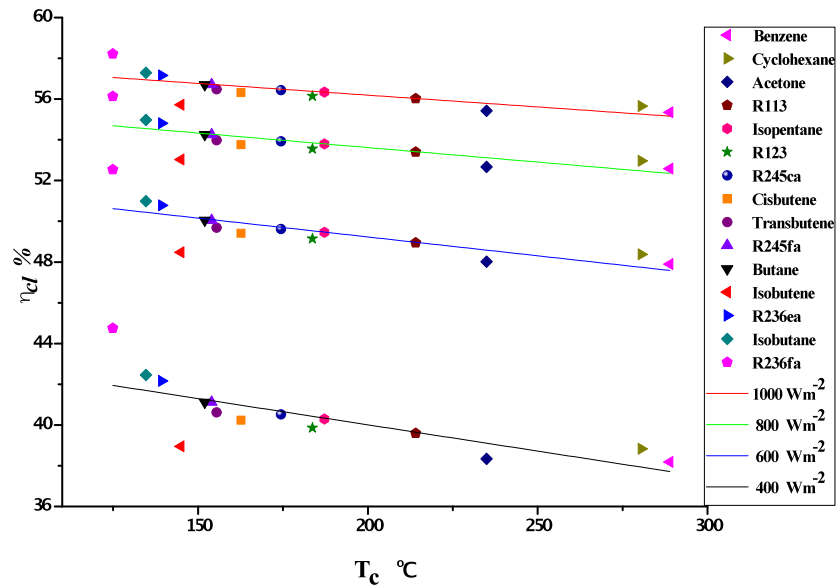


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572 Fig. 7. Influence of critical temperature of working fluid on on collector efficiency at evaporation

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temperature of 100°C

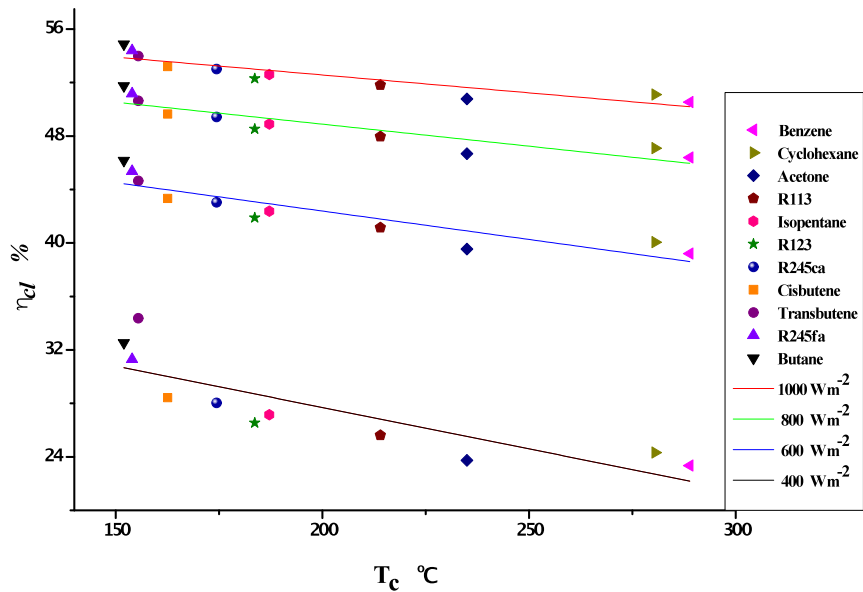


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575 Fig. 8. Influence of critical temperature of working fluid on collector efficiency at evaporation

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temperature of 120°C

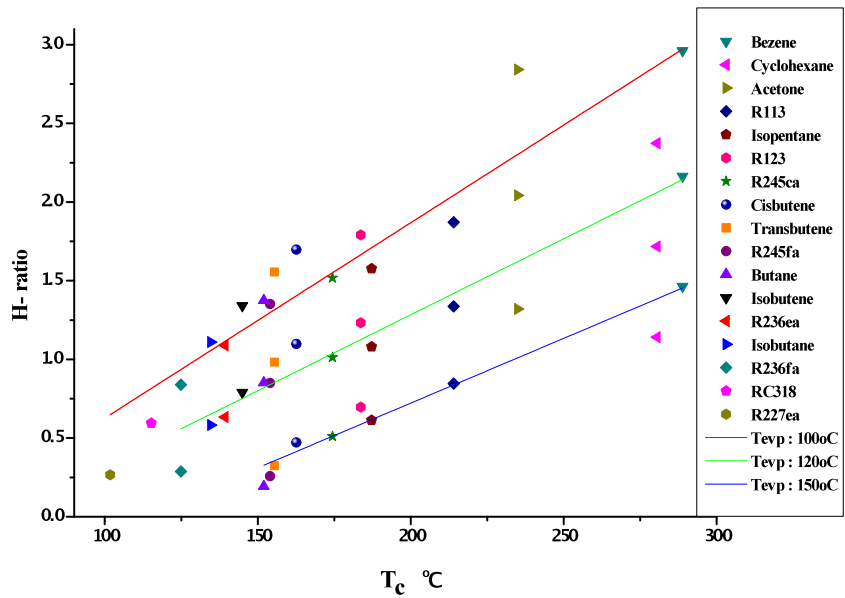


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578 Fig. 9. Influence of critical temperature of working fluid on collector efficiency at evaporation

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temperature of 150°C

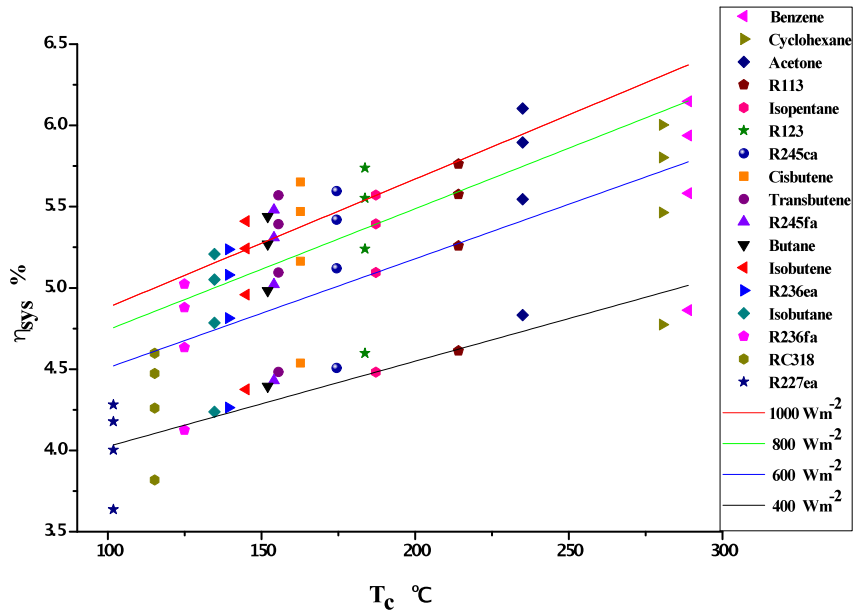


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581 Fig. 10. Influence of critical temperature of working fluid on enthalpy ratio at evaporation

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temperature of 100,120 and 150°C

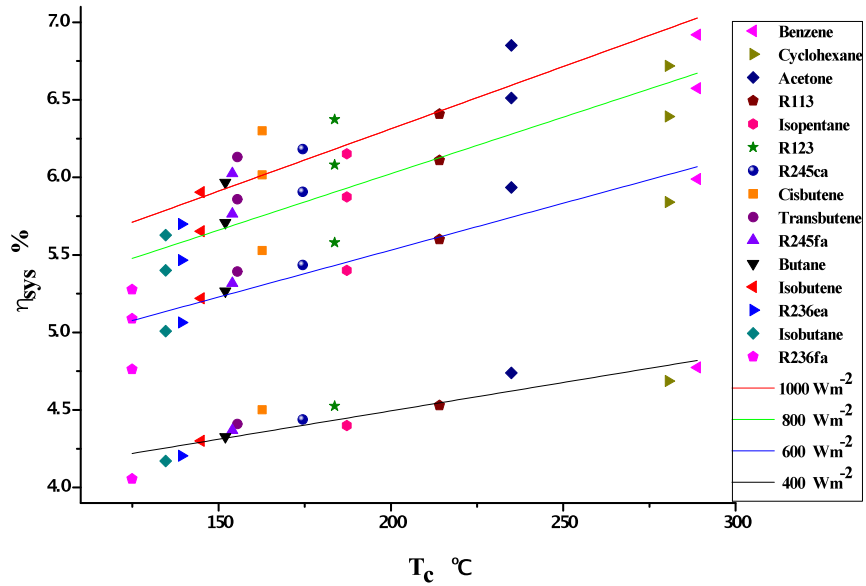


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584 Fig. 11. Influence of critical temperature of working fluid on system thermal efficiency at

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evaporation temperature of 100°C



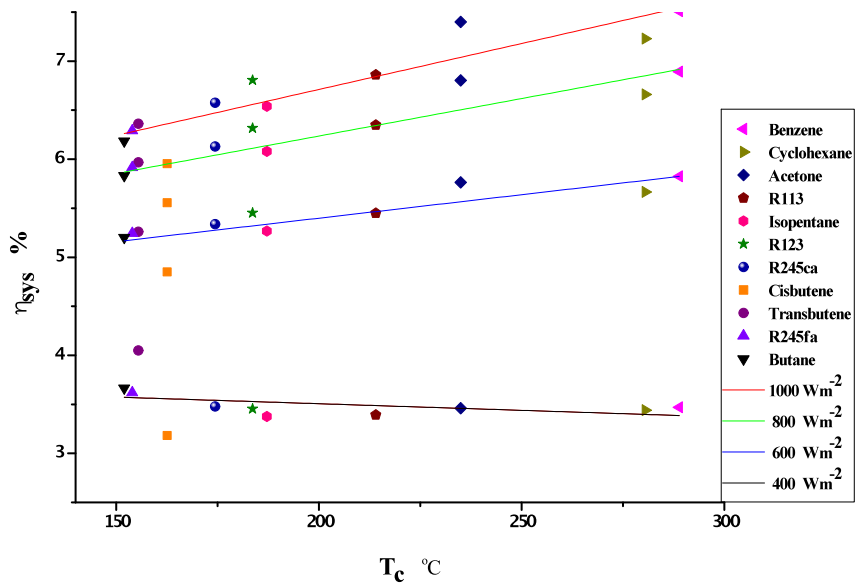
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Fig. 12. Influence of critical temperature of working fluid on system thermal efficiency at

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evaporation temperature of 120°C



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Fig. 13. Influence of critical temperature of working fluid on system thermal efficiency at

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evaporation temperature of 150°C

Table 1 Working fluid properties

Working fluid	Critical temperature °C	Critical pressure Mpa	Liquid thermal conductivity at 100°C (mW/m-K)	Semi empirical ODP	Net GWP	Toxicity	Flammability
Benzene	288.9	4.894	-	-	-	high	high
Cyclohexane	280.49	4.075	106.73	-	-	high	high
Acetone	234.95	4.7	-	-	-	low	high
R113	214.06	3.392	53.848	1.0	6130	low	non
Isopentane	187.2	3.378	83.018	0	4± 2	low	extremely
R123	183.68	3.6618	58.190	0.02	77	high	non
R245ca	174.42	3.925	76.127	0	693	-	-
Cis-butene	162.6	4.225	82.893	-	-	non	extremely
Trans-butene	155.46	4.027	81.357	-	-	-	extremely
R245fa	154.01	3.651	64.289	0	1030	low	non
Butane	151.98	3.796	78.234	0	4	low	extremely
Isobutene	144.94	4.009	76.945	0	3	non	extremely
R236ea	139.29	3.502	55.146	0	1370	-	-
Isobutane	134.66	3.629	66.572	0	3	low	extremely
R236fa	124.92	3.2	51.889	0	9810	low	non
R-C318	115.23	2.777	44.883	0	10300	low	non
R227ea	101.75	2.925	48.251	0	3220	low	non

Table 2 Relative increment in overall electricity efficiency of solar ORC with DVG, unit: %

Working fluid	Solar radiation			
	400 W/m ²	600 W/m ²	800 W/m ²	1000 W/m ²
Benzene	32.47	16.03	10.53	8.17
Cyclohexane	33.38	16.92	11.21	8.45
Acetone	33.44	16.42	10.86	8.27
R113	34.19	17.38	11.76	8.82
Isopentane	36.63	18.46	12.27	9.52
R123	35.11	17.86	11.97	9.11
R245ca	37.34	18.76	12.69	9.59
Cis-butene	36.40	18.41	12.38	9.40
Trans-butene	37.42	19.03	12.63	9.69
R245fa	38.97	19.75	13.27	10.08
Butane	39.04	19.87	13.21	10.08
Isobutene	31.00	15.68	10.62	8.11
R236ea	41.69	21.25	14.32	10.97
Isobutane	42.05	21.20	14.49	10.89
R236fa	49.63	25.08	15.77	12.76

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Nomenclature (in the sequence of first character of word)
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606 *Symbols*

607	A	Area, m ²
608	c_p	Specific heat, J / kg/°C
609	h	Enthalpy, J / kg
610	m	Working fluid mass flow rate, kg /s
611	Q	Heat transferred, J
612	s	Surface area, m ²
613	T	Temperature, °C
614	w	Work done, J

615 *Abbreviations*

616	G	Generator
617	P	Pump
618	V	Valve
619	CHP	Combined heat and power
620	CPC	Compound parabolic concentrator
621	CSP	Concentrated solar power
622	DSG	Direct steam generation
623	DVG	Direct vapor generation
624	ETC	Evacuated tube collector
625	FPC	Flat plate collector
626	GWP	Global Warming Potential
627	HTF	Heat transfer fluid
628	ODP	Ozone Depletion Potential

629	ORC	Organic Rankine Cycle
630	PCM	Phase change material
631	PTC	Parabolic trough concentrator
632	<i>Subscript</i>	
633	<i>b</i>	Binary
634	<i>c</i>	Critical
635	<i>cl</i>	Collector
636	<i>evp</i>	Evaporation
637	<i>g</i>	Generator
638	<i>i</i>	Inlet
639	<i>l</i>	Liquid
640	<i>max</i>	Maximum
641	<i>o</i>	Outlet
642	<i>Opt</i>	Optimum
643	<i>ORC</i>	Organic Rankine Cycle
644	<i>os</i>	Ideal thermodynamic process
645	<i>p</i>	Pump
646	<i>pp</i>	Pinch point
647	<i>Sys</i>	System
648	<i>t</i>	Expander
649	<i>0</i>	Reference state
650	Greek Symbols	
651	ε	Mechanical efficiency

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Δ	Change
η	Thermal Efficiency
α	Heat capacity coefficient, J / °C
θ	Arithmetic solution, °C