



Research Article

# ***N*-Pentane – Limonene Mixtures as Working Fluids for Organic Rankine Cycles**

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## **Abstract**

Mixtures of the orange-peel diterpene limonene with the fossil hydrocarbons pentane or isopentane were studied as potential working fluids for organic Rankine cycles. Evaporation rates of the mixtures at 22 °C and 87 kPa vary linearly with mass fraction of the alkanes in the liquid phase. The enthalpies of vaporisation of the mixtures also vary linearly with composition. When considered under the operation conditions of a binary geothermal plant in Costa Rica (pentane, 26% Carnot efficiency), mixtures with 20% content of limonene as ORC fluids show calculated overall Carnot efficiencies of 22% (pentane) and 24% (isopentane), a result to be used as benchmark for further thermal-efficiency study. The estimated flash points of the 20% limonene mixtures are ~30 °C higher than for the pure hydrocarbons.

**Keywords:** Organic Rankine cycles, multicomponent working fluids, limonene, pentane, isopentane.

## **Introduction**

Operation of binary-cycle power plants depends on different factors such as the chemical and physical features of the geothermal fluid used in the primary energy-conversion stage, nature of the working fluid

in the secondary stage, equipment, and local environmental features of the plant site.

The selection of the working fluid is of utmost importance in designing an organic Rankine cycle (ORC). Fluid properties such as thermodynamic, chemical stability, safety

and environmental aspects must be considered.

The use of zeotropic mixtures rather than single component working fluids has long been considered, mainly from a thermodynamic point of view (Iqbal, *et al.* 1976, Iqbal and Starling 1976, Angelino and Colonna di Paliano 1998, Wang, *et al.* 2010, Aghahosseini and Dincer 2013, Weith, *et al.* 2014), but also from the stand point of thermo-economics (Calm and Hourahan 2011, Heberle and Brüggemann 2016, Sarkar 2016, Astolfi *et al.* 2017).

ORC rigs are closed loops, but nevertheless daily losses of the organic fluid occur. For example, Moya and DiPippo (2007) have reported that 29 kg of *n*-pentane ( $n\text{-C}_5\text{H}_{12}$ ) are lost to the environment daily, in the Unit 5 bottoming binary plant at Miravalles geothermal field in north-western Costa Rica. One thought of identifying a renewable source for an organic liquid that would offer trade-offs between thermodynamic performance and environmental suitability, when forming part of zeotropic  $n\text{-C}_5\text{H}_{12}$  – “other component” working mixtures that offer a significant eco-friendly benefit.

Limonene was determined as a possibility, due to the local production of orange essential oil from which the diterpene limonene could be isolated on an industrial basis. Besides potential new value chains, it is expected that the use of  $n\text{-C}_5\text{H}_{12}$  – limonene

mixtures implies neither significant externalities associated to stratospheric ozone depletion nor contribution to global warming. In ecological eventualities such as massive spills, this renewable substance is readily biodegradable (41% – 98% degradation by biochemical oxygen demand in 14 days) under aerobic conditions in a standard test (Filipsson, Bard and Karlsson, 1998).

Modelling the performance of the working fluid mixtures in a certain setup can certainly give answers to technical scenarios, but we present here simple laboratory evaluations useful to carry out, prior to extensive computer modelling about mixed ORC working fluids.

### Statement of the Proposal

It is important to have data that allow numerical estimations of condensation temperatures of gas-phase mixtures, to intuit whether at the outlet of a turbine, the fluid may behave as *dry*, *isentropic* or *wet* because the first two conditions pose a minimum problem in preventing erosion and damage of turbine blades, due to liquid droplet impingement in the blades during expansion.

A model calculation can be carried out by assuming the mixed liquids obey Trouton’s rule (entropy of vaporisation,  $\Delta_{\text{vap}}S \sim 90 \text{ J K}^{-1} \text{ mol}^{-1}$ ):

$$\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T_{\text{boil}}} \quad (1)$$

The value of enthalpy of vaporisation ( $\Delta_{\text{vap}}H$ ) can be obtained from the thermal cubic-expansion coefficient ( $\alpha$ ) of the liquid mixtures, through the so-called soft-solid model for liquids (Castellón-Elizondo, *et al.*

2006). For simple molecules, the following relation between  $\alpha$  and  $\Delta_{\text{vap}}H$  holds:

$$\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \alpha = \frac{(4.30 \pm 0.05) \times 10^{-2}}{\Delta_{\text{vap}}H} \quad (2)$$

Acceptable estimations for  $\Delta_{\text{vap}}H$  are obtained in  $\text{kJ mol}^{-1}$ . Once  $T_{\text{boil}}$  is obtained for every mixture, it can be taken as the low

temperature of the heat sink. Thus, Carnot efficiency is calculated as

$$\eta \text{ (Carnot)} = 1 - \frac{T_{boil}}{T_{high}} \quad (3)$$

$\eta$  (Carnot) can be used as benchmark, before extensive thermodynamic model calculations are carried out.

## Materials and Methods

### Materials

*n*-Pentane, isopentane and limonene were obtained from *Sigma-Aldrich*, and used without any further treatment.

### Physical properties of mixtures

$\alpha$  values were determined from the densities of the mixtures ( $\rho$ ) at different temperatures by pycnometry, as described in standard textbooks of experimental analytical or physical chemistry. The best regression linear equations of  $\ln\rho$  vs.  $T$  give  $\alpha = -(\partial\ln\rho/\partial T)_p$ . Measurements were done by

triplicate, and average quantities include standard deviations from the mean.

Rates of evaporation were determined gravimetrically by following mass ( $m$ ) loss of samples contained in open Petri dishes under controlled laboratory conditions at 22 °C and 87 kPa, and in the absence of air currents. The loaded dishes were placed on an analytical balance pan, and the mass losses followed along time. The balance lateral lids were closed, leaving the upper lid open to prevent saturation of the space over the liquid. For mixtures, the time – mass data were conveniently fitted to cubic polynomials, and initial rates of evaporation calculated as:

$$\text{Initial rate of evaporation} = \lim_{t \rightarrow 0} \left( \frac{-dm}{dt} \right) \quad (4)$$

## Results and Discussion

### Volatility considerations

Leakage of organic working fluids poses a steady environmental risk, although substances such as *n*-C<sub>5</sub>H<sub>12</sub> (normal boiling point = 36 °C) or isopentane (*i*-C<sub>5</sub>H<sub>12</sub>, normal boiling point = 26 °C) have relative low environmental effect (global warming potential = 5) (Calm and Hourahan, 2011) and null ozone depletion potential. The

incorporation of limonene (normal boiling point = 176 °C) in the composition of working fluid aims to the reduction of the magnitude of leakage. Thus, the first issue to be considered is the volatility of mixtures at room temperature, say laboratory conditions at 22 °C.

The rate of isothermal evaporation of pure liquids follows zero-order kinetics, and is described at the molecular level by the Hertz-Knudsen equation:

$$\frac{-dn_{liq}/dt}{Area} = \kappa \frac{p_v}{\sqrt{2RTM}} \quad (5)$$

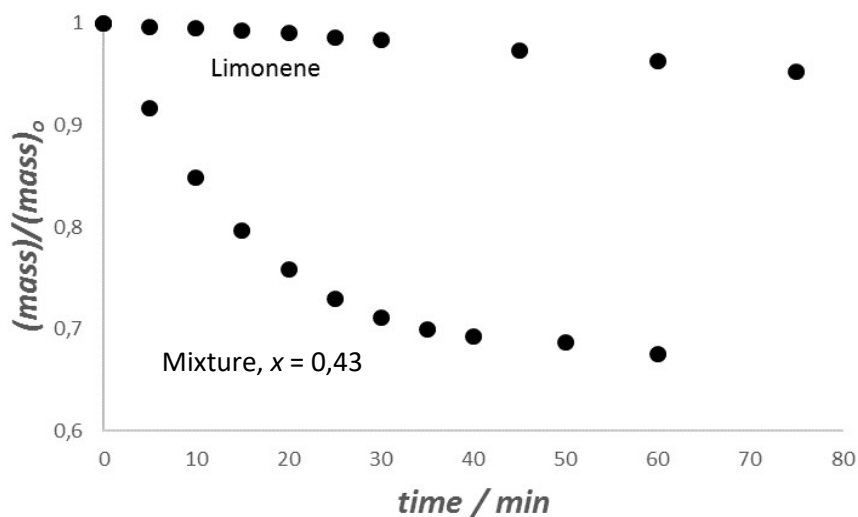
where  $p_v$  is the vapour pressure of the liquid substance,  $M$  its molar mass and the rest of symbols have their usual meaning.  $\kappa$  is the so-called evaporation coefficient, a correction for non-ideal chemical behaviour. Hołyst *et al.* (2015) have challenged the H-K equation on grounds that "... may not appropriately grasp the physical mechanism of evaporation". The authors propose that a very small difference between the vapour

pressure and the liquid pressure is the most probable driving force for evaporation of liquids. Their model implies that the pressure difference equals to the momentum flux of the leaving molecules (momentum associated to the molecules leaving the liquid surface whilst the phase change takes place). Nevertheless, their mechanistic proposal is corresponding to the straightforward molecular interpretation of the H-K equation.

Liquid-mixture evaporation deviates from linear kinetics. The rate of evaporation decreases as the less volatile components accumulate in the remaining liquid phase. Thus, a kinetic parameter such as initial rate of evaporation expressed in mass units such as  $\text{kg s}^{-1} \text{m}^{-2}$  must be used, because the

gaseous phase is composed of the different chemical species and the rate changes during the process.

Figure 1 shows the time profile for the evaporation of  $n\text{-C}_5\text{H}_{12}$  and a mixture with the alkane mass fraction ( $x$ ) of 0,43.

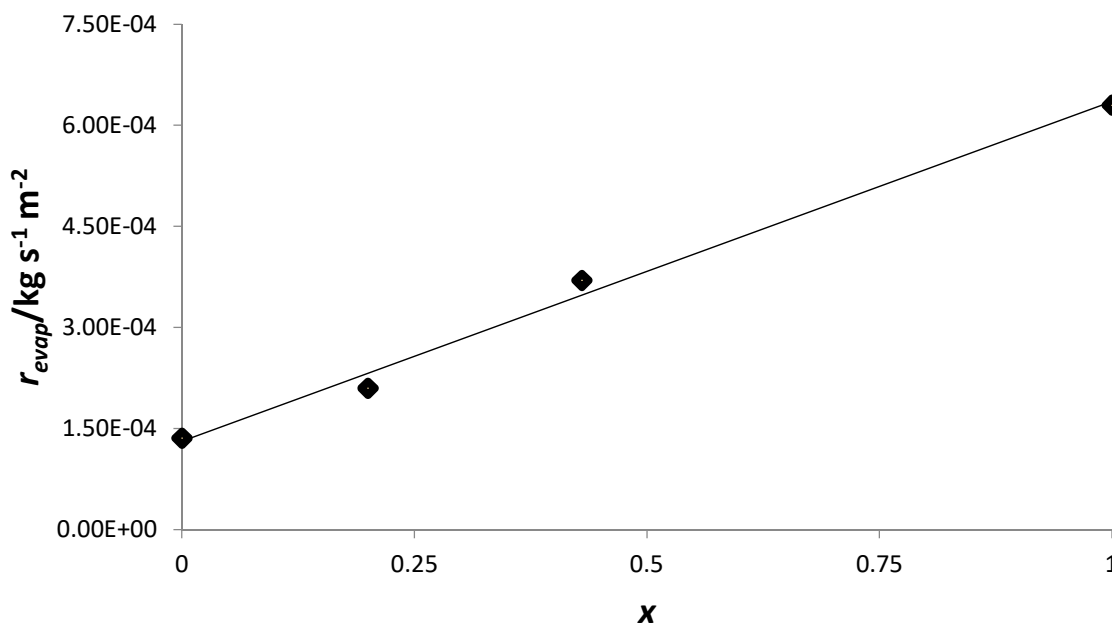


**Figure 1: Time profile for the evaporation of limonene and a 43% (by mass) mixture of  $n\text{-C}_5\text{H}_{12}$  -**

limonene, at 22 °C and 87 kPa

Non-ideal mixtures (Raoult's law not obeyed) may show evaporation rates (vapour pressures) that are faster or slower than either of the pure components. Table 1 and

figure 2 give the evaporation rates of mixtures, obtained by differentiation of the best cubic-fit polynomial for the mixtures studied, as explained above.



**Figure 2: Evaporation rates of  $n\text{-C}_5\text{H}_{12}$  – limonene mixtures as function of mass fraction of the alkane at 20 °C and 87 kPa atmospheric pressure**

**Table 1: Evaporation rates of  $n\text{-C}_5\text{H}_{12}$  – limonene mixtures as function of mass fraction of the linear alkane at 20 °C and 87 kPa atmospheric pressure**

Mass fraction of $n\text{-C}_5\text{H}_{12}$	$10^4 r_{evap} / \text{kg s}^{-1} \text{m}^{-2}$
0	0,136 ± 0.002
0,20	2,1 ± 0.2
0,43	3,7 ± 0.5
1	6,3 ± 0.9

A linear dependence is observed that fits acceptably ( $r_p^2 = 0,99$ ) the regression equation

$$r_{evap} / \text{kg s}^{-1} \text{m}^{-2} = 1,3 \times 10^{-4} + 5,0 \times 10^{-4} \times n\text{-C}_5\text{H}_{12} \text{ mass fraction} \quad (6)$$

Since  $i\text{-C}_5\text{H}_{12}$  is more volatile than the linear hydrocarbon isomer, one thought interesting to measure the evaporation kinetics of  $i\text{-C}_5\text{H}_{12}$  – limonene-rich mixtures, to learn

whether a linear  $x - r_{evap}$  relationship also existed. Table 2 gives the results for eight such mixtures.

**Table 2: Evaporation rates of *i*-C<sub>5</sub>H<sub>12</sub> – limonene mixtures as function of mass fraction of the branched alkane at 22 °C and 87 kPa atmospheric pressure**

Mass fraction of <i>i</i> -C <sub>5</sub> H <sub>12</sub>	10 <sup>4</sup> $r_{evap}$ / kg s <sup>-1</sup> m <sup>-2</sup>
0	0,136 ± 0,002
0,038	0,49 ± 0,06
0,041	1,01 ± 0,06
0,11	2,6 ± 0,3
0,17	3,3 ± 0,1
0,19	4,5 ± 0,2
0,23	4,4 ± 0,4
0,25	6,5 ± 0,2

A linear dependence is also observed that fits acceptably ( $r_p^2 = 0,94$ ) the regression equation

$$r_{evap} / \text{kg s}^{-1} \text{m}^{-2} = -7,8 \times 10^{-6} + 2,3 \times 10^{-3} \times i\text{-C}_5\text{H}_{12} \text{ mass fraction} \quad (7)$$

The empirical result suggests that both mixtures behave next to ideally, despite the differences in molecular size and shape of the components. Non-associated liquids form approximately ideal mixtures if their Hildebrand solubility parameters differ by small amounts (Hildebrand and Scott, 1964). The values for *i*-C<sub>5</sub>H<sub>12</sub>, *n*-C<sub>5</sub>H<sub>12</sub> and limonene are 13,8 (J cm<sup>-3</sup>)<sup>1/2</sup>, 14,4 (J cm<sup>-3</sup>)<sup>1/2</sup> and 16,4 (J cm<sup>-3</sup>)<sup>1/2</sup>, respectively. The values are close enough to render the chemical behaviour as ideal-like. Thus, if the degree of *ideality* of these mixtures is considerable, an approximately linear relationship is expected to exist between vapour pressure and composition (compliance with Raoult's law). Since the evaporation rate varies proportionally to the vapour pressure of the liquid, the linearity observed between  $r_{evap}$  and composition is understood.

According to the regression equations, for a *n*-C<sub>5</sub>H<sub>10</sub> – limonene mixture with 20% of limonene, there is a 16% decrease in the rate of evaporation at 22 °C and 87 kPa, relative to the pure hydrocarbon. For the case of *i*-C<sub>5</sub>H<sub>10</sub>, a 20% decrease in  $r_{evap}$  is to be observed, under the same conditions.

Another advantage of limonene is its flash point ( $Fp$ ) of 48 °C, relative to the same

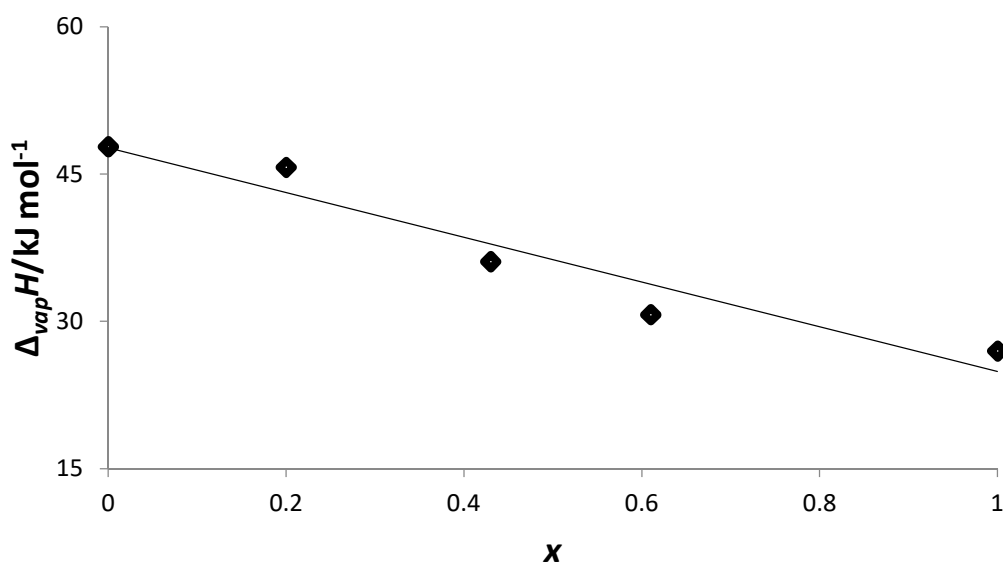
parameter for *n*-C<sub>5</sub>H<sub>12</sub> (-49 °C) and *i*-C<sub>5</sub>H<sub>12</sub> (-51 °C).

By interpolation,  $r_{evap}$  can be calculated as  $5,3 \times 10^{-4}$  kg s<sup>-1</sup> m<sup>-2</sup> for a mixture of *n*-C<sub>5</sub>H<sub>12</sub> containing 20 % limonene. Our experimental value for *n*-butyl acetate at 22 °C and 87 kPa of  $4,89 \times 10^{-5}$  kg s<sup>-1</sup> m<sup>-2</sup> yields  $r_{evap}$  (AcOBu = 1) = 11. This value allows the estimation of  $Fp$  equal to -18 °C (Mata-Segreda, 2017 unpublished results). For the case of an *i*-C<sub>5</sub>H<sub>12</sub> analogous mixture, the expected value is -14 °C. This effect shows a safety advantage for the mixtures, over the use of pure alkanes.

### Thermal Efficiency

Enthalpies of vaporisation can be estimated from the coefficient of thermal cubic expansion of liquids, as indicated in the *Materials and methods* section.

Figure 3 and table 3 give the enthalpies of vaporisation as function of composition for *n*-C<sub>5</sub>H<sub>10</sub> – limonene mixtures, by using the general relationship between  $\alpha$  and  $\Delta_{vap}H$  indicated by equation (2). Table 4 gives the enthalpies of vaporisation for *i*-C<sub>5</sub>H<sub>10</sub> – limonene mixtures.



**Figure 3: Enthalpies of vaporisation of  $n\text{-C}_5\text{H}_{12}$  – limonene mixtures as function of mass fraction of the alkane at 22 °C and 87 kPa atmospheric pressure**

**Table 3: Enthalpies of vaporisation of  $n\text{-C}_5\text{H}_{12}$  – limonene mixtures as function of mass fraction of the alkane at 22 °C and 87 kPa atmospheric pressure**

Mass fraction of $n\text{-C}_5\text{H}_{10}$	$\Delta_{vap}H / \text{kJ mol}^{-1}$
0	$47,8 \pm 0,9$
0,20	$45,7 \pm 0,8$
0,43	$36,1 \pm 0,4$
0,61	$30,7 \pm 0,7$
1	$27 \pm 3$

As expected from the previous kinetic results shown above, this linear regression also gives a relationship between heat of vaporisation

and composition, at an acceptable degree of significance ( $r_p^2 = 0,96$ ):

$$\Delta_{vap}H / \text{kJ mol}^{-1} = 48 - 23 \times n\text{-C}_5\text{H}_{10} \text{ mass fraction} \quad (8)$$

The values for pure  $n\text{-C}_5\text{H}_{12}$  and limonene are somehow deviant from the data obtained from the well-known collection of Chickos and Acree, Jr. (2003):  $26 \text{ kJ mol}^{-1}$  and  $46 \text{ kJ mol}^{-1}$ , respectively but the aim of this

experiment holds from a semiquantitative point of view.

Table 4 gives the corresponding values for the  $i\text{-C}_5\text{H}_{10}$  – limonene mixtures.

**Table 4: Enthalpies of vaporisation of *i*-C<sub>5</sub>H<sub>12</sub> – limonene mixtures as function of mass fraction of the alkane at 22 °C and 87 kPa atmospheric pressure**

Mass fraction of <i>i</i> -C <sub>5</sub> H <sub>10</sub>	$\Delta_{vap}H / \text{kJ mol}^{-1}$
0	47,8 ± 0,9
0,038	48,0 ± 0,6
0,11	45 ± 1
0,17	41,7 ± 0,6
0,19	40,4 ± 0,5
0,23	38,7 ± 0,6
0,25	41,0 ± 0,9
1 (From Chickos and Acree, Jr.)	[24]

The linear relationship is also qualitatively satisfactory ( $r_p^2 = 0,96$ ) for *i*-C<sub>5</sub>H<sub>12</sub>:

$$\Delta_{vap}H / \text{kJ mol}^{-1} = 47 - 23 \times i\text{-C}_5\text{H}_{10} \text{ mass fraction} \quad (9)$$

Taking the Miravalles Unit 5 as model (Moya and DiPippo, 2007), Carnot efficiencies are calculated for 20% limonene mixtures by using the temperature of the residual brine (heat source) as 147 °C, and the lower temperatures are the corresponding boiling point of the mixtures.

If *n*-C<sub>5</sub>H<sub>12</sub> is used at a level of 80% by mass,  $\Delta_{vap}H = 29,6 \text{ kJ mol}^{-1}$ ,  $T_{boil} = 329 \text{ K}$  and  $\eta$  (Carnot) = 0,22. The case for *i*-C<sub>5</sub>H<sub>12</sub> results as  $\Delta_{vap}H = 28,8 \text{ kJ mol}^{-1}$ ,  $T_{boil} = 320 \text{ K}$  and  $\eta$  (Carnot) = 0,24.

The Carnot efficiency of Miravalles Unit 5 is set by the heat-source temperature of 147 °C and the waste heat given off at 38 °C. Thus,  $\eta$  (Carnot) = 0,26, but the actual thermal performance is 15%, due to the internal irreversibilities of the rig. Nevertheless, the use of limonene in mixtures of either of the two pentanes suggests that a complete thermodynamic analysis is valuable to carry out.

### Conclusion

Mixtures of *n*-C<sub>5</sub>H<sub>12</sub> or *i*-C<sub>5</sub>H<sub>12</sub> with up to 20% of limonene by mass may be considered for extensive thermodynamic evaluation as working fluids in ORC operations, because

their volatility implies acceptable Carnot efficiencies as benchmark for further thorough model studies. Environmental and safety aspects of their use and storage are better than for the two pure hydrocarbons.

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