David Tomás Sánchez Martínez
Lourdes García Rodríguez
(coordinadores)

Proceedings of the 7th International Seminar on

ORC Power Systems

Editorial Universidad de Sevilla

Proceedings of the 7th International Seminar on

ORC Power Systems

David Tomás Sánchez Martínez
Lourdes García Rodríguez
(coordinadores)

Proceedings of the 7th International Seminar on

ORC Power Systems

(ORC2023)

4th to 6th
SEPTEMBER
SEVILLE 2023

EUS EDITORIAL UNIVERSIDAD DE SEVILLA

Sevilla, 2024

Colección Actas
Núm.: 91

ISBN 978-84-472-2745-7
DOI: https://dx.doi.org/10.12795/9788447227457

Diseño de cubierta y maquetación: los autores

INDEX OF CONTRIBUTIONS

ORC SEVILLE 2023
7th International Seminar on O.R.C. Power Systems

DOI: https://dx.doi.org/10.12795/9788447227457_54

INFLUENCE OF DOPANT FLUORINATION ON THE HEAT TRANSFER BEHAVIOUR OF CO_2-BASED MIXTURES IN TRANSCRITICAL POWER CYCLES

Michele Doninelli*, Gioele Di Marcoberardino, Costante Mario Invernizzi, Paolo Giulio Iora

Università degli Studi di Brescia, Dipartimento di ingegneria meccanica e industriale, Via Branze 38, 25123 Brescia, Italy

*Corresponding Author: m.doninelli002@unibs.it

ABSTRACT

CO_2-based mixtures are recognized to be an effective working fluid to overcome the limitations of pure sCO_2 cycles for power production in high-temperature environments. Based on the temperature level of the heat source, several dopants, characterized by high critical temperature, can be adopted for blending CO_2. As thermal stability is one of main concern in the working fluids selection, fluorinated compounds have been considered in the recent years as potential solution due to high C-F chemical bond energy. However, the available thermodynamic and transport properties of CO_2 mixtures with fluorinated hydrocarbons are relatively scarce, thus further experimental and theoretical investigations are necessary to properly design the power cycle components.
The CO_2-based mixtures are considered in this work for high-temperature heat recovery to assess the influence of fluorine atoms substitution to hydrogen atoms both on cycle efficiency and heat exchangers size. Benzene (C_6H_6) and two fluorinated derivatives (fluorobenzene C_6H_5F, hexafluorobenzene C_6F_6) are considered here to assess the influence of the presence of fluorine atoms in the molecule of the dopant on the transport properties of the CO_2-mixtures and their heat transfer behaviour. These three halogenated aromatic dopants possess good thermal stability related with the benzene ring structure and could be potentially exploited for medium-high temperature level applications (350-550°C) such as waste heat recovery and concentrated solar power.
Specific models for transport properties implemented in Matlab codes are optimized for the considered mixtures with a novel approach, and the design of the PCHE recuperator has been carried out. It turns out that the use of fluorobenzene as CO_2 dopant in medium-high temperature heat recovery can be a good solution in terms of heat exchangers sizes, efficiency, cost, and environmental characteristics (GWP and toxicity).

1 INTRODUCTION

CO_2-mixtures are recently studied as a valid alternative to sCO_2 as working fluid for closed power cycles to turn the supercritical recompressed cycle into a transcritical cycle even at high ambient temperatures, by enhancing the working fluid critical temperature with the addition of a proper amount of selected dopants.
The main fields of application of CO_2 mixtures are Concentrated Solar Power (CSP), with the aim at reducing the Levelized Cost of Electricity (LCOE), (see for instance the H2020 projects Scarabeus and Desolination), but also waste heat recovery (WHR) applications for the combined heat and power production (Morosini et al., 2023) or electricity and desalinated water production (Michele Doninelli et al., 2023), as well as for trigeneration. The dopant selection to be mixed with CO_2 is a critical aspect to be properly evaluated for the specific application, where the main drivers are the critical temperature and the thermal stability. Since CO_2-based cycles could potentially be competitive in WHR applications where the heat source is higher than 400°C (Astolfi et al., 2017), it is necessary that the dopant overcomes the actual limits of thermal stability of the fluids typically employed in Organic Rankine Cycles. In this scenario, fluorinated dopants such as C_6F_6 (Di Marcoberardino et al., 2022), C_4F_{10} and

C_6F_{14} (Di Marcoberardino et al., 2020) have been proposed, since perfluorocarbons possess good thermal stability thanks to the combination of high energy of the C-F chemical bond and high electronegativity of fluorine atoms.
However, it should be noted that the presence of fluorine atoms has also an impact on the viscosity, thermal conductivity, and density. From previous studies, the viscosity of fluorinated compounds resulted to be considerably higher than their hydrocarbon homologues (Freire et al., 2008), while the thermal conductivity decreases with the number of fluorine atoms (Irving & Jamieson, 1975). Three dopants are here considered to investigate the impact of fluorination on the heat exchangers: benzene (C_6H_6), fluorobenzene (C_6H_5F), hexafluorobenzene (C_6F_6). In particular, fluorobenzene is proposed for the first time as potentially applicable dopant in WHR applications. In fact, the expected thermal stability is high due to the aromatic stability of benzene structure, although reasonably lower than C_6F_6 which was proved to be thermally stable at 550-600°C in Inconel 625 (Di Marcoberardino et al., 2022). Additional advantages of fluorobenzene is a lower cost and global warming potential (GWP) compared to C_6F_6 and a much lower toxicity compared to benzene. In fact, the radiative efficiency (RE) of fluorobenzene is reported to be 0.07 (Hodnebrog et al., 2020), compared to 0.15 of C_6F_6. The medium-high flammability of the three dopants is comparable, but it is a minor drawback in mixtures with high-CO_2 content.
The Friction-Theory model for viscosity (Quiñones-Cisneros et al., 2001) and thermal conductivity (Quiñones-Cisneros et al., 2021) are tuned based on the experimental data of the pure components and used to predict the transport properties of the mixtures for a realistic Printed Circuit Heat Exchanger (PCHE) recuperator design. The objectives of this work are a detailed description of the heat transfer behaviour of the selected CO_2 blends, the influence of fluorination on both cycle efficiency and thermal properties, the introduction of fluorobenzene as interesting CO_2 dopant for WHR applications.

2 FINE-TUNING OF TRANSPORT PROPERTIES OF THE INVESTIGATED BLENDS

334

The dynamic viscosity and thermal conductivity are fluid properties related to momentum and heat transfer and are key properties for the determination of the heat transfer coefficients. The prediction of transport properties of mixtures is difficult due to non-ideal behaviour. Almost all the methods available to estimate the transport properties of dense pure fluids and mixtures are empirical or semi-theoretical (Poling & Prausnitz, 2001).
The generic transport property π is calculated as a sum of a "zero-density" property π_0 and a "residual property" $\Delta\pi$:

$$\pi(T,p) = \pi_0(T) + \Delta\pi(T,p) \quad (1)$$

The zero-density term can be calculated with methods that are derived from the rigorous kinetic theory of gases, whilst almost all the methods available to describe the residual property are empirical or semi-theoretical (Poling & Prausnitz, 2001), with the corresponding-state (CS) based methods being the most applied. The zero-density viscosity and thermal conductivity of the mixture are computed here with the Wilke (Wilke, 1950) and the Wassiljewa-Mason-Saxena (Mason & Saxena, 1959) equations, respectively, with the zero-density properties of the pure components obtained with the Chung model (Chung et al., 1988)(Chung et al., 1984). About the residual term, when the two components in the mixture are very different in size and shape, the CS approach tends to fail since the reference fluid cannot be "conformal" with both the components in the mixture. As highlighted in a previous work (M. Doninelli & Di Marcoberardino, 2023), the transport properties of CO_2 complex mixtures are potentially better described with the use of the relatively recent friction-theory models (Quiñones-Cisneros et al., 2000)(Quiñones-Cisneros et al., 2021), which relies on an equation of state to describe the residual transport property of the mixture. The f-theory models can provide good results for mixtures even if the optimization is carried out only on pure component experimental data: no binary interaction parameters are involved in the model.

2.1 Friction Theory model for viscosity and thermal conductivity

The residual dynamic viscosity of the mixture has been calculated with the viscosity model developed by Quiñones-Cisneros et al. (Quiñones-Cisneros et al., 2001), as in the following quadratic relation:

$$\Delta\eta(T,p) = k_a p_a + k_r p_r + k_{rr} {p_r}^2 \quad (2)$$

where k_a, k_r, k_{rr} are friction factors, obtained with mixing rules, related to the attractive (subscript "a") and repulsive (subscript "r) pressure terms. In the general one-parameter model, the pure-component friction factors are obtained only as function of a critical characteristic viscosity $\eta_{c,i}$:

$$k_{j,i} = \frac{\eta_{c,i}\ \hat{k}_{j,i}}{P_{c,i}} \quad (3)$$

while the reduced coefficient $\hat{k}_{j,i}$ depends only on the EoS selected for the calculation of the attractive (p_a) and repulsive (p_r) pressure terms - see Table 2 of (Quiñones-Cisneros et al., 2001). The critical characteristic viscosity formally represents the viscosity of the fluid at the critical point, but it is in fact the only adjustable parameter of the model, which is based on corresponding states behaviour, and can be tuned on available experimental data once selected the thermodynamic model to obtain attractive and repulsive pressures. Thus, only one parameter has to be regressed based on experimental data available for the pure fluid, which is beneficial especially for fluids with scarce experimental viscosities. A one-parameter model for thermal conductivity is still lacking, so the model presented in (Quiñones-Cisneros et al., 2021) has been used with a second-order truncation:

$$\Delta\lambda = \lambda_c + \phi_{a,1} s_a + \phi_{a,2} {s_a}^2 + \phi_{r,1} s_r + \phi_{r,2} {s_r}^2 \quad (4)$$

where the attractive and repulsive residual entropy of the mixture has been computed with the PR EoS. The friction coefficients $\phi_{j,i}$ and the critical enhancement term λ_c contain nine coefficients (a_i, b_i, A_0, B_0, ϕ_c) that must be regressed for each pure compound on available experimental data in dense conditions (residual term). Then, mixing rules are applied to have mixture's friction coefficients.

335

2.2 Friction Theory models optimization for the fluids of interest

Friction coefficients for thermal conductivity are already available in (Quiñones-Cisneros et al., 2021) for many compounds including CO_2. In this work, the coefficients of benzene, fluorobenzene and hexafluorobenzene are regressed in Matlab environment by using Levenberg-Marquardt algorithm and presented in Table 1. As innovative outcome of this work, a temperature-dependent critical characteristic viscosity is found to best reproduce the experimental data: the simplicity of the one-parameter model has been compensated by a temperature dependence to improve the accuracy. The critical characteristic viscosity of the pure dopant (Eq. 3) has been expressed in the form of the Uyehara and Watson (Uyehara, OA and Watson, 1944) equation with a temperature dependent factor k(T) fitted on experimental data (validity range of the factor [280-700 K]):

$$\eta_c = k(T) \cdot MM^{\frac{1}{2}} \cdot P_c^{\frac{2}{3}} \cdot T_c^{-\frac{1}{6}} \quad (5)$$

This approach has been tested on pure benzene, where the mean percentage error decreases from 5.77% (constant temperature parameter) to 1.94% in comparison with the reference correlation for the viscosity of benzene (Avgeri et al., 2014), in the 320-650 K and 1-200 bar range. In case of hexafluorobenzene and fluorobenzene a substantial improvement is observed too. The expressions for the factor k(T), which best reproduce the critical characteristic viscosity of the three dopants, are reported in Tables 2. The well-known constant value of characteristic critical viscosity for pure CO_2 (376.872 μP) has been used (Quiñones-Cisneros et al., 2001).

Table 1: optimised parameters for f-theory thermal conductivity model.

	Thermal Conductivity Model								
	a_0	a_1	a_2	b_0	b_1	b_2	A_0	B_0	Φ_c
CO_2	0.3868	35.6309	15.9827	3.6295	2.6629	-2.6629	0.2274	0.3120	-0.6579
C_6H_6	-3.2476	2.8255	0.9565	0.2035	2.4728	0	0.0010	0.0022	0.001
C_6H_5F	-4.3332	0.1001	-0.8412	5.5838	1.7321	-1.8845	0.0272	0.2826	-0.05
C_6F_6	0.9287	5.5583	-1.8031	0.0344	0.0022	0	0.0142	0.0018	0.0408

Table 2: optimised k(T) factor for Eq. (5) – viscosity model.

	Viscosity model – k(T) coefficient optimised
C_6H_6	$k(T[K]) = -0.0000000293\ T^3 + 0.0000688326\ T^2 - 0.0526172200\ T + 20.6066312478$
C_6H_5F	$k(T[K]) = -0.0000000216\ T^3 + 0.0000493068\ T^2 - 0.0360406074\ T + 16.2908833076$
C_6F_6	$k(T[K]) = -0.0000001877\ T^3 + 0.0003181158\ T^2 - 0.1770737101\ T + 42.4647664823$

The comparison for thermal conductivity is reported in Figure 1. The liquid field is characterized by high intermolecular interactions, and the comparison shows the capability of the models to describe the departure from ideal gas conditions.

336

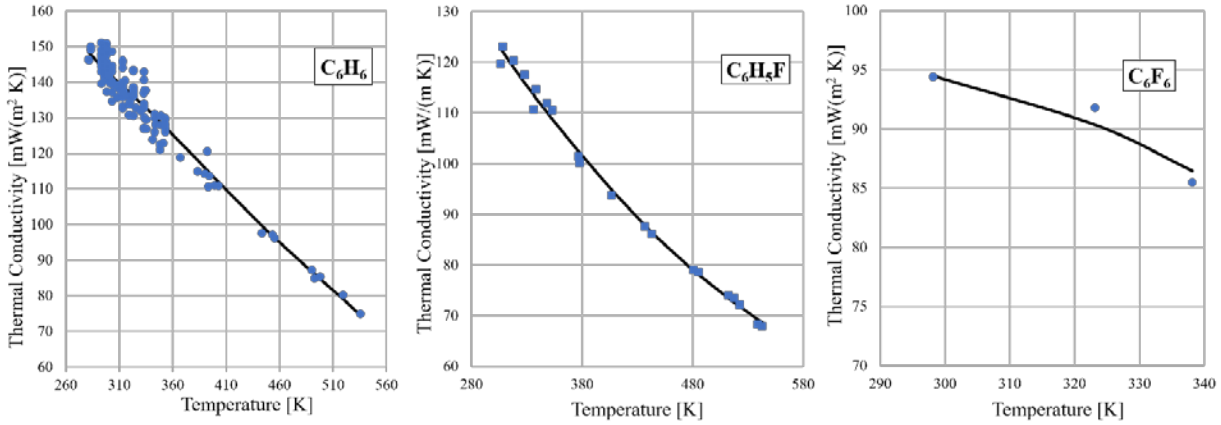

***Figure 1**. Experimental liquid thermal conductivity (dots) vs optimised model (solid lines).*

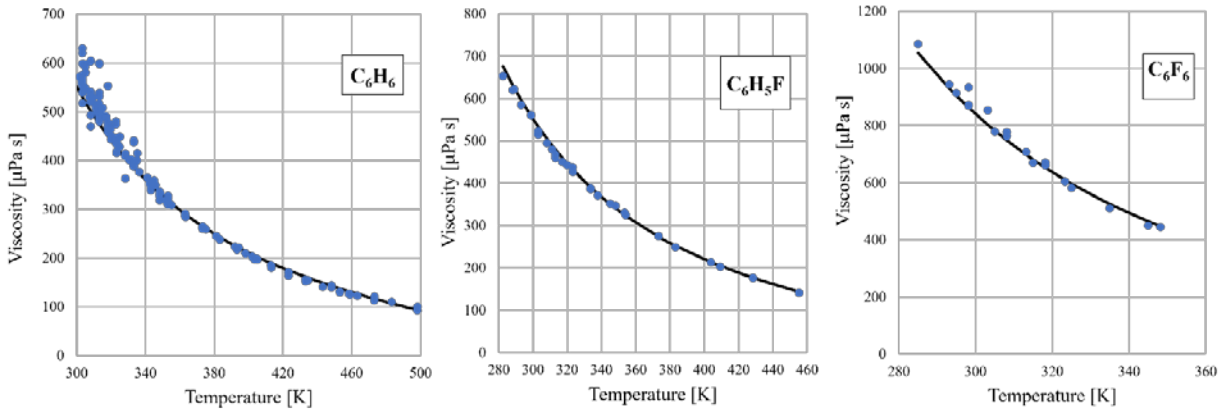

***Figure 2**. Experimental liquid dynamic viscosity (dots) vs optimised model (solid lines).*

Only three liquid thermal conductivity data at ambient pressure available for C_6F_6 from (Irving & Jamieson, 1975), while the rest of liquid viscosities and thermal conductivities presented in Figure 1 and 2 are saturated liquid data available from the NIST database available in Aspen Plus environment. Notably, the dynamic viscosity increases with fluorine content while the thermal conductivity decreases at the same reduced conditions. The increase in the viscosity of fluorinated dopants, compared to their hydrocarbon homologues, relies in the stronger intermolecular interactions in fluorinated compounds (which is reflected also in smaller vapour pressures of the pure dopants and bubble pressure for the mixtures). In general, highly viscous fluids possess also large thermal conductivities. However, it is generally known that for non-polar fluids the dimensionless ratio $M\lambda / R\eta$ is approximately constant value between 2-3 (Poling & Prausnitz, 2001), which means that the thermal conductivity is inversely proportional to the molar mass, that is larger for C_6F_6 (186.96 g/mol) compared to C_6H_6 (78.11 g/mol).

3 CASE STUDY: HIGH-TEMPERATUER HEAT RECOVERY

337

The considered case study is the exploitation of available heat from the exhaust gases of a commercial 12.9 MW_{el} gas turbine, representative of a high-temperature heat source. The adoption of a CO_2-based power cycle in the high-temperature heat recovery market represents a competitive alternative to the state-of-the-art ORCs, which are limited below 350°C due to thermal stability limit. From a study of (Papapetrou et al., 2018), around the 40% of the total waste heat potential in EU is available in the range 500-1000°C, then it is necessary to improve the efficiency of the technologies employed for the conversion of such waste heat to reduce the impact of fossil fuels consumption. For this reason, it is relevant to identify innovative working fluids that could be applied in high-temperature applications.
Fluorobenzene has been considered for the first time as potential CO_2 dopant, and the relevance of this dopant relies on the capability of this mixture to compromise on GWP, ODP, toxicity, cost, thermal stability, availability, compared to more fluorinated dopants typically considered in the literature.
The heat is recovered from the flue gases by the CO_2-based power cycle in the upper temperature range (with direct heat transfer) to produce additional electric power, and by a heat transfer fluid (HTF) in the lower temperature range for cogeneration purposes. The simple recuperated layout is selected even if it cannot guarantee a good degree of cooling of the sensible heat source if compared to other layouts (Morosini et al., 2023). However, the fraction of available heat that is introduced into the primary heat exchanger (PHE) is converted with high thermodynamic efficiency and the rest of heat can be exploited in to produce useful heat at a good thermal level in cogenerative mode. This case could be representative of cogeneration for district heating or for industries that requires valuable heat in the temperature range 100-200°C to satisfy processes like distillation, evaporation, sterilization, vulcanization, etc. About the 20% of the primary energy demand for industrial heating is within the 100-200°C temperature range. For this reasons, the proposed technology could be an important step towards the decarbonization. In this study, both the dopant molar fraction and the turbine inlet temperature (TIT) are optimised to achieve the maximum electrical output, but the optimal cycle configuration can be adjusted to satisfy the specific thermal and electrical demand.

3.1 Power Cycles and Heat Source Description

The exhaust gases have been simulated with molar fractions that are representative of a typical composition of gas turbine exhausts (Scholes et al., 2016), and the temperature level (555°C) and mass flow rate (40 kg/s) are representative of a commercially available 12.9 MW_{el} gas turbine: considering a stack temperature of 120°C, the total available thermal duty is 19.81 MW_{th}.
The power cycle assumptions are in Table 3, where both the mixture's composition and the TIT have been optimized on the total heat recovery efficiency, i.e., the electric output of the cycle has been maximized. An 89% molar content of CO_2 results to be the optimal composition for the mixtures with both C_6F_6 and C_6H_5F. In case of C_6H_6, for the sake of comparison it is considered a 89% composition too even in the optimum results to be 88% since the output differences are negligible (3.51 MW_{el} and 3.514 MW_{el} respectively). The cycle minimum pressure is the bubble pressure of the mixture (87.1 bar for CO_2+C_6H_6, 85.1 bar for CO_2+C_6H_5F ,84.4 bar for CO_2+C_6F_6) at the considered minimum cycle temperature (50°C). The simulations are carried out in Aspen Plus V12 with the Peng Robinson EoS and optimized binary interaction parameters (BIP) K_{ij} regressed on vapour-liquid equilibrium (VLE) data where available (for CO_2+C_6H_6 k_{ij}=0.0774 available in Aspen database, for CO_2+C_6F_6 $k_{ij}(T)$= 0.16297-0.0003951·T[K] from (Di Marcoberardino et al., 2022)). A BIP equal to zero is used for the CO_2+C_6H_5F since there are no VLE data available.

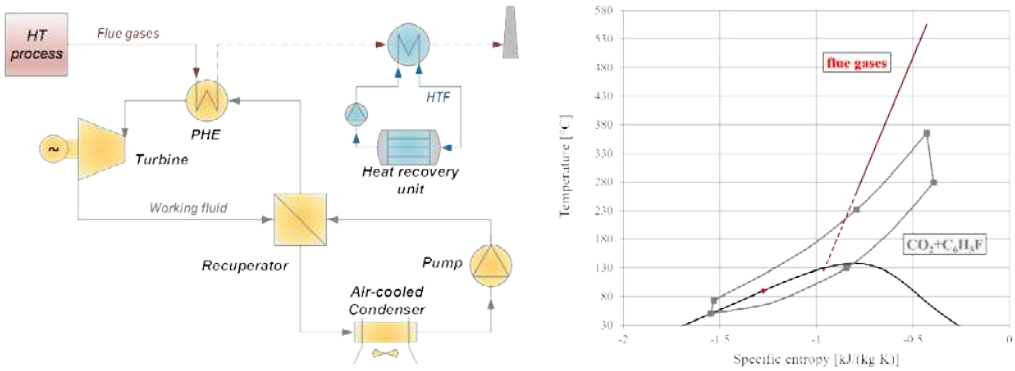

***Figure 3**. System layout for cogeneration scope (left) and T-s diagram (right).*

The assumptions on the simple recuperated power block are summarized in Table 3.

Table 3: power cycle operating conditions.

Parameter	Value
TIT	365°C
Cycle minimum temperature	50°C
Cycle maximum pressure	250 bar
Dopant molar fraction	11%
PHE approach temperature	30°C
Recuperator MITA	10°C
Pump/Expander isentropic efficiency	80/85%
Pressure drops (PHE/HRU)	3/1 bar
Pressure drops recuperator (HP/LP)	0.3/1 bar
Generator/Motor efficiency	97/97%

3.2 Heat recovery results

The results of the cogenerative case-study are represented in Table 4. Since the electrical power production has been maximized, the main key performance index of the system is the electrical efficiency defined as:

$$\eta_{el} = \frac{\dot{W}_{net}}{\dot{Q}_{available,flue\ gases}} \tag{6}$$

Table 4: Cogeneration results.

Parameter	CO_2+C_6H_6	CO_2 + C_6H_5F	CO_2 + C_6F_6
Mass flow rate [kg/s]	64.4	65.5	75.5
Net electric power $\dot{W}_{net}$ [MW]	3.51	3.51	3.35
Electrical efficiency η_{el} [%]	17.7	17.7	16.9
Flue gases PHE outlet T [°C]	261.4	261.8	265.6

4 RECUPERATOR DESIGN COMPARISON

The printed circuit heat exchanger (PCHE) technology has been selected for the design of the recuperator at such high pressures (up to 250 bar) since the manufacturing process (diffusion bonding) gives to the material its parental strength and allows for good compactness. Conventional straight semi-circular channels with 2 mm width are considered, a roughness of 0.1 μm and the metal block made of SS316. A local balance approach has been used to compute the local area required since the thermodynamic and transport properties varies along the heat exchanger. In the one-phase field, the well-known Gnielinski correlation (1976, (Gnielinski, 1975)) is used for the calculation of the heat transfer coefficient while the Darcy friction factor calculated with the correlation of Chen (1979, (Chen, 1979)) is used for the pressure drop. The Cavallini-based model of Deng et al. (2019, (Deng et al., 2019)) has been used for the heat transfer coefficient in the two-phase field since it has been validated by Illyes et al.(Illyés et al., 2022) for a condensing CO_2-rich mixture. The Del Col model (2013, (Del Col et al., 2013)) was therefore considered to compute the two-phase pressure drops.
The T-Q diagram of the recuperator for the CO_2+C_6H_6 is represented in Figure 4, with the local global heat transfer coefficient (solid lines) and the temperature difference (dashed lines) along the heat exchangers for the three dopants.

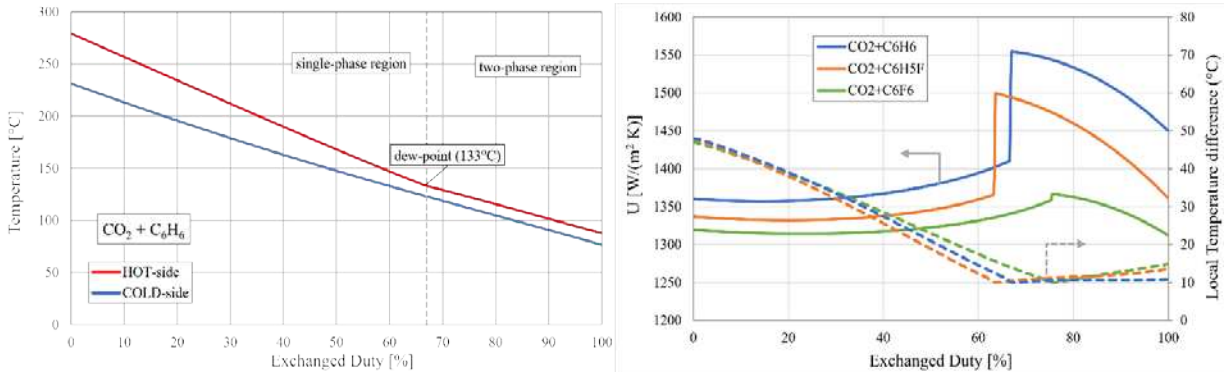

***Figure 4**. T-Q diagram (left) and local U and LMTD for the three mixtures (right).*

The results of the design of the PCHE recuperator for the considered mixture under the same MITA (10°C), hot-side pressure drop (1 bar), and with almost the same thermal duty is reported in Table 5.

Table 5: PCHE recuperator design results (89% CO_2, ΔP_{hot}=1 bar).

Parameter	CO_2+C_6H_6	CO_2 + C_6H_5F	CO_2 + C_6F_6
M_{cycle} [kg/s]	65.45	65.49	75.51
G [kg/(m^2 s)]	635	626	700
Thermal duty exchanged [MW]	19.74	20.23	19.87
LMTD [°C]	17.24	17.42	19.39
Length [m]	2.36	2.42	2.17

Number of channels hot/cold [-]	65'615	66'596	51'574
Heat transfer area (hot/cold side) [m^2]	794.7	828.51	767.1

For C_6F_6, the mass flux to achieve the thermal duty at the constrained pressure drop increase with fluorine content due to higher mass density compared to C_6H_6, and this is reflected in the lower number of plates (frontal area) required to accommodate the total mass flow. At almost the same dynamic viscosity (Figure 5) in the single-phase field, the fluorine content in C_6F_6 promotes higher Reynolds numbers that are compensated by the lower thermal conductivity of fluorinated dopant, and the resulting overall heat transfer coefficient is inferior to the hydrocarbon dopant (Figure 4). The effect of more unbalanced heat capacities (high local temperature differences) of CO_2+C_6F_6 is that the channels are shorter (see Table 5) and the total area required for the CO_2+C_6F_6 mixture is 3.6% lower than the CO_2+C_6H_6 mixture. In other words, the worsening of the heat transfer behaviour that is evident in the global heat transfer coefficient is counterbalanced by the higher LMTD, at the same MITA, and the most fluorinated dopant provides the most compactness but the lowest cycle efficiency.
In case of C_6H_5F, the density gain is not so relevant as for C_6F_6, while the lower thermal conductivity (Figure 5) entails a slight reduction of the heat transfer coefficients, resulting in a total heat transfer area only 4.25% higher than the benzene case.

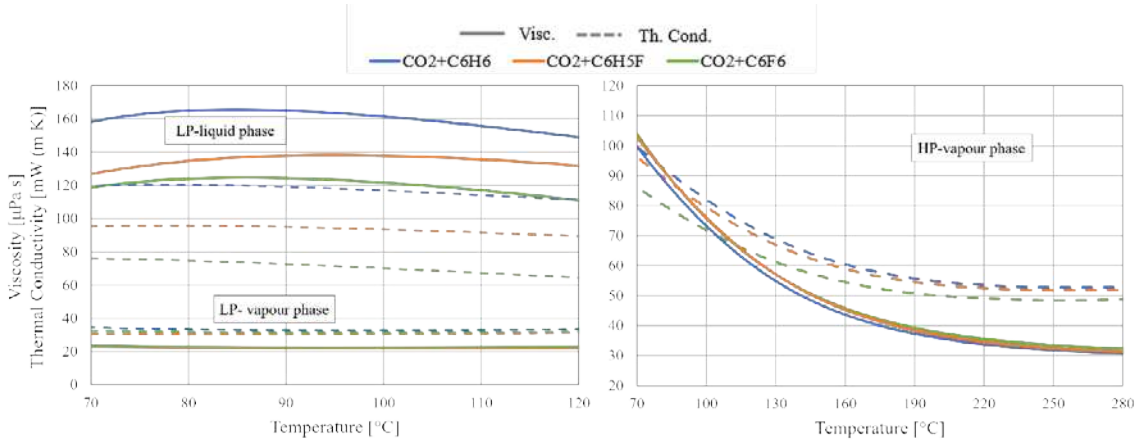

Figure 5. Thermal conductivity and viscosity in the HP supercritical side and two-phase field.

As the viscosity is a molar-based property, at the same molar content (89% CO_2) the influence of the dopant is limited in the high-pressure side. Deviations in dynamic viscosity are relevant in the two-phase field where the first liquid droplet of the CO_2+benzene, in equilibrium with its vapour phase, is at high dopant molar content (64%) compared to the fluorinated mixtures (47%): the molar content of the viscous dopant in the liquid phase is considerably higher, even if the dopant itself (benzene) is less viscous than the fluorinated dopants.
The thermal conductivity is more mass fraction-based (for that reason the mixing rules applied are based on the mass fractions (Quiñones-Cisneros et al., 2021)), and the influence of heavier fluorine atoms is evident at the same molar content, even at 89% molar CO_2. The penalization of the global heat transfer coefficient (Figure 4) in fluorinated dopants is mainly due to lower thermal conductivity. However, for CO_2+C_6F_6, this is compensated by a higher local temperature difference at the same MITA, at almost equal thermal duty exchanged, which leads to a more compact heat exchanger but lower cycle efficiency. In case of CO_2+C_6H_5F, the heat transfer behaviour is only partially deteriorated by fluorination, and the LMTD (Table 5) is similar to CO_2+C_6H_6 leading to a slightly larger heat exchanger, nevertheless keeping a good cycle efficiency.

5 CONCLUSIONS

In this paper, benzene and two fluorinated derivates were investigated as CO_2 dopants in high-temperature heat recovery application to evaluate the impact of fluorination on cycle efficiency and on heat exchangers by sizing the PCHE recuperator. Proper transport properties models have been tuned, with an innovative approach, based on experimental data to carry out a realistic heat exchanger design.

For the first time, the adjustable parameter of the one-parameter friction theory model for viscosity has been tuned with a temperature-dependent approach, to compensate for the incapability of the equation of state to describe the severe increase of intermolecular forces in the liquid dense phase region, at low temperatures, with clear benefits in the properties prediction.

The thermal conductivity drop (also associated with the increase of the viscosity) of fluorinated compounds is reflected in a decline of the global heat transfer coefficient (-8.3% for C_6F_6 compared to C_6H_6), which is compensated by more unbalanced heat capacities (higher local temperature differences) in the recuperator. In case of C_6F_6, the divergence of the heat capacities in single-phase and VLE regions leads to higher local temperature differences and a slightly more compact heat exchanger, though with a negative effect on the cycle efficiency. This work provides insights on the heat transfer behaviour of CO_2 mixtures within the internal heat recovery process, which is the key factor that determines the cycle efficiency.

Fluorobenzene C_6H_5F is proposed for the first time as potential CO_2 dopant. Its adoption results to be an interesting solution for heat recovery and solar applications in the medium-high temperature range since it guarantees high efficiency similar to that of benzene (+1% compared to C_6F_6) with a slight penalization in the heat transfer behaviour due to the fluorine atom, relatively-low GWP and low cost (compared to C_6F_6), low toxicity (compared to C_6H_6), zero ODP. Future works will be intended to fill the gap on experimental VLE data of the CO_2+C_6H_5F mixture and to assess its thermal stability limit.

NOMENCLATURE

Acronyms

BIP	Binary Interaction Parameter
CS	Corresponding States
LCOE	Levelized Cost of Electricity
LMTD	Logarithmic mean temperature difference
LP	Low pressure
HP	High Pressure
MITA	Minimum Internal Temperature Approach
ODP	Ozone Depletion Potential
PHE	Primary Heat Exchanger
PCHE	Printed Circuit Heat Exchanger
TIT	Turbine Inlet Temperature
VLE	Vapour-Liquid Equilibrium
WHR	Waste Heat Recovery

Roman and Greek letter

G	Mass Flux	kg/(m^2 s)
M	Mass Flow Rate	kg/s
MM	Molar Mass	kg/mol
P	Pressure	bar
T	Temperature	°C
U	Overall Heat Transfer Coefficient	W/(m^2 K)]
$\dot{Q}$	Thermal power	MW
$\dot{W}$	Mechanical Power	MW
ΔT	Temperature difference	°C
η	Dynamic viscosity	Pa s
λ	Thermal Conductivity	W/(m K)

Subscript

a	attractive
c	critical
i,j	species
r	repulsive
th	thermal
0	zero-density conditions

REFERENCES

Astolfi, M., Lasala, S., & Macchi, E. (2017). Selection Maps for ORC and CO2 Systems for Low-Medium Temperature Heat Sources. *Energy Procedia*, *129*, 971–978. https://doi.org/10.1016/j.egypro.2017.09.217

Avgeri, S., Assael, M. J., Huber, M. L., & Perkins, R. A. (2014). Reference Correlation of the Viscosity of Benzene from the Triple Point to 675 K and up to 300 MPa. *Journal of Physical and Chemical Reference Data*, *43*(3). https://doi.org/10.1063/1.4892935

Chen, N. H. (1979). An Explicit Equation for Friction Factor in Pipe. *Industrial &*

Engineering Chemistry Fundamentals, *18*(3), 296–297. https://doi.org/10.1021/i160071a019

Chung, T. H., Ajlan, M., Lee, L. L., & Starling, K. E. (1988). Generalized multiparameter correlation for nonpolar and polar fluid transport properties. *Industrial \& Engineering Chemistry Research*, *27*(4), 671–679. https://doi.org/10.1021/ie00076a024

Chung, T. H., Lee, L. L., & Starting, K. E. (1984). Applications of Kinetic Gas Theories and Multiparameter Correlation for Prediction of Dilute Gas Viscosity and Thermal Conductivity. *Industrial and Engineering Chemistry Fundamentals*, *23*(1), 8–13. https://doi.org/10.1021/i100013a002

Del Col, D., Bisetto, A., Bortolato, M., Torresin, D., & Rossetto, L. (2013). Experiments and updated model for two phase frictional pressure drop inside minichannels. *International Journal of Heat and Mass Transfer*, *67*, 326–337. https://doi.org/10.1016/j.ijheatmasstransfer.2013.07.093

Deng, H., Rossato, M., Fernandino, M., & Del Col, D. (2019). A new simplified model for condensation heat transfer of zeotropic mixtures inside horizontal tubes. *Applied Thermal Engineering*, *153*(December 2018), 779–790. https://doi.org/10.1016/j.applthermaleng.2019.02.128

Di Marcoberardino, G., Invernizzi, C. M., Iora, P., Ayub, A., Di Bona, D., Chiesa, P., Binotti, M., & Manzolini, G. (2020). Experimental and analytical procedure for the characterization of innovative working fluids for power plants applications. *Applied Thermal Engineering*, *178*, 115513. https://doi.org/10.1016/j.applthermaleng.2020.115513

Di Marcoberardino, G., Morosini, E., Di Bona, D., Chiesa, P., Invernizzi, C., Iora, P., & Manzolini, G. (2022). Experimental characterisation of CO2 + C6F6 mixture: thermal stability and vapour liquid equilibrium test for its application in transcritical power cycle. *Applied Thermal Engineering*, 118520. https://doi.org/10.1016/j.applthermaleng.2022.118520

Doninelli, M., & Di Marcoberardino, G. (2023). On the design of recuperator for transcritical cycle adopting CO2-based mixture as working fluid: a focus on transport properties prediction - under review. *Applied Thermal Engineering*.

Doninelli, Michele, Morosini, E., Gentile, G., Putelli, L., Di Marcoberardino, G., Binotti, M., & Manzolini, G. (2023). Thermal desalination from rejected heat of a transcritical cycle working with a CO2-based mixture in CSP application: a focus on the MED technology. *Sustainable Energy Technologies and Assessments*.

Freire, M. G., Ferreira, A. G. M., Fonseca, I. M. A., Marrucho, I. M., & Coutinho, J. A. P. (2008). Viscosities of liquid fluorocompounds. *Journal of Chemical and Engineering Data*, *53*(2), 538–542. https://doi.org/10.1021/je700632z

Gnielinski, V. (1975). New equations for heat and mass transfer in the turbulent flow in pipes and channels. *NASA STI/Recon Technical Report A*, *41*(1), 8–16.

Hodnebrog, Aamaas, B., Fuglestvedt, J. S., Marston, G., Myhre, G., Nielsen, C. J., Sandstad, M., Shine, K. P., & Wallington, T. J. (2020). Updated Global Warming Potentials and Radiative Efficiencies of Halocarbons and Other Weak Atmospheric Absorbers. In *Reviews of Geophysics* (Vol. 58, Issue 3). https://doi.org/10.1029/2019RG000691

Illyés, V., Morosini, E., Doninelli, M., David, P.-L., Guerif, X., Werner, A., Di Marcoberardino, G., & Manzolini, G. (2022). *Design of an Air-Cooled Condenser for CO2-Based Mixtures: Model Development, Validation and Heat Exchange Gain with Internal Microfins*. 1–11. https://doi.org/10.1115/gt2022-82438

Irving, J. B., & Jamieson, D. T. (1975). Thermal conductivity of 13 fluorocarbon liquids. *Journal of Fluorine Chemistry*, *5*(5), 449–456. https://doi.org/https://doi.org/10.1016/S0022-1139(00)82503-8

Mason, E. A., & Saxena, S. C. (1959). Thermal Conductivity of Multicomponent Gas Mixtures. II. *The Journal of Chemical Physics*, *31*(2), 511–514. https://doi.org/10.1063/1.1730386

Morosini, E., Doninelli, M., Alfani, D., Astolfi, M., Di Marcoberardino, G., & Manzolini, G. (2023). Analysis of the potential of CO2 based mixtures to improve the efficiency of cogenerative waste heat recovery power plants. *The 5th European SCO2 Conference for Energy Systems*.

Papapetrou, M., Kosmadakis, G., Cipollina, A., La Commare, U., & Micale, G. (2018). Industrial waste heat: Estimation of the technically available resource in the EU per industrial sector, temperature level and country. *Applied Thermal Engineering*, *138*(July 2017), 207–216. https://doi.org/10.1016/j.applthermaleng.2018.04.043

Poling, B. E., & Prausnitz, J. M. (2001). The Properties of Gases and Liquids. In *Solutions*.

Quiñones-Cisneros, S. E., Pollak, S., & Schmidt, K. A. G. (2021). Friction Theory Model for Thermal Conductivity. *Journal of Chemical and Engineering Data*, *66*(11), 4215–4227. https://doi.org/10.1021/acs.jced.1c00400

Quiñones-Cisneros, S. E., Zéberg-Mikkelsen, C. K., & Stenby, E. H. (2000). The friction theory (f-theory) for viscosity modeling. *Fluid Phase Equilibria*, *169*, 249–276.

Quiñones-Cisneros, S. E., Zéberg-Mikkelsen, C. K., & Stenby, E. H. (2001). One parameter friction theory models for viscosity. *Fluid Phase Equilibria*, *178*(1–2), 1–16. https://doi.org/10.1016/S0378-3812(00)00474-X

Scholes, C., Ho, M., & Wiley, D. (2016). Membrane-Cryogenic Post-Combustion Carbon Capture of Flue Gases from NGCC. *Technologies*, *4*(2), 14. https://doi.org/10.3390/technologies4020014

Uyehara, OA and Watson, K. (1944). A universal viscosity correlation. *National Petroleum News*, *36*, 714–722.

Wilke, C. R. (1950). A viscosity equation for gas mixtures. *The Journal of Chemical Physics*, *18*(4), 517–519. https://doi.org/10.1063/1.1747673

This book contains the compilation of works contributed to the *7th International Seminar on Organic Rankine Cycle Power Systems* (ORC 2023), held in Seville between the 4th and 6th of September 2023. The event was hosted by Universidad de Sevilla on behalf of the Knowledge Centre on Organic Rankine Cycle Technology (KCORC), incorporated in The Netherlands.

The ORC conference, organized biennially, stems as the only conference that is specific to ORC technology, therefore gathering a diverse community whose affiliation spans across all the interested stakeholders, not only in this particular technology but also and in a broader context, in the energy transition. Original equipment manufacturers, professional associations, end-users, investors, policy makers, academics, scientists feel at home at ORC 2023.

The almost 100 proceedings in this book cover a wide variety of topics, from fundamentals to system integration through component design, accounting for thermodynamic performance as well as component design. In addition to this, and as a new track in 2023, works on heat pump technology were also accepted in order to raise awareness of the strong ties between both technologies, specifically in energy storage applications.

This book provides an excellent overview of the current maturity of power systems based on Organic Rankine Cycle technology for applications as diverse as geothermal and waste heat recovery in industry or downstream of other prime movers (e.g., marine applications). It is also an excellent source of information to understand the current challenges faced by the technology, stemming from a very competitive market and increasingly stringent environmental regulations.

The organizers of ORC 2023 hope that the reader finds this work as exciting as the attendees to the conference and, maybe, make the decision to join the 8th edition to the conference in 2025.

KCORC
KNOWLEDGE CENTER
ORGANIC RANKINE CYCLE

eus EDITORIAL
UNIVERSIDAD DE SEVILLA