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Proceedings of the 7th International Seminar on

ORC Power Systems

Editorial Universidad de Sevilla

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(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_80

Prediction of the ideal maximum operational temperature of hydrocarbon and HFCs as working fluids of organic Rankine cycle power plants based on transition state theory

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ABSTRACT

The use of organic working fluids in organic Rankine cycle (ORC) power plants may lead to thermal decomposition, which can negatively impact system performance and safety. Therefore, it is essential to determine the safe operating temperature range of the working fluids. In this paper, a simplified theoretical method based on the transition state theory is proposed to predict the ideal maximum operational temperature of working fluids. This method involves considering the initial decomposition reaction of the working fluids and calculating the total reaction rate of the initial decomposition using the transition state theory. By setting an acceptable decomposition rate, the ideal maximum operational temperature of the working fluid can be determined. Using this method, the total reaction rate constants of several typical hydrocarbon and hydrofluorocarbon working fluids, including n-butane, isobutane, n-pentane, isopentane, neopentane, n-hexane, HFC-245fa, HFC-134a, HFC-125, HFC-236fa, HFC-227ea, HFC-143a, and HFC-152a, were obtained in the temperature range of 300~700K. The predicted maximum operational temperatures were in good agreement with most experimental results. Furthermore, by analyzing the branch ratio of each initial decomposition path of these working fluids, it was found that C-C bond cleavage contributed mainly to the decomposition of hydrocarbons, while the removal of HF and C-C bond cleavage contributed mainly to the decomposition of HFCs. As the C-C bond breakage paths and HF removal reaction paths have high branching ratios (>99%), only considering these reactions in the reaction rate calculation can greatly reduce the calculation cost without significantly impacting the prediction accuracy.

1 INTRODUCTION

When organic Rankine cycle (ORC) system is applied to medium-high temperature heat sources, the organic working fluids will face the risk of thermal decomposition, which results in performance loss and many important operation problems (Niggemann, 1969; Koplow et al., 1984). Therefore, in the practical application of ORC systems, the thermal stability of organic working fluids is vital important. Obtaining the maximum safe use temperature is the focus of the research on the thermal stability of working fluids.

At present, the most effective method is to obtain the decomposition rate data of the working fluids at relatively high temperature by experiment, and obtain the correlation between the decomposition rate

and temperature by fitting the decomposition rate at different temperatures. By analyzing the impact of the pyrolysis of working fluids on the system performance and determining the acceptable decomposition rate threshold of working medium in the life cycle of ORC, the maximum safe operation temperature of working fluids can be determined (Pereira et al., 2022).

(Dai et al., 2016a) obtained the decomposition kinetics correlation of n-pentane through experiments. Under the condition of 1% threshold of acceptable decomposition rate within the life of ORC, the evaluated upper limit operation temperature of n-pentane in ORC systems is 280 ℃~300 ℃. Although this method is very effective, it requires a high cost to determine the kinetics correlation. (Dai et al., 2016b) further proposed a fast pyrolysis experiment method to determine the pyrolysis temperature of hydrocarbon. By this method, the decomposition temperature of n-pentane, n-hexane, isopentane, cyclopentane, n-butane and isobutane are obtained. Using the same method, (Dai et al., 2018) measured the pyrolysis temperatures of HFC-245fa, HFC-152a, HFC-134a, HFC-236fa and HCFC-123. Compared with the experimental results of (Calderazzi and di Paliano, 1997) and (Angelino and Invernizzi, 2003), the pyrolysis temperature measured by (Dai et al., 2018) is relatively low. This is due to differences in experimental conditions and judgment indicators. (Dai et al., 2016a, 2018) also carried out an analysis of the influence of pressure on the decomposition rate of n-pentane and HFC-245fa. The results showed that at 340 ℃, pressure has little effect on the decomposition rate of n-pentane, and the correlation equation for fitting the reaction rates measured in the experiment conforms to the first-order reaction kinetics; At 320 ℃, the pressure has little effect on the decomposition of HFC-245fa. This indicate that under these temperatures, the second order reaction has little effect on the decomposition of these working fluids. Therefore, the pyrolysis can be reasonably described by first-order reaction kinetic model.

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Since the working fluids are usually operating in a high-pressure environment greater than atmospheric pressure in ORC systems, the rate constants of each decomposition reaction path can be reasonably evaluated by the high-pressure limit transition state theory (TST) (Eyring, 1935; Nikitin, 1974) which is established based on statistical thermodynamics and quantum mechanics. By considering the structure and energy of the reactants at the transition state, as well as the vibrational frequencies between the reactants and the transition state, the prediction and interpretation of chemical reaction rates can be made. In present work, we carried out high-precision quantum chemical calculations on the initial pyrolysis reaction paths of several hydrocarbon working fluids and HFCs working fluids commonly used in ORC systems (Wang et al., 2022). Based on the first-order reaction kinetic model and the transition state reaction rate calculation, the decomposition kinetic correlations of these working fluids in temperature range of 300~700 K were obtained. The contribution of different reaction paths in the decomposition process is further analyzed, and the main contribution path is determined. This work provides a novel method for determining the thermal stability temperature of working fluids under ideal conditions (without considering the impact of impurities and contact materials on thermal stability).

2 COMPUTATIONAL DETAILS

2.1 Quantum chemical calculation

The geometry optimization, frequency calculations and transition state searches have been carried out at the density functional theory (DFT), M062x/def2-TZVP level (Weigend and Ahlrichs, 2005; Zhao

and Truhlar, 2008) with ZPE scale factor of 0.971 (Alecu et al., 2010), and single point energy calculations were carried out at CCSD(T)/cc-PVTZ level. All the DFT calculations were accomplished using Gaussian-16 software package (Frisch et al.) at temperature of 298.15K and at pressure of 0.1MPa. In the frequency analysis, all the molecular and radical optimized structures have no imaginary frequency, while the transition state structure has only one imaginary frequency. For the transition state structure, the correctness is further guaranteed by the calculation of intrinsic reaction coordinates (IRC). The thermodynamic parameters at different temperatures are calculated using Shermo software package (Lu and Chen, 2021).

2.2 Reaction rate constant calculation

The reaction rate constants were calculated by using the high-pressure limit transition state theory (TST) (Eyring, 1935; Nikitin, 1974). The TST calculation can be expressed as follows (Al-Otaibi et al., 2021),

$$k^{TST}(T) = \sigma \frac{k_B T}{h} \left(\frac{RT}{P^0} \right)^{\Delta n} e^{\frac{-\Delta^{\neq} G^0(T)}{k_B T}} \tag{1}$$

where, σ is degeneracy of the reaction path; k_B, h, R and T are the Boltzmann constant, Planck constant and general gas constant, temperature in Kelvin, respectively; P^0 is the standard pressure; $\Delta^{\neq} G^0(T)$ is the Gibbs free energy barrier of the reaction path at a given temperature and standard atmospheric pressure; For monomolecular decomposition reaction, $\Delta n = 0$.

Due to the study of the reaction rate at relative low temperatures, the quantum tunneling effect correction is carried out for the reaction path containing transition states, the Wigner correction method (Wigner, 1937) was used to calculate the tunneling correction factor (κ), 478

$$\kappa = 1 + \frac{1}{24} \left(\frac{h v^{\neq}}{k_B T} \right)^2 \tag{2}$$

where, $v^{\neq}$ is the imaginary frequency of transition state. Then, the reaction rate considering tunneling correction can be expressed as:

$$k^{TST,\kappa}(T) = \kappa k^{TST}(T) \tag{3}$$

After obtaining the reaction rate of each path, the total reaction rate of the initial decomposition reaction can be obtained as follows,

$$k_{total}^{TST,\kappa}(T) = \sum_i^n k_i^{TST,\kappa}(T) \tag{4}$$

The reaction branching ratio is used to measure the contribution of each reaction path to decomposition. The branching ratio is calculated as follows,

$$BR(i)\% = \frac{k_i^{TST,\kappa}(T)}{k_{total}^{TST,\kappa}(T)} \times 100 \tag{5}$$

3 RESULTS AND DISCUSSION

3.1 Decomposition kinetics of six hydrocarbon working fluids

Six common hydrocarbon working fluids including n-butane, isobutane, n-pentane, isopentane, neopentane and n-hexane were used as research objects. In the initial stage of decomposition, the weaker chemical bond in the molecule breaks, resulting in the initial decomposition of molecule. For these

hydrocarbons, mainly considers two types of initial decomposition reactions (Xin et al., 2020): C-H bond cleavage reactions and C-C bond cleavage reactions. Taking n-pentane as example, the initial reaction paths and degeneracy of reaction paths (σ) are shown in Table 1.

Table 1: Initial reaction paths of n-pentane.

Reaction path	Reaction	σ
RP1	$n-C_5H_{12} \rightarrow CH_3\bullet + C_4H_9\bullet$	2
RP2	$n-C_5H_{12} \rightarrow C_2H_5\bullet + C_3H_7\bullet$	2
RP3	$n-C_5H_{12} \rightarrow H\bullet + \bullet CH_2(CH_2)_3CH_3$	6
RP4	$n-C_5H_{12} \rightarrow H\bullet + CH_3\bullet CH(CH_2)_2CH_3$	4
RP5	$n-C_5H_{12} \rightarrow H\bullet + CH_3CH_2\bullet CHCH_2CH_3$	2

The branching ratio reflects the contribution of each reaction path to the total reaction rate, which is shown in Fig.1. As shown in Fig.1a, the reaction rate of each path follows the following order: deethylation reaction rate (RP2) > demethylation reaction rate (RP1) >> C-H bond cleavage reaction rate (RP3, RP4 and RP5). As shown in Fig. 1b. In the temperature range of 300K~700K, the branching ratio of the reaction path for the deethylation reaction (RP2) is about 99.5%, the branching ratio of the demethylation reaction (RP1) is about 0.5%~0.4%, and the branching ratio of the reaction paths for the C-H bond cleavage (RP3, RP4 and RP5) is less than 0.1%.

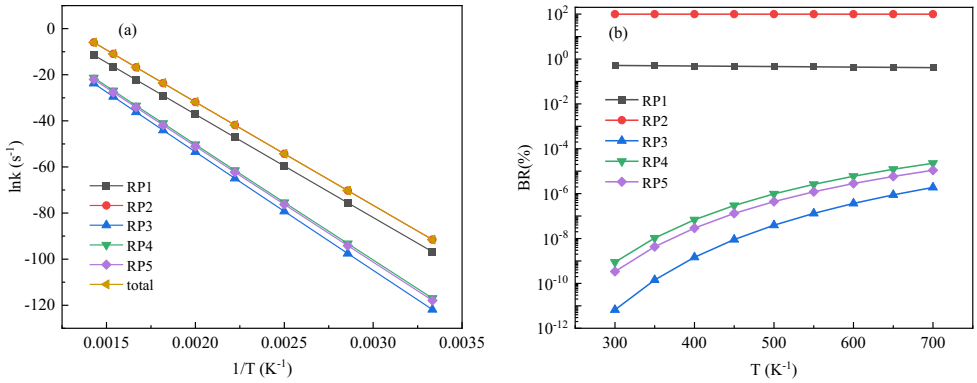

Figure 1: Reaction rate (a) and branching ratio (b) of each reaction path of n-pentane.

The total reaction rate fitting correlations of six hydrocarbon working fluids are shown in Fig. 2. In order to evaluate the accuracy of these fitting correlation equations in predicting the decomposition reaction rates, a comparison was made with experimental data from existing literature, and the results are shown in Table 2. As shown in Table 2, for n-pentane, compared with experimental data, the correlation equation overestimates the reaction rate at 603.15 K and below, while it underestimates the reaction rate above 603.15 K; at temperature of 588.15 K, the correlation equation overestimates the reaction rate of isopentane, while show excellent prediction accuracy of neopentane. Overall, the obtained correlation shows good prediction accuracy. Further, with 1% annual decomposition as the threshold, the ideal maximum operational temperatures of six hydrocarbon working fluids are predicted by using the obtained kinetic correlations, and compared with the ideal maximum operational temperatures recommended in the literature (Dai et al., 2016b), which was obtained through rapid pyrolysis experiments. The lower limit of the range corresponds to the highest temperature at which no

decomposition products are detected after 24 hours of heating, while the upper limit corresponds to the lowest temperature at which decomposition products are detected after 24 hours of heating, with a temperature interval of 20 K. The results are shown in Table 3. For n-butane, isobutane and isopentane, the predicted temperature is within the ideal maximum operational temperature range recommended by the experiment; for isobutane and n-hexane, there are deviations of -3.27 K and 32.5 K. On the whole, the obtained kinetic expressions have good performance in predicting the ideal maximum operational temperature of hydrocarbon working fluids. Moreover, it is worth mentioning that due to the high branching ratio of RP1 and RP2, the contribution of RP3, RP4 and RP5 can be ignored when fitting the kinetic correlation, which has little impact on the prediction of ideal maximum operational temperature.

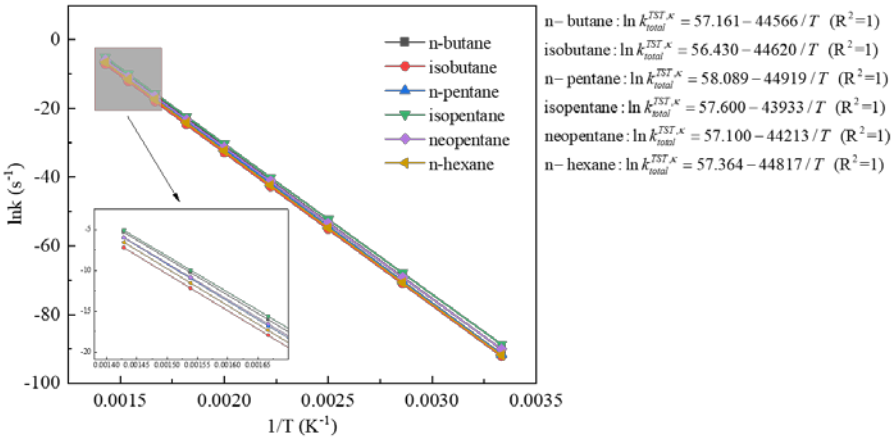

Figure 2: Total reaction rate of six hydrocarbon working fluids.

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Table 2: Comparison of reaction rate predicted by correlation equation with experimental data.

Working fluid	Temperature (K)	Reaction rate predicted by correlation equation (s^{-1})	Reaction rate obtained by experiment (s^{-1})
n-pentane	588.15	1.15×10^{-8}	$(4.07\pm0.70)\times10^{-9}$ (Andersen and Bruno, 2005)
	603.15	7.67×10^{-8}	$(3.2998\pm0.1971)\times10^{-8}$ (Dai et al., 2016a)
	613.15	1.15×10^{-8}	$(1.4246\pm0.1176)\times10^{-8}$(Dai et al., 2016a)
	623.15	2.58×10^{-7}	$(6.1062\pm0.4748)\times10^{-7}$(Dai et al., 2016a)
isopentane	588.15	3.76×10^{-8}	$(7.9\pm1.6)\times10^{-9}$(Andersen and Bruno, 2005)
neopentane	588.15	1.48×10^{-8}	$(1.5\pm0.3)\times10^{-8}$((Andersen and Bruno, 2005)

Table 3: Ideal maximum operational temperature predicted by obtained kinetics correlations.

Working fluid	Predicted T_{max} (K)	Recommended T_{max} by experiment (K) (Dai et al., 2016b)
n-butane	563.93	573.15~593.15
isobutane	569.88	573.15~593.15
n-pentane	561.79	553.15~573.15
isopentane	552.85	533.15~553.15

neopentane	559.60	-
n-hexane	565.65	533.15~553.15

3.2 Thermodynamic and kinetics of decomposition of seven HFCs working fluids

In this part, seven HFCs working fluids (HFC-245fa, HFC-134a, HFC-227ea, HFC-236fa, HFC-143a, HFC-152a, HFC-125) commonly used in ORC were selected as research objects. For HFCs, the initial pyrolysis has the following reaction paths: C-C bond cleavage, C-H bond cleavage, C-F bond cleavage and HF removal. Taking HFC-245fa as an example, the initial reaction paths and degeneracy of reaction paths are shown in Table 3.

Table 4: Initial reaction paths of HFC-245fa.

Reaction path	Reaction	σ
RP1	$CF_3CH_2CF_2H \rightarrow \bullet CF_3 + \bullet CH_2CF_2H$	1
RP2	$CF_3CH_2CF_2H \rightarrow CF_3CH_2\bullet + \bullet CF_2H$	1
RP3	$CF_3CH_2CF_2H \rightarrow H\bullet + CF_3CH\bullet CF_2H$	2
RP4	$CF_3CH_2CF_2H \rightarrow H\bullet + CF_3CH_2CF_2\bullet$	1
RP5	$CF_3CH_2CF_2H \rightarrow F\bullet + \bullet CF_2CH_2CF_2H$	3
RP6	$CF_3CH_2CF_2H \rightarrow F\bullet + CF_3CH_2CFH\bullet$	2
RP7	$CF_3CH_2CF_2H \rightarrow CF_3CH_2CF_2H(TS_1) \rightarrow HF + CF_2 = CHCF_2H$	6
RP8	$CF_3CH_2CF_2H \rightarrow CF_3CH_2CF_2H(TS_2) \rightarrow HF + CF_3CH = CFH$	4

Fig. 5 shows the reaction rate and branching ratio of each reaction path. As shown in Fig.5a, In the temperature range of 300~500 K, the reaction rate of each path follows the following order: HF removal (RP7 and RP8) > C-C bond cleavage (RP1 and RP2) > C-H bond cleavage (RP3 and RP4) > C-F bond cleavage (RP5 and RP6). However, because the reaction rate of C-C bond cleavage increases faster with temperature, when the temperature is higher than 500 K, the reaction rate of C-C bond cleavage gradually exceeds that of HF removal. As shown in Fig. 5b, in the temperature range of 300~550 K, the branching ratio of the HF removal reactions is nearly 100%. In the temperature range of 550~700 K, the branching ratio of the HF removal reactions decrease, and that of C-C bond cleavage reactions increase. When the temperature exceeds 650 K, the branching ratio of C-C bond cleavage reaction exceeds HF removal reaction, the cleavage of the C-C bond will become the dominant reaction for the initial decomposition of HFC-245fa. In the temperature range of 300~700 K, the branching ratio of C-F bond and C-H bond cleavage reaction are close to 0, which is difficult to occur.

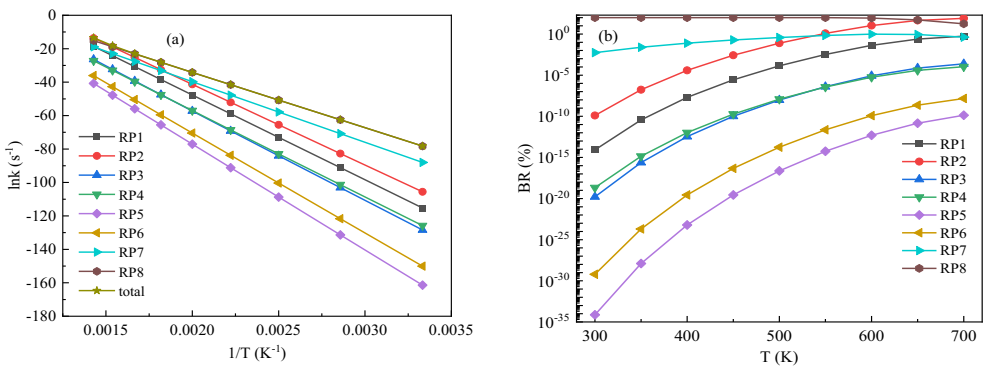

Figure 5: Reaction rate (a) and branching ratio (b) of each reaction path of HFC-245fa.

The total reaction rate fitting correlations of seven HFCs working fluids are shown in Fig. 6. As shown in Fig. 6, the decomposition rate of each working fluids varies greatly with temperatures. Further analysis shows that in the temperature range of 300~700 K, the decomposition of the seven working fluids is almost all contributed by HF removal and C-C bond, as shown in Fig. 7. Therefore, for HFCs, the reaction of C-H bond and C-F bond breaking can be ignored when calculating the decomposition rate. To evaluate the accuracy of the obtained kinetic correlations, the ideal maximum safe operational temperatures of seven HFCs working fluids are calculated with the annual decomposition amount of 1% as the threshold, and compared with the literatures. The results are shown in Table 5. For the temperature range given in the literature, the lower limit value was used as the ideal maximum operational temperature for comparison. According to Table 5, except for HFC-152a, HFC-227ea and HFC-134a, which have large deviations from the experimental results, 179.29 K, 91.56 K and 58.46 K, respectively, the other four working fluids are in good agreement with the experimental values, and the deviations are within 35 K. In addition to the inherent error in calculating energy using DFT, the deviation between the predicted values and the experimental ones may be caused by the following reasons: (1) The experimental values are determined by the fluoride ion concentration (Dai et al., 2018) or pressure deviation (Angelino and Invernizzi, 2003) after the thermal stress experiment, which is somewhat different from the decomposition rate of the reactant; (2) The metal surface under experimental conditions have a certain catalytic effect on the decomposition of HFCs (Dai et al., 2017; Huo et al., 2019). Due to the high branching ratio of the C-C bond cleavage reaction paths and HF removal reaction paths, the contribution of the C-H bond and C-F bond cleavage can be ignored when fitting the kinetic correlation, which has little impact on the prediction of ideal maximum operational temperature.

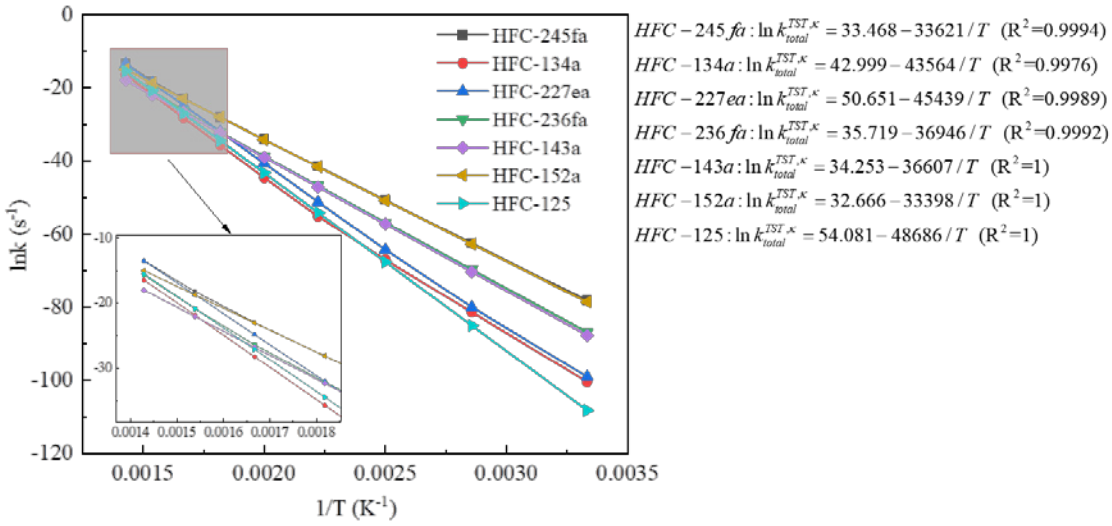

Figure 6: Total reaction rate of seven HFCs working fluids.

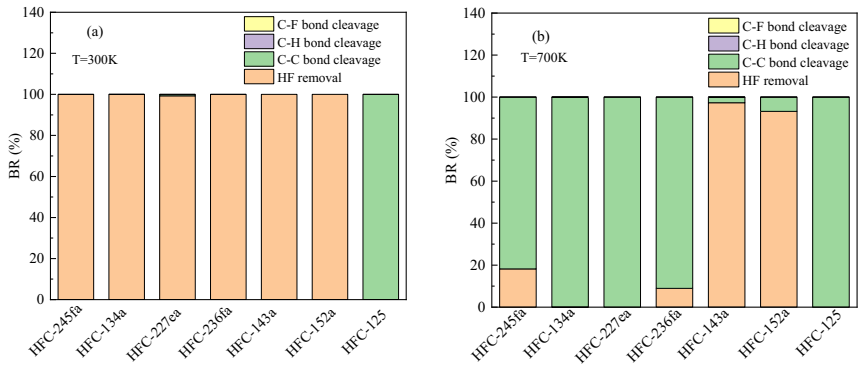

Figure 7: Reaction path branching ratios at different temperatures: (a) 300K; (b) 700K.

Table 5: Ideal maximum operational temperature predicted by obtained kinetics correlations.

Working fluid	Predicted T_{max} (K)	Recommended T_{max} by experiment (K)
HFC-245fa	606.59	573.15~593.15 (Dai et al., 2018)
HFC-134a	671.60	613.15~633.15 (Dai et al., 2018)
HFC-227ea	626.59	698.15 (Angelino and Invernizzi, 2003)
HFC-236fa	641.58	673.15 (Angelino and Invernizzi, 2003)
HFC-143a	652.30	623.15 (Calderazzi and di Paliano, 1997)
HFC-152a	612.44	433.15~453.15 (Dai et al., 2018)
HFC-125	641.05	669.15 (Calderazzi and di Paliano, 1997)

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4 CONCLUSIONS

In present work, combining high-precision quantum chemical calculations and transition state theory, a simplified method for predicting the ideal maximum operational temperatures of hydrocarbon and HFCs working fluids in ORC power plants was proposed, and its prediction effect was evaluated. The main conclusions are drawn as follows:

- For the decomposition of hydrocarbon working fluids, using the obtained decomposition kinetics correlations, accurate ideal maximum operational temperature prediction can be achieved. The ideal maximum operational temperature of n-butane, isobutane, n-pentane, isopentane, neopentane, and n-hexane predicted with the annual decomposition rate of 1% as the threshold value is 563.93 K, 569.88 K, 561.79 K, 552.8 K, 559.60 K and 565.65 K, respectively.
- For the decomposition of HFCs working fluids, the ideal maximum operational temperatures of HFC-245fa, HFC-134a, HFC-227ea, HFC-236fa, HFC-143a, HFC-152a and HFC-125 predicted by the obtained decomposition kinetics correlations are 606.59 K, 671.60 K, 626.59 K, 641.58 K, 652.30 K, 612.44 K and 641.05 K, respectively.
- For hydrocarbon working fluids, the initial decomposition is mainly contributed by the C-C bond cleavage reaction paths, while for HFCs working fluids, the initial decomposition is mainly contributed by the C-C bond cleavage and HF removal reaction paths.

NOMENCLATURE

BR	branching ratio	(%)
DFT	density functional theory	(-)
HFCs	hydrofluorocarbons	(-)
h	Planck constant	(J·s)
k_B	Boltzmann constant	($J \cdot K^{-1}$)
k	reaction rate constant	(s^{-1})
ORC	organic Rankine cycle	(-)
R	general gas constant	($J \cdot mol^{-1} \cdot K^{-1}$)
RP	reaction path	(-)
R^2	mean square error	(-)
T	temperature	(K)
TST	transition state theory	(-)
σ	degeneracy of the reaction path	(-)

Subscript

max	Ideal maximum operational temperature

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ACKNOWLEDGEMENT

This work was financially supported by the National Natural Science Foundation of China (No. 52076018) and the Chongqing Graduate Research and Innovation Project (No. CYB22020).

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.

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