Energy 153 (2018) 422–430

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Influence of alkane working fluid decomposition on supercritical organic Rankine cycle systems

Xiaoye Dai [a], Lin Shi [b,*], Qingsong An [c], Weizhong Qian [a]

[a] Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing, China
[b] Key Laboratory of Thermal Science and Power Engineering of Ministry of Education of China, Department of Energy and Power Engineering, Tsinghua University, Beijing, China
[c] Key Laboratory of Efficient Utilization of Low and Medium Grade Energy, MOE, School of Mechanical Engineering, Tianjin University, Tianjin, China

ARTICLE INFO

Article history:
Received 21 December 2016
Received in revised form
1 April 2018
Accepted 14 April 2018

Keywords:
Organic Rankine cycle (ORC)
Thermal stability
Alkanes
Influence mechanism

ABSTRACT

The supercritical Organic Rankine Cycle (ORC) develops rapidly due to its low exergy loss, high thermal efficiency and high work output. The thermal stability of working fluid is the major limitation when selecting the working fluid for high temperature heat sources (150–350 °C). The influence mechanisms of the working fluid decomposition are important considerations when evaluating the thermal stability for ORCs. This study analyzed the influence of alkane working fluid decomposition on ORCs with n-pentane as the test fluid. The compositions of the gaseous and solid products were confirmed by experiments. The experiments and ORC system model were designed to analyze the different influence mechanisms of gaseous and solid products on the ORCs. The results showed that the main influence is the condensation pressure rise caused by non-condensable gases in gaseous decomposition products. Studies on methods for predicting the long-term thermal stability are also significant and merit further work.

1. Introduction

Organic Rankine Cycle (ORC) systems are widely used for industrial waste heat recovery and renewable energy utilization due to their good performance and high efficiencies for low grade heat sources. Subcritical ORC systems are used commercially in solar power [1], geothermal power [2], biomass power [3] and industrial waste heat recovery systems [4]. Supercritical ORCs with high temperature heat sources (150–350 °C) have attracted much interest due to their potential advantages compared with subcritical ORCs. Studies have shown that supercritical ORCs can obtain better thermal efficiencies than subcritical ORCs under some conditions with appropriate fluids [5]. The exergy losses of supercritical ORCs can be lower than those of subcritical ORCs because supercritical ORCs better match with the heat resources due to the smaller temperature differences between fluids and heat resources [6].

The thermal stability is the primary limiting condition of working fluid selection due to the possible decomposition at cycle operating temperatures. Initial ORC studies (1970s) recognized the importance of the thermal stability [7]. Badr et al. [8] summarized the thermal stability results for 68 working fluids, including hydrocarbons, HFCs, and other species. However, most of these thermal stability results were not obtained under ORC conditions and contained large deviations. The thermal stability results for a certain working fluid had considerable variations because of differences in the experimental systems, procedures, and conditions. The variations could even be hundreds of degrees for the decomposition temperature and a factor of 10^2 to 10^4 for the decomposition rate. For example, the decomposition temperatures for R12 were 102 °C [9], 204 °C [10] and 300 °C [11] in different studies.

However, the heat source temperatures were usually lower than 150 °C in early studies and most working fluids were stable at such low temperatures. The thermal stability did not get much attention in the early studies. As heat source temperatures have risen, there have been more studies on the fluid thermal stability. Alkanes are considered to be potential working fluids for supercritical ORCs due to their high critical temperatures, good thermal performance and environmental friendliness. Most available thermal stability studies have focused on alkanes. There have been many studies on the thermal stability of alkanes in the research fields of chemical engineering, petroleum, and fuels [12–15]. However, these thermal

* Corresponding author.
E-mail address: rnxsl@mail.tsinghua.edu.cn (L. Shi).

https://doi.org/10.1016/j.energy.2018.04.083
0360-5442/

Nomenclature

Symbols

u	Uncertainty of measurements
h	Enthalpy (kJ/kg)
W	Power (kW)
$\dot{m}$	Mass flow (kg/s)
Q	Heat flow (kW)
T	Temperature (K, °C)
U	Mean overall heat transfer coefficient (W/m^2-K)
Nu	Nusselt number
Re	Reynolds number
Pr	Prandtl number
g	Gravitational acceleration (m/s^2)
r	Latent heat (kJ/kg)
d	Diameter (m)
t_s	Saturation temperature (K, °C)
η	Efficiency
α	Thermal conductivity (W/m-K)
δ	Wall thickness (m)
λ	Convection heat transfer coefficient (W/m^2-K)
ρ	Density (kg/m^3)
μ	Dynamic viscosity (N-s/m^2)

Subscripts

1, 2, 3, 4	State points of the ORC system
t	Turbine
f	Working fluid
C	Cold source
O	Outlet
I	Inlet
P	Pump
H	Heat source
net	Net
ORC	Organic Rankine Cyle
Pinch	Pinch point
W	Wall

stability results were almost all obtained for long chain molecules at high temperatures (>400 °C), which are not suitable for ORC working fluids. Specialized experimental methods for ORC working fluids under given pressure and temperature conditions are needed. Andersen and Bruno [16] measured the reaction rate constants of some alkane working fluids at 315 °C. The pressure was experimentally confirmed to be irrelevant to the decomposition. Ginosar et al. [17] measured the decomposition of cyclopentane at 240, 300, and 350 °C in a cyclical test system and confirmed the existence of solid deposits. Pasetti et al. [18] used pressure changes to imply the decomposition and identify safe temperatures for some alkanes. Dai et al. [19,20] presented a chemical kinetics method for evaluating the thermal stability of ORC working fluids and measured the safe temperatures of some alkanes. However, these previous studies only focused on the extents or conditions needed for decomposition and did not consider the influences of the working fluid decomposition on ORC systems. The previous studies only emphasized the importance of the thermal stability and listed possible damages from decomposition. The possible mechanisms include the following.

1) The decomposed working fluid cannot match the original system conditions, which may lead to output losses [16–21]. Angelino and Invernizzi [21] considered the decomposition products and original pure fluid as mixture fluids and calculated the decomposition cycle efficiency changes. The results showed that volatile gases such as methane and tetrafluoromethane had very large effects on the cycle performance.
2) The gaseous decomposition products may create non-condensable gases that increase the condensation pressure [17,19,20]. This high condensation pressure can then lead to lower thermal efficiencies and system outputs. This mechanism mainly influences the condenser in ORC systems.
3) Solid decomposition products may block the tubes in ORC systems and cause safety problems. Moving components like the expander may also be damaged by solid deposits [16,18–20,22]. This mechanism mainly influences the expander, fluid pump, and tubes in ORC systems.
4) Decomposition products may cover the heat exchanger surfaces and degrade the heat transfer, which will also reduce the ORC system efficiency [7,8,17–20,22]. This mechanism mainly influences the evaporator and condenser in ORC systems.
5) Decomposition products may have corrosive effects on ORC system materials, which can cause serious safety problems [7,8,16,22]. For example, fluorinated hydrocarbons may form HF during decomposition, which has significant corrosive effects on most materials [22]. This mechanism can influence all components in ORC systems.

However, these possible mechanisms have not been discussed in detail, and few reported studies have focused on further analyses of these possible influences. The main influences have not been confirmed experimentally or theoretically, and the extents of these influences have not been quantified. Even though the decomposition rates have been measured, previous studies have not evaluated the influences on the ORC system design because the mechanism and quantitative influences have not been known. Thus, the influences of working fluid decomposition on ORC systems are very important and further studies are required.

This study analyzed the influences of alkane working fluid decomposition on ORCs. Decomposition experiments were first designed to qualitatively and quantitatively confirm the composition of the decomposition products, which included gaseous and solid products (Section 2). The possible influence mechanisms were then analyzed to confirm the main mechanism by considering the experimental results and ORC system characteristics (Section 3). The extent of the main influence mechanism was calculated using the ORC model, and the results are discussed (Section 4).

2. Experiments

2.1. Experimental systems and methods

2.1.1. Test fluid

Alkane is the acyclic saturated hydrocarbon and consists of only elements carbon and hydrogen. The decompositions of alkanes are mainly primary reactions in ORC temperature ranges [19]. Thus, all kinds of alkane working fluids have similar species of the decomposition products, which are smaller acyclic hydrocarbons and hydrogen. The similar species of the decomposition products lead to similar influence mechanisms, so the study method for a certain alkane fluid can be extended to other alkanes. N-pentane was selected as test fluid to be the representative of alkane working fluids. N-pentane was obtained from commercial suppliers with