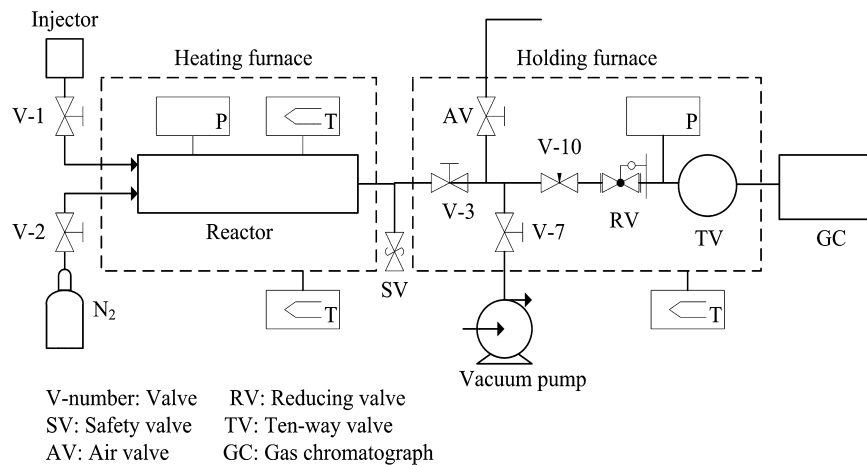Research Paper

Chemical kinetics method for evaluating the thermal stability of Organic Rankine Cycle working fluids

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HIGHLIGHTS

- A chemical kinetics method for evaluating the thermal stability of ORC working fluids.
- An experimental system to obtain the apparent kinetic parameters.
- An apparent chemical kinetics model to predict the thermal stability.
- The n-pentane pre-exponential factor was 7.5275×10^{12} s^{-1} and the activation energy was 227.57 kJ/mol.

GRAPHICAL ABSTRACT

V-number: Valve   RV: Reducing valve
SV: Safety valve   TV: Ten-way valve
AV: Air valve   GC: Gas chromatograph

ARTICLE INFO

ABSTRACT

Organic Rankine Cycle (ORC) systems are widely used to generate electricity with industrial waste heat and renewable energy. Transcritical ORCs with high temperature heat sources are more attractive than subcritical ORCs due to their lower exergy losses, higher thermal efficiencies and higher work outputs. The working fluid thermal stability is the primary consideration in the working fluid selection due to decomposition at high temperatures. This paper presents a chemical kinetics method for evaluating the thermal stability of ORC working fluids. A chemical kinetics experimental system was built with n-pentane as the test working fluid. The influences of pressure and temperature were analyzed experimentally and theoretically. An apparent chemical kinetics model was established to predict the thermal stability with the apparent kinetic parameters of n-pentane measured experimentally. This apparent chemical kinetics model gives significant guidance for the working fluid selection and ORC system design.

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1. Introduction

The Organic Rankine Cycle (ORC) is a promising technology for industrial waste heat recovery and renewable energy utilization. Subcritical ORCs have been widely used in the geothermal power, solar power, biomass power and industrial waste heat recovery systems [1–4]. Subcritical ORC heat source temperatures are usually less than 150 °C, which limits their thermal efficiencies and leads to high costs. Transcritical ORCs, which use high temperature heat sources (150–350 °C), are more efficient and less expensive. The literature suggests that transcritical ORCs have much better efficiencies than subcritical ORCs with the same working fluids and heat source temperatures. Karellas and Schuster [5] calculated the thermal efficiencies of transcritical ORCs with R134a and R245fa to show that the thermal efficiencies were 10–20% higher than subcritical ORCs. Similar results were obtained by Chen et al. [6] for transcritical ORCs with mixture working fluids with 10~30% improvements. Transcritical ORC temperatures match better with the heat sources, so they have lower exergy losses. Higher thermal efficiencies and work outputs are then obtained because of the higher temperature heat sources, and the system costs are reduced by smaller heat exchanger areas.

However, some new problems have not been addressed in the studies of transcritical ORCs. The primary problem is the thermal stability of the ORC working fluids at high temperatures. All organics decompose at high temperatures. If decomposition occurs in the ORC system, the thermal efficiency and work output will decrease because of the different working conditions. Decomposition products like non-condensable gases and deposits can seriously damage the components and compromise safety. Thus, thermal stability is the primary consideration for working fluid selection and ORC system design. Studies of working fluid thermal stability have been conducted since the early 1970s [7]. However, the heat source temperatures were usually less than 150 °C and the working fluids were found to be stable in early ORC studies. Working fluid thermal stability has attracted much interest recently because of the higher temperature heat sources. Andersen and Bruno [8] presented a method for rapid screening of the working fluid thermal stability for ORCs. The reaction rate constants of some hydrocarbon working fluids were measured. Ginosar et al. [9] measured the thermochemical decomposition of cyclopentane at 240, 300, and 350 °C at 4.3 MPa in a glass-lined heated tube. Air was found to have a large effect on the decomposition. Pasetti et al. [10] used pressure changes to imply decomposition to identify safe temperatures for cyclopentane, iso-pentane and n-butane. However, previous studies have not considered the relationships between thermal stability and temperature or time. Previous studies only considered special working conditions and cannot be applied to other general conditions. Thus, more thermal stability experimental data and a universal evaluation method are needed.

This paper presents a chemical kinetics method for thermal stability to evaluate the ORC working fluids. A chemical kinetics measurement system was used to get the data for an apparent chemical kinetics model. The model could predict the thermal stability at different temperatures and times. N-pentane was used as the test fluid because it was one of the most desirable ORC working fluids.

2. Theory

Thermochemical decomposition of a simple substance is a unimolecular reaction in terms of the chemical kinetics. Unimolecular reactions are usually first order reactions except in some extreme conditions. The reaction rate of a first order reaction is proportional to the reactant concentration as

$$\frac{dC_A}{dt} = -kC_A \tag{1}$$

where C_A is the reactant concentration, t is the time and k is the reaction rate constant which is only related to the reaction temperature. Equation 1 can also be written as

$$-\ln\frac{C_A}{C_0} = -\ln C = -\ln(1-x) = kt \tag{2}$$

where C_0 is the original reactant concentration, T is the reaction time, C_A is the concentration at time t, C is the concentration ratio and x is the reactant decomposition concentration. Equation 2 shows that $\ln C$ is related linear with t because k is constant at a given temperature. Thus, the reaction rate constant, k, can be calculated from $\ln C$-t curves if the reactant concentrations are measured at different times at a given temperature. The reaction rate constant can then be used to predict the reactant decomposition concentration at different times at the same temperature. The decomposition products may also decompose and the reaction mechanism becomes more complex when the reactant is mixed with products. The product influence is ignored in this paper because the reactant decomposition rate is very slow in the measured temperature range. The assumption that the decomposition is a first order reaction is accurate enough for stability studies.

The Arrhenius Equation is used to describe the reaction ratio at different temperatures.

$$k = Ae^{-E_a/RT} \tag{3}$$

where k is the reaction rate constant, A is the pre-exponential factor, Ea is the activation energy, R is the gas constant and T is the temperature. The pre-exponential factor, A, and the activation energy, Ea, are normally assumed to be constants in the Arrhenius Equation, and they are independent of any environmental condition. The Arrhenius Equation is a classical equation in chemical kinetics and can be used in most practical environmental conditions. The Arrhenius Equation can also be written as

$$\ln k = -\frac{Ea}{R}\frac{1}{T} + \ln A \tag{4}$$

Equation 4 shows that $\ln k$ is linearly related with $1/T$ because the pre-exponential factor, A, and activation energy, Ea, are constant for given reactant. Thus, the pre-exponential factor and the activation energy can be calculated from the $\ln k$-$1/T$ curve if the reaction rate constants are measured at different temperatures. The apparent chemical kinetics model can then be obtained by combining Equations 2 and 4.

$$\ln(1-x) = -Ate^{-E_a/RT} \tag{5}$$

This apparent chemical kinetics model can be used for all the ORC working fluids because the derivational process in theory is suitable for any organic. The model is accurate enough when the experimental temperature is not very high (to ensure the condition of the Arrhenius Equation) and the decomposition concentration is not very big (to ensure the condition of first order reactions). Equation 5 shows that the variables in the model are the reactant decomposition concentration, time and temperature. Thus, the reactant decomposition concentration at any time and temperature conditions can be calculated once the pre-exponential factor and the activation energy are measured.

3. Experiment

3.1. Chemicals

N-pentane was chosen as the working fluid because it is one of the most promising ORC working fluids. The n-pentane samples were