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Group contribution methods in thermodynamic cycles: Physical properties estimation of pure working fluids

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ABSTRACT

Thermodynamic cycles consist of reverse cycles, such as refrigeration and heat pump, and positive cycles, such as organic rankine cycle. These cycles have been widely applied for cooling, heating and power generation. In general, the involved energy transfer in the thermodynamic cycles can be realized by the continuous change of physical properties of working fluids. Thus, the physical properties of working fluids are the foundation of cycle analysis. Furthermore, working fluids with appropriate properties can assure high-efficient, safe and economic operation of cycles.

Over the past few decades, a large number of group contribution methods (GCMs) have been developed to estimate properties of compounds. Therefore, in this paper, GCMs, which are applied to estimate the properties of working fluids for the evaluation of cycle performance, are reviewed. The considered properties include thermodynamic, transportive, environmental, physicochemical and economic properties. Furthermore, the knowledge gaps and development directions of GCMs are presented as well. The reviewed GCMs in this work can be employed to make quick estimations of properties from molecular structures of working fluids, and find working fluids with desired properties via computer-aided molecular design.

1. Introduction

1.1. Background

Over the past decades, the global demand for energy has grown substantially with industrial development and population growth. This has led to many serious problems, such as energy crisis, air pollution and global warming. Therefore, the waste or renewable heat sources such as solar energy, biomass and geothermal energy have attracted widespread attention. These heat sources belong to the low and medium grade of energy. So far, the power cycles represented by Organic Rankine Cycle (ORC) and the vapor compression reverse cycles represented by refrigeration/ heating cycles, are commonly employed to develop the waste or renewable heat. ORC can convert low-temperature heat source into power in the kW and MW range [1] and has the characteristics of simplicity and flexibility. Therefore, it can be easily combined with other industrial processes such as seawater desalination system [2], carbon capture [3,4] and internal combustion engine [5,6]. Vapor compression reverse cycle can transfer the heat from the low temperature to the high temperature. It generally consists of refrigeration which provides cooling [7,8], and heat pump which supplies heating [9,10].

For thermodynamic cycles, working fluids are employed to generate work or transfer heat. The thermodynamic processes of working fluid in the ORC and the refrigeration/heat pump are shown in Fig. 1. It can be seen that the working fluid is the core of thermodynamic cycles. The employed working fluid has a significant effect on the design of components, the cycle efficiency, the cycle stability and safety. Thus, fundamental problems of thermodynamic cycles lie in the measurement of physical properties and the selection of working fluids.

Nowadays, physical properties such as the boiling temperature, the freezing temperature and the critical parameters have been measured and published for various working fluids in the literatures [11–13]. A large number of experimental data have been digitized into the databanks, such as the Design Institute for Physical Properties (DIPPR) [14] and the Dortmund Data Bank (DDB) [15]. These databanks contain physical properties for more than 6000 compounds. Furthermore, for the experimentally unmeasured properties such as the enthalpy, the entropy and the internal energy, many researchers have contributed to develop equations of state or estimation formulas for different working fluids based on the general thermodynamic relations [16–18]. The required parameters are generally obtained from the fitting with the experimentally measured properties. However, it is unrealistic to acquire the properties from the experiment for

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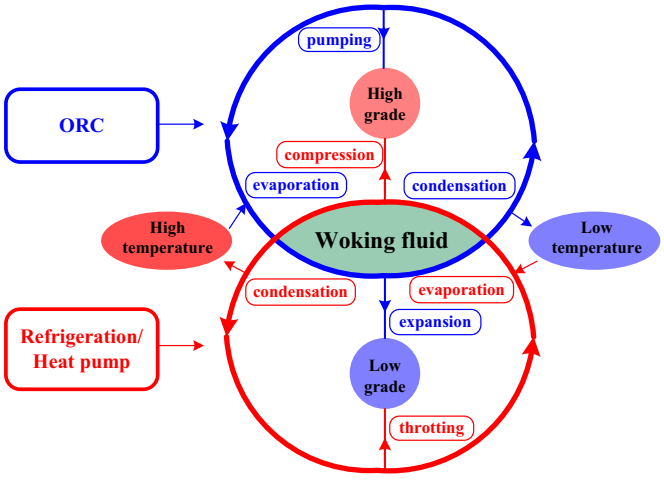

Fig. 1. Thermodynamic processes of working fluid for thermodynamic cycles.

thousands of working fluids, considering that experimental measurement often takes a lot of time and cost. Therefore, predictive models with high accuracy have been developed to estimate the properties of working fluids.

1.2. Predictive models

In general, there are three types of predictive models, namely computational chemistry method [19–21], group contribution method [22–24] and equation of state [12,25,26], as shown in Fig. 2. Computational chemistry method (CCM) is based on quantum chemistry, so that it can determine the properties of working fluids at the atomic scale. However, computational effort of CCM may range from hours to days, even when simulating one molecule [19,20]. Thus, it's not appropriate to use CCM in the thermodynamic analysis. Furthermore, for equation of state (EOS), hundreds of EOSs have been proposed from molecular statistical thermodynamics. A little computational effort is required to calculate the physical properties of working fluids. However, the physical constants and correlation parameters involved in these equations have been experimentally determined only for a small amount of molecules [26]. Thus, the semi-empirical EOSs can't be efficiently applied for the property estimation of new working fluids.

Another predictive model-group contribution method (GCM) is based on the assumption that the property of a compound is a function of structurally-dependent parameters. The property can be determined by summing the frequency of each group occurring in the molecule times its contribution [27]. For organic compounds, a certain number of groups can generate a vast number of substances, as indicated in Fig. 3. Furthermore, the contribution of each group in a particular property is assumed to be constant regardless of the molecular

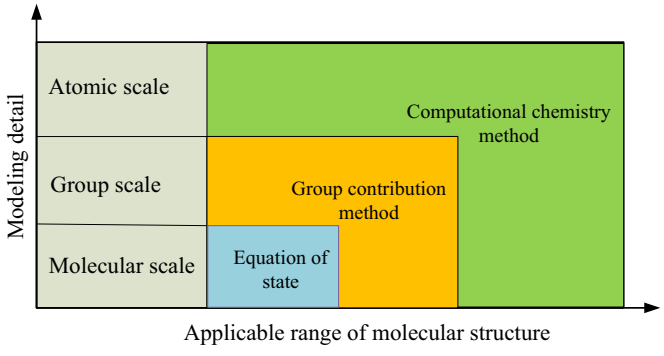

Fig. 2. Property prediction models with respect to modeling detail and range of molecular structure.

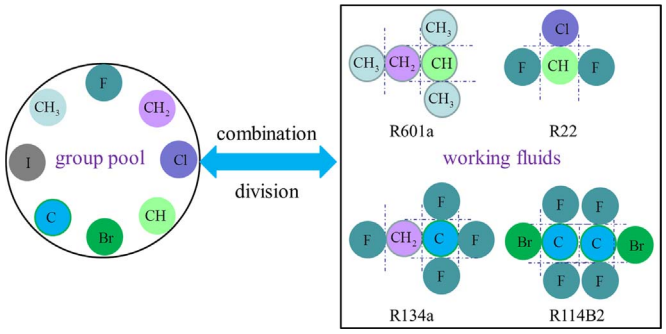

Fig. 3. Schematic diagram of molecular groups and working fluids.

structure in which the group is considered. Therefore, based on the molecular structure, GCM can quickly estimate the properties of working fluids. It can not only improve the computational efficiency compared with the CCM, but also solve the data unavailability compared with the EOS. Over the past few decades, many GCMs have been proposed to estimate various physical properties of working fluids [28–32].

1.3. GCM and CAMD

GCM generally consists of three parts, namely group division, group estimation formula, and group contribution value. In the process of developing a GCM for a desired property, the group division is firstly conducted. The divided groups can be atoms, chemical bonds or functional groups. Thereafter, the estimation formula, which establishes the relationship between the occurrences of groups and the physical property, is proposed on the basis of the chemical structure theory. Finally, the group contribution values of divided groups are determined from the experimental data by regression techniques [33,34].

Based on the proposed GCMs for physical properties of working fluids, a systematic approach called computer-aided molecular design (CAMD) has been developed to design alternative working fluids for thermodynamic cycles [35,36]. CAMD can generate a vast number of conventional or novel working fluids which may exhibit favorable characteristics in the cycles [36–39]. In conventional practice, novel working fluids can only be found through experimental work. However, the experiment generally takes a lot of time and cost. Therefore, through the predictive capability of CAMD, experimental work on searching alternative working fluids can be greatly reduced.

For thermodynamic cycles, suitable working fluids must exhibit favorable thermodynamic, transportive, environmental, physicochemical and economic properties [40–43]. Table 1 presents the considered properties in the design and selection of working fluids. Thus, in this work, an overview of GCMs for the estimation of these properties is presented. GCMs for thermodynamic properties are summarized and discussed in Section 2. In Section 3, we review GCMs for transport properties. GCMs for environmental properties are presented in Section 4. In Section 5, physicochemical and economic properties, such as stability, compatibility and cost are discussed. In Section 6, we present the knowledge gaps and development directions of GCMs. A conclusion of this review on GCMs for the considered properties is given in Section 7.

2. Thermodynamic properties

2.1. Boiling temperature

Boiling temperature (T_b) is defined as the temperature at which a liquid's vapor pressure equals to an atmospheric pressure. From the simulated results on thermal efficiency of ORC for R113, R123, R245ca