High-Throughput Screening of ORC Fluids for Mobile Applications

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Abstract. Although huge effort has been invested in research and development of Organic Rankine Cycle (ORC) systems for mobile applications, it was not possible so far to identify a working fluid which covers nearly all of the requirements defined by OEMs and component suppliers. Therefore, the intention of this work was the identification of a so-called "superfluid" by screening the complete chemical space of more than 72 million chemical substances given by the PubChem© database. For this purpose, a fast simulation tool (DetailSimORC) was programmed in Matlab®. The thermodynamic properties were gained by the COSMOtherm software with a combination of the COSMO-RS theory and a cubic equation of state. The subsequent evaluation was based on a scoring system taking into account constructional aspects (e.g. minimum pressure level), safety issues (e.g. flammability) and regulatory requirements (e.g. ozone depletion potential, ODP) in addition to the thermodynamic performance. The results revealed that a conflict occurs between optimal thermodynamic performance and safety issues. Fluids showing a high net power output and low ODP are often highly flammable, whereas well-performing non-flammable working fluids have drawbacks concerning environmental and toxico-logical issues. Keeping these conflicting priorities in mind, it is possible to select a set of diverse best-ranked fluids for further investigation: the alcohol ethanol, the linear siloxane hexamethyldisiloxane, as well as the refrigerant R-152 (1,2-difluoroethane).

Keywords: Organic Rankine Cycle · Mobile sector · COSMO-RS · Scoring system · PubChem · Screening

1 Introduction

The mobile sector is driven by legislation and economics to reduce fuel consumption constantly. To meet future targets on fuel savings in heavy duty truck, passenger cars and the marine sector, waste heat recovery by means of Organic Rankine Cycle has gained increased interest in the last years. A crucial aspect for the efficiency and, therefore, for the profitability of such systems is the working fluid. Mostly, common databases for thermodynamic properties of organic fluids like RefProp® are applied

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with the goal of identifying a suitable working fluid. However, results of a number of publications as well as two research projects of the Research Association of Combustion Engines (FVV) eV revealed that among the investigated fluids no fluid meets nearly all requirements set by OEMs and component supplier. Therefore, this projects deals with the search for an ideal fluid based on a highly innovative methodology: High-Throughput-Screening of potential working fluids using a combination of Computational Chemistry and thermodynamic process simulations. The goal of the project was nothing less than finding an ideal fluid for the exhaust gas usage in mobile applications by screening the complete chemical space defined by the PubChem database that covers around 72 million chemical substances at the moment. Possible advantages of such a fluid could be:

- higher net power output and, therefore, higher CO_2-reduction
- lower costs and reduced weight and size of the Rankine-system
- lower additional costs for condensation/cooling of the working fluid

To find the ideal fluid, a simulation tool in Matlab is programmed and combined with thermodynamic properties from COSMOtherm to ensure that the complete chemical space given by the PubChem database can be investigated. This work summarizes the main methods and results; more information can be found in a previous publication [1].

2 Theory and Methods

2.1 Organic Rankine Cycle

Although the mobile sector summarizes three different applications, namely heavy duty trucks, passenger cars and the marine sector, thermodynamically only two cases have to be distinguished: internal combustion engines using heat from exhaust gas recirculation (EGR) and the ones just using heat downstream of exhaust gas aftertreatment (EGA). The layout for cases including EGR is displayed in Fig. 1.

Boundary conditions for the simulation of all cares are selected according to discussions in the working committee of the research project. Furthermore, the working committee provided heat source characteristics based on real engine operation points. Based on these assumption, the simulation tool “DetailSimORC” is programmed within the simulation environment Matlab®. DetailSimORC is based on steady state simulations and the principle of conservation of energy. Radiation losses in the heat exchangers as well as pressure drops in the cycle are neglected. Figure 2 shows a simplified flow chart.

2.2 Computational Chemistry Methods (COSMOtherm)

The quantum chemically based Conductor-like Screening Model for Realistic Solvation (COSMO-RS) is a rather general method for predicting the chemical potentials of almost arbitrary molecules in almost any dense pure or mixed liquid. This chemical potential difference can be transformed into properties such as vapor pressures, activities or solubilities. In general, COSMO-RS is composed of two fundamental steps:

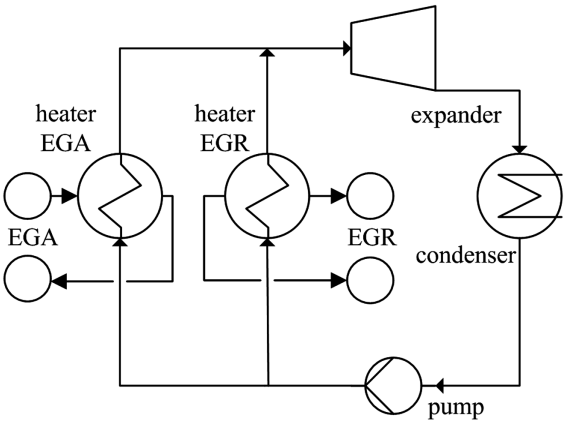

Fig. 1. Layout of Organic Rankine Cycle with exhaust gas recirculation

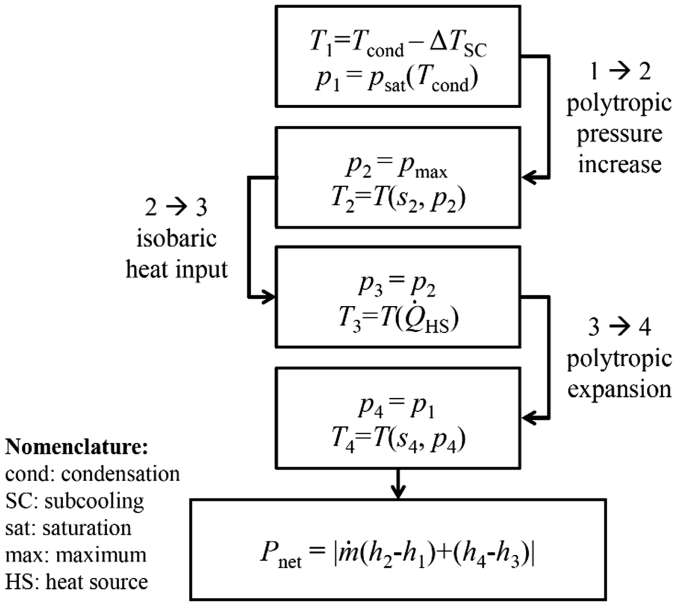

Fig. 2. Simplified flow chart of DetailSimORC

At first, quantum chemical calculations have to be performed for all compounds of interest. In these calculations a virtual conductor embedding the molecule is taken into account by the continuum solvation model COSMO [2]. In the second step of COSMO-RS, the statistical thermodynamics of the molecular interactions, this polarization charge density is used for the quantification of the interaction energy of pairs of surface segments. As most important molecular interaction modes, electrostatics and hydrogen bonding are taken into account in this way.

The classic COSMO-RS theory is based on the assumption of incompressible liquids and ideal gases. The ORC process, however, uses temperatures and pressures up to the critical point. In this range of application, the treatment of both liquid phase compressibility and real gas behaviour is essential. In order to extend the applicability range of COSMO-RS, the theory is combined with the Patel-Teja equation of state within this study [3].

The ORC fluid screening requires a preferably diverse chemical structure dataset. Here, the PubChem database has been chosen as the largest inventory publically available. In an automatized workflow, the molecular structures are fetched from the database, quantum chemical calculations are initiated for appropriate compounds and the thermodynamic properties are predicted via the COSMOtherm software, as depicted in Fig. 3. DetailSimORC simulations are then performed for a filtered set according to suitable thermodynamic properties for the ORC process (critical temperatures, vapor pressures…) as described above.

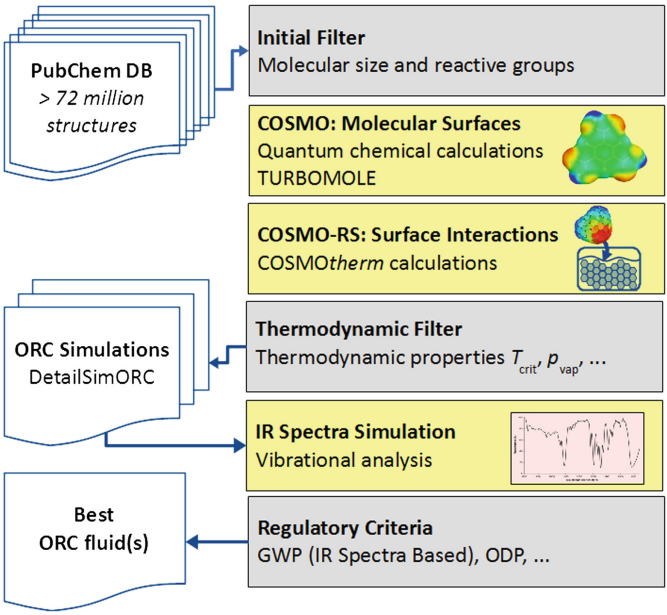

Fig. 3. Schema of the PubChem database screening by COSMOtherm calculations and DetailSimORC simulations

3 Results and Discussion

In total, 3,175 working fluids are simulated in DetailSimORC based on accurate thermodynamic properties from COSMOtherm (TZVPD-FINE level, see also Preißinger et al. [1]). Each working fluid is considered for two different applications (heavy

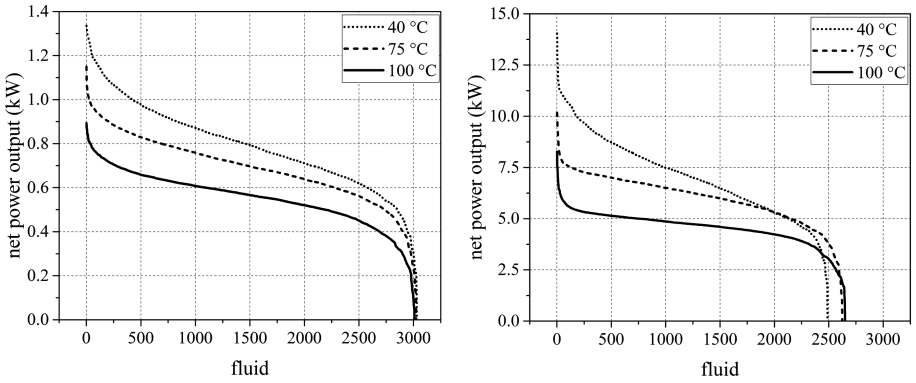

Fig. 4. Net power output for various working fluids depending on condensation temperature for application passenger car (left) and heavy duty truck (right)

duty truck, passenger car) and three different condensation temperatures (40 °C, 75 °C, 100 °C).

Figure 4 shows the expected decreasing net power output with increased condensation temperature. Furthermore, a steep increase in net power output for the best 50 working fluids is observed.

It is obvious that several working fluids reach high net power output. In a next step an overall evaluation by summing up the ranking of each fluid within each of the six cases. An ideal working fluid would come up with an overall scoring of 6 (being ranked on 1st place for all six cases), the least efficient working fluid would lead to a value of 19050 (begin last ranked for all six cases). It can be seen that the working fluid with the best overall ranking is acetaldehyde with an overall score of 27. This shows that the methodology of combining a fast simulation environment with computational chemistry is an effective way to find ideal working fluids from a thermodynamic point of view.

However, based on security aspects like flammability, autoignition temperature and the formation of highly explosive peroxides, acetaldehyde cannot be applied under real world conditions. Therefore, a more comprehensive evaluation method is developed which takes into account constructional aspects, safety issues, regulatory parameters and thermodynamic efficiency.

Constructional aspects include minimum and maximum pressure, maximum temperature, heat flux in the condenser and pressure ratio in the expansion unit. Flammability, mutagenicity, carcinogenicity, acute toxicity and aquatic toxicity are investigated among other as safety issues. Regulatory parameters include global warming potential GWP, ozone depletion potential ODP, freezing point as well as structure analysis concerning e.g. reactive substructures and stability analysis by autoignition temperature. The overall results reveal that a conflict occurs between optimal thermodynamic performance and safety issues. Fluids with high net power output and low ODP are often highly flammable, whereas well-performing non-flammable working fluids have drawbacks concerning environmental and toxicological issues.

Nevertheless, a set of diverse best-ranked working fluids can be selected for further investigation. Ethanol combines high thermodynamic efficiency in different cases with a

lack of special toxicological or ecotoxicological issues. Hexamethyldisiloxane is especially attractive for high condensation temperatures (above 100 °C). R-152 is a synthetic refrigerant that combines an excellent net power output with reasonable constructional parameters. Alternatively, 1-propanol and cyclopentane are well-performing in a specific range of boundary conditions, whereas 1-propanol should be favored for high condensation temperature, cyclopentane for low ones.

4 Summary and Outlook

The complete PubChem database with more than 72 million chemical substances were screened to find an ideal working fluid for Organic Rankine Cycle in mobile applications like heavy duty trucks, passenger cars and the marine sector. The main results can be summarized as follows:

- Based on different filter criteria the set of suitable working fluids can be brought down to 3,175 chemical substances.
- Acetaldehyde can be identified as a thermodynamic "superfluid", however, it cannot be applied in real world conditions due to security aspects.
- A scoring system has been implemented to allow for a holistic evaluation of ORC working fluids based on thermodynamic, constructional, safety and regulatory aspects.
- Screening the complete chemical space of the PubChem database leads to well-performing and unconventional working fluids partly not known so far.
- A diverse set of best-ranked working fluids including alcohols (ethanol), refrigerants (R-152) as well as siloxanes (hexamethyldisiloxane) is suggested.

In a next step, the selected working fluids should be tested in small-scale test rigs and demonstration units. Furthermore, dynamic simulations are necessary to give more information about the behavior of the working fluids under typical operating conditions.

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