Applied Energy 206 (2017) 887–899

Contents lists available at ScienceDirect

Applied Energy

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

Multi-criteria evaluation of several million working fluids for waste heat recovery by means of Organic Rankine Cycle in passenger cars and heavy-duty trucks

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HIGHLIGHTS

- 72 million working fluids are screened for their use in mobile ORC systems.
- Realistic boundary conditions from series engines of different manufacturers are used.
- A multi-criteria approach evaluates thermodynamic, constructional and regulatory aspects.
- An objective scoring systems to find optimal working fluids is developed.
- So far unknown ORC working fluids can be identified by the large-scale screening.

ARTICLE INFO

Keywords:
Organic Rankine Cycle
COSMO-RS
PubChem
Working fluid
Automotive application
Multi-criteria evaluation

ABSTRACT

Automotive industry is driven by economic and legislative constraints to increase fuel efficiency and reduce CO_2-emissions to a certain extend. To reach the required threshold values, manufacturers consider waste heat recovery by means of Organic Rankine Cycle (ORC) in passenger cars and heavy-duty trucks. This work deals with the crucial issue of identifying an optimal working fluid which is flexible in terms of application and condensing temperature and which is applicable in real systems. For this purpose, a large-scale screening based on computational chemistry and thermodynamic process simulation is coupled with a multi-criteria evaluation. In total, about 72 million chemical substances provided by the PubChem database are screened and more than 3000 promising candidates are evaluated considering COSMO-RS based thermodynamic data as well as constructional, regulatory and security aspects. Five promising working fluids are identified and it is shown that these fluids outperform widely discussed candidates like synthetic refrigerants. Even more remarkably is the fact that within the TOP 100 working fluids only twelve have already been reported in ORC literature. However, the optimal set of working varies as it depends on configuration (with and without mass flow splitting) and condensing temperature. In general, the study demonstrates that a large-scale screening of the complete chemical space can reveal unconventional working fluids for thermodynamic cycles.

1. Introduction

Transport system is driven by economic and legislative constraints to increase fuel efficiency and reduce CO_2-emissions. Manufacturers of passenger cars and trucks consider waste heat recovery by means of Organic Rankine Cycle (ORC) to reach these goals [1,2]. The main differences between the reported systems include the following aspects (Table 1 gives a comprehensive overview about main research work carried out in the last decade without claim of completeness):

- *Application:* Waste heat recovery by means of ORC is relevant for light and heavy duty trucks as well as for automotive applications.
- *Heat sources:* Depending on the application, exhaust gas can be used within the exhaust gas recirculation (EGR) and after the exhaust gas aftertreatment (EGA). Further heat sources are the compressed air charger (CAC) and the cooling loop. If more than one heat source is

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http://dx.doi.org/10.1016/j.apenergy.2017.08.212
Received 3 July 2017; Received in revised form 16 August 2017; Accepted 27 August 2017
Available online 09 September 2017

Nomenclature

Ar	argon
CO_2	carbon dioxide
$\dot{m}$	mass flow rate (kg/s)
N_2	nitrogen
O_2	oxygen
P	electric power (kW)
p	pressure (bar, kPa)
$\dot{Q}$	heat flux (kW)
s	specific entropy (kJ/kg K)
T	temperature (°C, K)

Abbreviations

AIT	autoignition temperature
ASHRAE	American Society of Heating, Refrigerating and Air-Conditioning Engineers
CAMD	Computer Aided Molecular Design
ECHA	European Chemical Agency
EGA	exhaust gas aftertreatment
EGR	exhaust gas recirculation
GWP	Global Warming Potential
ODP	Ozone Depletion Potential
OP	Operational Point
ORC	Organic Rankine Cycle
R	refrigerant
REG	regulatory
TD	thermodynamic

Greek letters

Δh	specific enthalpy difference (kJ/kg)

Subscripts

cond	condenser
net	net power output
ORC	Organic Rankine Cycle

utilized, split circuits are often used as ORC configuration.

- *Condensation:* Condensation can be realized by ambient air but also by the available cooling water circuit.

Main objectives of available simulative and experimental analyses are first and second law efficiency and in some publications also technical aspects of the system. The selection of an appropriate working fluid is hardly investigated for mobile applications. The publications given in Table 1 select working fluids based on main publications from stationary applications, which might be inappropriate due to different boundary conditions in mobile compared to stationary applications. Few research groups investigate working fluid selection with special concern to mobile applications. Glover et al. [3,4] carried out a working fluid selection based on process simulation of sub- and supercritical mode of operation. They screened 95 pure fluids and 10 azeotropic blends from the RefProp database regarding critical temperature and pressure, toxicity and flammability. They identified 18 possible working fluids without defining an optimal one. Lang et al. [5] suggested 3 working fluids (hexamethylcyclotrisiloxane D3, octamethycyclotetrasiloxane D4, water) out of 32 candidates. They included melting temperature, thermal stability, pressure levels, environmental impact, toxicity, flammability, availability, costs, material compatibility, and lubrication properties into account during the screening and evaluation process. Shu et al. [6] considered off-design behavior of seven different working fluids for harvesting of marine engine's exhaust waste heat, Girgin and Ezgi [7] emphasized for the same application how important it is to include safety aspects into the working fluid selection as even in the shipping industry benzene as efficient but carcinogenic working fluid would be a problem. A large-scale screening is carried out by Panesar et al. [8,9]. They investigated water/alcohol-mixtures as working fluid for a novel system whereas a large database of possible second constituents of water blends has been screened. The exact number of screened constituents is not given. Wang et al. [10] investigated nine working fluids from the RefProp database and took safety aspects, environmental impact and performance into account. R245fa and R245ca seem to be promising based on their results. Yang et al. [11–13] investigated ethanol, zeotropic mixture R416A and R245fa/R152a-mixtures. Furthermore, they evaluated eight fluid mixtures based on performance, heat transfer, physical and chemical properties, intersolubility with lubrication oil, security aspects, environmental aspects, electrical isolation capability, and economic aspects. Further studies include fully dynamic ORC simulations for ethanol in heavy duty trucks [14,15], investigation of hot-spots for dynamic operation [16], cascade systems with two expansion units [17] and dynamic response characters for 14 working fluids in engine waste heat recovery [18].

Based on the available studies, the following shortcomings in the available literature are identified:

- It has not been investigated if split cycles with two heat sources (mostly used in trucks) and basic cycles with one heat source (mostly used in automotive industry) require different working fluids or if one working fluid is efficient for both applications.
- It has not been investigated if working fluid selection is influenced by the choice of the condensation temperature.
- The number of investigated working fluids is rather small and depends on the available database.
- A multi-criteria evaluation of working fluids including thermodynamic, constructional, safety, regulatory and environmental aspects has not been carried out.

This leads to the research question, which is addressed in our contribution:

> Is it possible to identify an optimal working fluid, which is suitable for split and basic ORCs at different condensation temperatures in real mobile applications?

To answer this question, we screened about 72 million chemical structures given in the PubChem database by application of the COSMO-RS methodology [19] and evaluated them for two different ORC configurations and three different cooling concepts to get a multi-criteria ranking based on ten different criteria. Our work aims to increase the number of screened working fluids and their chemical classes tremendously compared to group contribution methods (e.g. screening of hydrofluorocarbons [20,21]) or available thermodynamic databases. Furthermore, we intend to increase the number of different evaluation parameters especially concerning construction issues compared to other publications [22]. As the evaluation criteria are discussed and selected together with an industrial advisory board, the study aims for a highly practical approach. To summarize, it is our goal to give a contribution to ORC application in real mobile systems by identifying more elaborate working fluids which are able to fill the gap to profitability of such systems reported recently by Pili et al. [23].

Table 1
Main research work for waste heat recovery in vehicles (applications: A: automotive, HDDE: heavy duty diesel engine; HDT: heavy duty truck; LDDE: light duty diesel engine heat source/sink: CAC: compressed air charger; EGA: exhaust gas aftertreatment; EGR: exhaust gas recirculation, EC: engine cooling).

Authors	Application	Focus	Heat source and sink	Working fluid	Selection process
Arsie et al. [24]	A	Modeling and optimization	Source: EGA Sink: air	R123	Literature survey (not further specified)
Bettoja et al.[1]	HDT	Technical configuration, experimental testing, cost analysis	Source: EGA and/or EGR	ethanol, water-ethanol-mixtures	Process simulation, safety issues
Boretti [25]	A	Cycle simulation concerning fuel saving	Source: EGA Sink: air	R245fa	Literature survey (not further specified)
Capata and Toro [26]	A	Preliminary design of main components	Source: EGA Sink: well water	R245fa, steam	Market inquiry, availability, cost, thermal properties
Cipollone et al. [27]	HDDE	Experimental investigation	Source: EGA Sink: water T_{cond} = 45 °C	R245fa, R1233zd	5 possible fluids, process simulation, flammability
Di Battista et al. [28]	LDDE	Experimental study, effect of heat recovery system on engine performance	Source: EGA Sink: air or water	R236fa	No argument
Dominguez et al. [29]					
Guillaume et al. [30]	truck	Experimental comparison between R245fa and R1233zd	Source: EGA Sink: water T_{cond} > 45 °C	R245fa, R1233zd	Toxicity, flammability, GWP, ODP, availability
Kim et al. [31]	A	Thermodynamic process simulation; single loop ORCs	Source: EGA and EC Sink: T_{cond} = 40 °C	R245fa, R134a	Efficiency, environmental friendliness, flammability, GWP
Luong and Tsao [32]	HDT	Control strategy for base load and load-following ORC	Source: EGR	mixture of ethanol and water (52/48)	No argument
Mastrullo et al. [33]	HDT, A	Modeling and optimization of heat exchangers	Source: EGA Sink: air T_{cond} = 30 °C	R245fa	Literature survey: risk analysis, efficiency, pressure level, GWP
Pradhan [34]	HDTE	Theoretical analysis, real engine data	Source: EGR, EGA, CAC Sink: water, T_{cond} = 36 °C	R123, R245fa, R134a	Literature survey: thermodynamic properties, safety aspects, environmental aspects
Shu et al. [35]	HDTE	Experimental analysis, broad range of engine speed	Source: EGA, Sink: water	R123, R245fa	Literature survey: thermal stability, evaporating temperature, pressure level, toxicity, flammability, cost, environment, dry fluid
Skarke et al. [36]	A, hybrid	First and second law analysis	Source: EGA Sink: air	R245fa	Literature survey
Teng et al. [37,38]	HDTE	Process simulation, supercritical ORC	Source: EGA, EGR, CAC Sink: T_{cond} = 90 °C	Water, R34a, R245fa	Literature survey
Usman et al. [39]	LDTE	Positive and negative aspects of ORC for WHR	Source: EGA Sink: air	R245fa	Literature survey
Wiedemann and Span [40]	HDTE	Potential analyses, dimensioning of system components	Source: EGA	Ethanol	Literature survey

2. Methodology

2.1. Simulation model and thermodynamic properties

First, 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. Thermodynamic properties are gained by the COSMO*therm* software [41] in form of look-up-tables. The underlying Conductor-like Screening Model for Realistic Solvation (COSMO-RS) is a general thermodynamic theory for almost any dense pure or mixed liquid phase with accurate treatment of all interactions on a molecular scale (hydrogen bonds, electrostatic and van der Waals) [42–44]. To extend the applicability range of COSMO-RS up to the critical point, the theory has been combined with a cubic equation of state. Further details on DetailSimORC and the COSMO-RS methodology can be found in our previous publications [45,46]

2.2. ORC configuration

Two different ORC configurations are investigated (Fig. 1). Waste heat recovery from passenger cars takes place after the exhaust gas aftertreatment (EGA) and is realized by a basic ORC consisting of pump, heater (preheating, evaporation, superheating), expander and condenser. Additional heat recovery in a separate branch is investigated, as exhaust gas recirculation (EGR) is standard for heavy duty trucks. It is

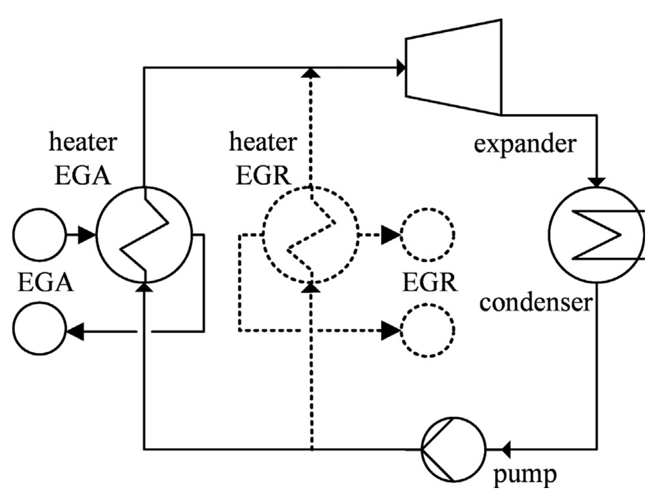

Fig. 1. ORC configuration for car (only exhaust gas aftertreatment, EGA) and truck (EGA and exhaust gas recirculation, EGR).

Table 2
Boundary conditions for ORC simulation.

Parameter	Value	Unit
Maximum working pressure	40	bar
Maximum volume flow ratio	100	–
Minimum condensation pressure (at corresponding condensation temperature)	0.75	bar
Isentropic efficiency of expander	70	%
Isentropic efficiency of pump	80	%
Mechanical efficiency expander	95	%
Mechanical efficiency pump	70	%
Maximum temperature of working fluid	227	°C
Condensing temperatures	40, 75, 100	°C
Degree subcooling	8.15	K
Pinch point temperature difference (condenser)	10	K
Pinch point temperature difference (other heat exchangers)	20	K

important that the exhaust gas temperature after the EGR heater is less than 100 °C to ensure secure and efficient operation of the main combustion engine. Therefore, full exchange of the heat flux within the EGR is ensured in a first step. Afterwards, heat from the EGA is coupled to the ORC until thermodynamic limitations occur. The fraction of working fluid through the EGR path as well as the fraction through the EGA path must be fully evaporated and are mixed subsequently.

2.3. Boundary conditions

Discussions with the industrial advisory board involved in the project led to the boundary conditions for ORC simulation summarized in Table 2. Three different condensation temperatures are investigated within the study. 40 °C is characteristic for direct contact cooling with a separate radiator for the ORC system. For a combined radiator for engine cooling and ORC, the condensing temperature is higher and set to 75 °C. Last, cooling via the cooling loop of the engine with a condensing temperature of 100 °C is investigated. Heat source data are provided by the industrial partners as well (Table 3). As a fully dynamic simulation of a typical drive cycle mode is not possible for such a large number of working fluids, we have chosen two characteristic engine operational points as reference for the simulation, one for the application car and one for the application truck. The operational points were taken from a operational engine map (real test data) as the operational points with the highest share during a typical driving cycle. Therefore, the operational points can be seen as characteristic for the specific application. Another operational point for the application car is chosen and represents the behavior on the highway. This alternative operational point is used for sensitivity analysis.

Table 3
Characteristic engine operational points for application car and truck.

heat source parameter	unit	car (reference)	truck (reference)	car (alternative)
EGA inlet temperature	°C	440.0	270.0	689.0
EGA mass flow rate	kg/h	60.3	870.0	150.1
EGA inlet pressure	bar	1.00	1.00	1.00
EGR inlet temperature	°C	–	453.0	–
EGR outlet temperature	°C	–	100.0	–
EGR mass flow rate	kg/h	–	243.0	–
EGR inlet pressure	bar	–	2.3	–
mass fraction CO_2	%	12.30	15.23	12.30
mass fraction O_2	%	0.70	7.74	0.70
mass fraction H_2O	%	13.80	6.76	13.80
mass fraction N_2 + rest	%	73.20	70.27	73.20

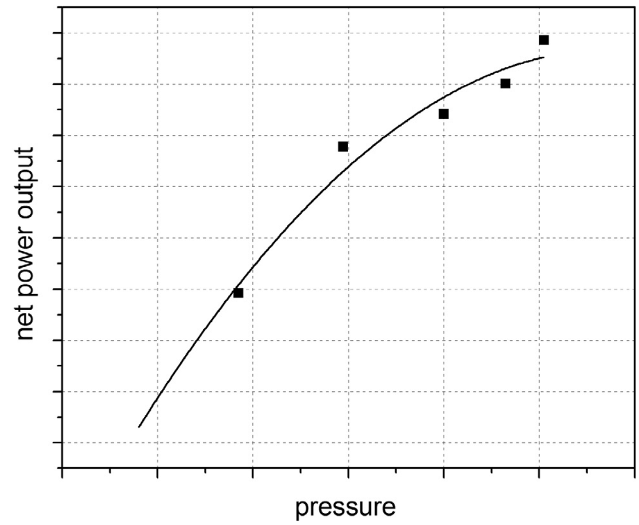

Fig. 2. Qualitative behavior of net power output depending on pressure (discrete simulation values and polynomial description).

2.4. Evaluation criteria

The most important evaluation criterion for waste heat recovery in mobile applications is the net power output as it is directly related to fuel saving and reduction of CO_2-emission. As the net power output of an ORC strongly depends on the working pressure within the system, two predominant kinds of behavior must be considered: a bell-shaped curve and a steady increase of net power output with increasing working pressure [47]. To reduce simulation time but accounting for both cases, an optimization strategy for the working pressure is implemented in DetailSimORC. The method is based on the discrete calculation of different working pressures (maximum pressure p_{max}, $0.95{\cdot}p_{max}$, $0.75{\cdot}p_{max}$, $0.50{\cdot}p_{max}$, $0.25{\cdot}p_{max}$). Subsequently, a polynomial fit leads to the optimal working pressure with respect to maximum net power output (Fig. 2). Based on the optimized system pressure, a temperature-heat flux-diagram is automatically created to evaluate the process graphically (Fig. 3).

Relative evaluation of net power output is realized based on the efficiency index EI_i:

$$EI_i = \frac{1}{N_C}\sum_{j=1}^{N_C}\frac{P_{i,j}}{P_{max,j}} \tag{1}$$

EI_i gives the relative difference between the net power output of a specific working fluid i, and the maximum net power output in each of the six investigated cases j. Efficiency index is of high applied interest as net power output – compared to thermal efficiency – is directly proportional to fuel savings in mobile applications.

The developed multi-criteria evaluation considers constructional, safety and regulatory parameters next to net power output. Five constructional parameters are evaluated: minimum working pressure is a key issue related to possible air entry into the system during operation; maximum pressure is related to the costs of heat exchangers; pressure ratio is an important design criteria for expanders; maximum temperature in the system influences material selection for heat exchangers and thermal degradation of working fluids; heat flux in the condenser is highly relevant in mobile applications as space for heat exchange surface of condenser is limited.

The European Union bans organic substances with influence on global warming and ozone due to the Montreal Protocol. Therefore, the regulatory parameters global warming potential (GWP) and ozone depletion potential (ODP) are simulated, as described by Kazakov et al. (using the more accurate MOOH method to estimate atmospheric lifetime and the PM7 functional for the simulation of IR spectra) [48–52]

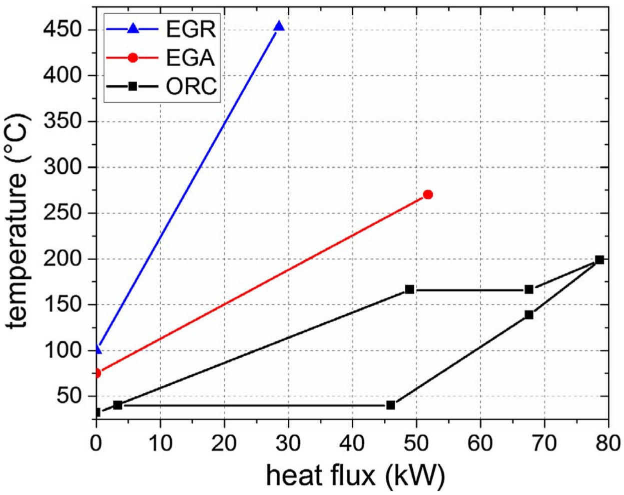

Fig. 3. Graphical evaluation of ORC (thermodynamic state changes of the whole cycle) in a temperature-heat flux-diagram (working fluid: R245fa, PubChem ID 68030).

and by Solomon et al. (slightly adapted according to WMO recommendations) [53,54]. Furthermore, freezing at motor downtime should be avoided. For this reason, the melting point is calculated as evaluation criterion using the COSMO*quick* software [55,56]. It should be noted that the melting point is not treated as filter but as evaluation criterion, as additives would allow to lower the melting point easily. Finally, the autoignition temperature (AIT) range is predicted in a semi-quantitative way as a measure of stability, using the lowest value of systematical radicalic hydrogen abstraction in a molecule, and binning them according to threshold values below 370 kJ/mol (associated with low AITs), between 370 and 407 kJ/mol (intermediate AITs), and above 407 kJ/mol (high AITs).

3. Results

3.1. Application of filter criteria

First, the initial data set of 72,725,677 PubChem entries is filtered by industrial relevant filter criteria. The following compounds are excluded from further investigation by structural analysis and COSMO-RS calculations, as they are not suitable for industrial applications:

1. too large compounds associated with low vapor pressures (i.e., compounds having more than 15 atoms, not counting hydrogen and fluorine)
2. compounds with unsuitable substructures (multi compound structures; ionic structures; metal or isotope containing compounds; reactive substructures, e.g., nitro groups or multiple unsaturated bonds; sulfur containing compounds for olfactory reasons)
3. stereoisomers (i.e., enantiomers, as R- and S-isomers provide the same thermodynamic efficiency)
4. compounds with vapor pressure below 75 kPa for a condensation temperature of 100 °C
5. compounds with critical temperature below 70 °C

Vapor pressure above 75 kPa is taken to avoid extensive air entry into the system during operation. Lastly, subcritical processes are the focus of the study fixing the necessary critical temperature. Application of the filter criteria leads to a final dataset of 3174 working fluids which are evaluated within the following chapters.

3.2. Thermodynamic evaluation

First, net power output is taken as a single criterion as it is directly connected to fuel savings and reduction of CO_2 emission. As this study intends to find an optimal working fluid which can be applied in both applications (truck and passenger car) and for three different condensation concepts, six different simulations are carried out. ORC with and without exhaust gas recirculation in combination with each of the chosen condensation temperatures (40 °C, 75 °C, 100 °C). Simulation of each of the cases leads so six lists which are sorted according to net power output. If one builds a list of the TOP 50 performing working fluids for all six cases, 78 working fluids are at least in one of the six TOP 50 lists, 29 are in two lists, 17 are in 4 lists, 9 are in five lists.

Only one working fluid is among the TOP 50 in all six cases. The working fluid is ranked no. 3, no. 4 and no. 2 for 40 °C, 75 °C, and 100 °C condensation temperature in passenger cars. For heavy-duty trucks, it is ranked no. 15, no. 2 and no. 1 for the different condensation temperatures. Thus, it reaches an efficiency index EI_i according to Eq. (1) of 95 %, outperforming all other investigated working fluids. The PubChem identifier of the working fluid is 177, hence, being acetaldehyde. From a thermodynamic point of view, this result is in accordance with other theories of fluid selection like CAMD as Papadopoulos et al. [57] identified acetaldehyde as highly efficient for low-temperature ORCs as well. However, according to common security data of acetaldehyde, it is extremely flammable, the vapor phase leads to highly explosive vapor-air-mixtures, highly explosive peroxides occur in combination with air and the auto-ignition temperature is just about 155 °C. Hence, we can sum up that acetaldehyde may be an optimal working fluid from a thermodynamic point of view, however, it cannot be used in serial-produced cars and trucks due to security aspects. Based on this result, we stated in our previous publication [45,46] that next to acetaldehyde no other working fluid can be identified as exceptionally efficient compared to the others. However, six further working fluids exceed an efficiency index of 90% and further 33 working fluids are above 80%.

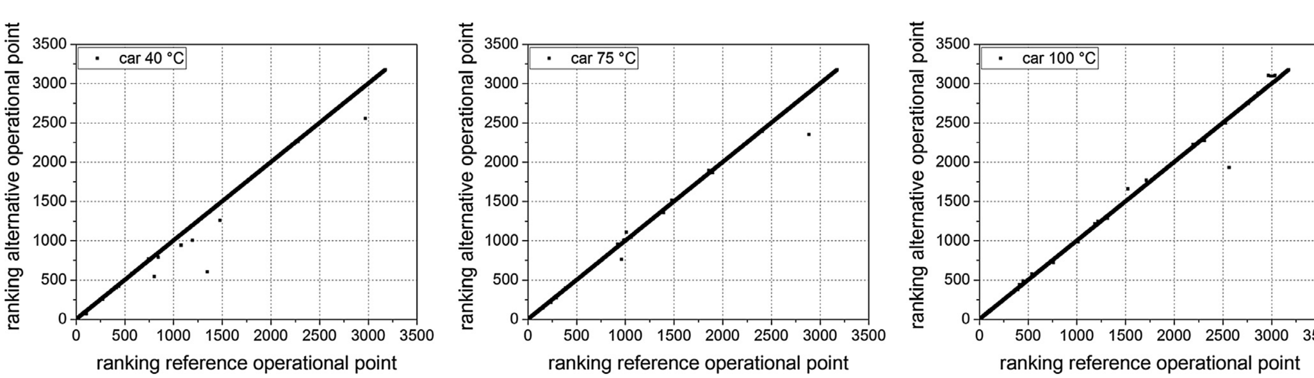

Fig. 4. Ranking for alternative engine operational point compared to reference operational point (application car, three different condensation temperatures).

3.3. Sensitivity analyses

The results in Section 3.2 are gained with the boundary conditions displayed in Table 2 and the reference engine operational points of Table 3. Subsequently, the thermodynamic results are tested concerning their sensitivity. Exemplarily, Fig. 4 compares the ranking of the working fluids for the reference operational point with the ranking if one assumes an alternative operational point with higher temperature and load as it occurs for example on a highway drive (right column in Table 3). It is obvious that the operational point does not change the ranking except for a few working fluids. All working fluids among the TOP 50, however, are still in the TOP 50 regardless which operational point is chosen. The ranking is almost independent on the temperature and load of the operational point.

The working pressure is a crucial parameter in the design of ORC systems (compare Fig. 2), so further sensitivity analyses concerning the maximum pressure in the system are carried out. First, the maximum pressure is increased from 4000 kPa to 5000 kPa, second, the maximum pressure is decreased to 3000 kPa. Fig. 5 compares the ranking for a maximum pressure of 4000 kPa with the ranking for a maximum pressure of 5000 kPa. Condensation temperature is chosen to 75 °C and both applications are investigated. Although the ranking among the TOP 50 working fluids change slightly, 47 of the working fluids remain in the TOP 50. For the case of lower pressures (3000 kPa) the trend is similar, whereas more than 60% of the working fluids remain in the TOP 50. We can summarize that the thermodynamic fluid selection process is a robust method even for alternating boundary conditions and heat source characteristics. As the method leads to a diverse set of well-performing working fluids, non-thermodynamic criteria have to be taken into account in a next step.

3.4. Constructional criteria

Net power output alone is not an appropriate objective function (Section 3.2). Hence, constructional parameters have been investigated as well. Exemplarily, results for net power output and five additional constructional parameters are shown for the TOP 50 working fluids of the application car at a condensation temperature of 75 °C. Net power output drops by 13.0% within the TOP 50 working fluids. Median value is 1.04 kW whereas all working fluids exceed a minimum value of 1.01 kW. Most of the working fluids have a minimum pressure between 75 kPa and 150 kPa, just a few working fluids condense at pressures above 250 kPa. The median value for the minimum pressure is 125 kPa. The maximum pressure is generally higher than 2000 kPa, however, just 10% of the working fluids reach their highest net power output at the maximum working pressure of 4000 kPa. The median value for the maximum working pressure is 2850 kPa. Regarding the expansion unit, the pressure ratio within the system is relevant. It is shown that the TOP 50 working fluids reach values between 10 and 36 with a median value of 25. For the maximum temperature in the system a clear trend occurs as more than 65% of the TOP 50 working fluids reach their highest net power output with the highest possible temperature of 500 K. Last, the heat flux in the condenser is evaluated. Within the TOP 50 working fluids, the heat flux is almost constant with a slight increase of about 3.3%. Based on Fig. 6 it is deduced that constructional aspects are highly significant for fluid selection in real systems. If one compares for example working fluids ranked no. 1–5, minimum pressure ranges from 75 kPa to 375 kPa, maximum pressure from 2000 kPa to 4000 kPa and, therefore, pressure ratio from 11 to 34.

3.5. Regulatory and safety parameters

Besides thermodynamic and constructional parameters, regulatory acceptance of the potential working fluid is a crucial aspect for its application in industry. Global warming potentials (GWP) and ozone depletion potentials (ODP) of the best ranked working fluids are displayed in Fig. 7. Nine working fluids have a GWP higher than the allowed threshold value of 150 (according to the EU regulation EG-VO 517-2014), whereas one of these fluids is just slightly higher (335). Comparison of OPD shows that 30 of the 50 fluids have an ODP of zero. Note that these fluids have not been excluded so far as the large-scale screening in this study follows the rule “exclude fluids due to just one critical parameter as late as possible”. However, ODP issues are highly relevant for the discussion and the multi-criteria approach in Section 4.

Next to ODP and GWP, two further fluid properties in vehicle ORCs are considered: autoignition temperature and melting point (Fig. 8). Autoignition temperature is subdivided into three classes (see Section 2.4). 27 working fluids have a low autoignition temperature, 15 are in the class of intermediate values and only eight working fluids reach high values for this safety criterion. Eleven working fluids have a melting point higher values than -40 °C which is set as threshold value to prevent the working fluid of freezing during standstill in winter even in northern European countries.

4. Multi-criteria approach and discussion

Section 3 has given a broad overview about relevant thermodynamic, constructional, regulatory and safety parameters. However, the evaluation has been carried out as “single criterion evaluation”.

So far, the results are based on net power output, however, net power output just slightly decreases from one to the other working fluids. Hence, it is possible that a fluid which is ranked number 65 for car 75 °C is still the best choice as in combination with all other parameters it gives the best overall behavior. Furthermore, we want to find

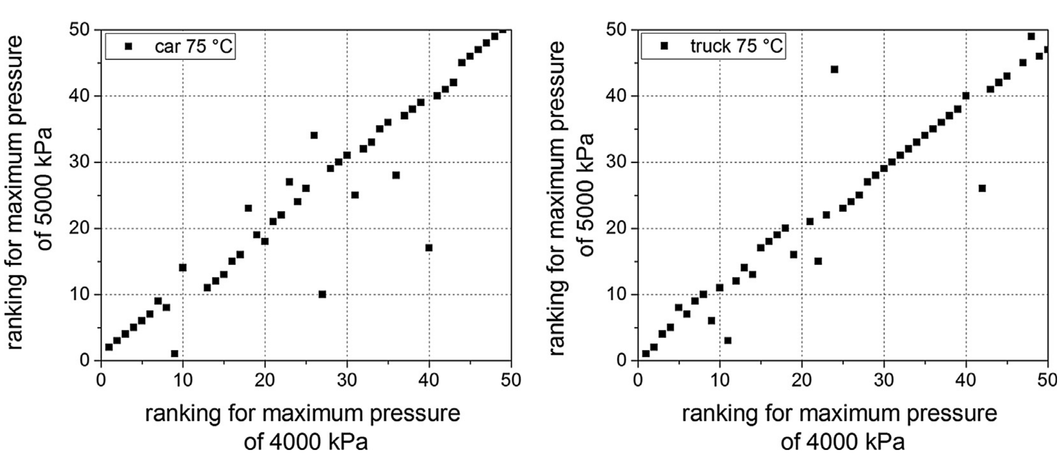

Fig. 5. Ranking for increased maximum pressure compared to reference pressure.

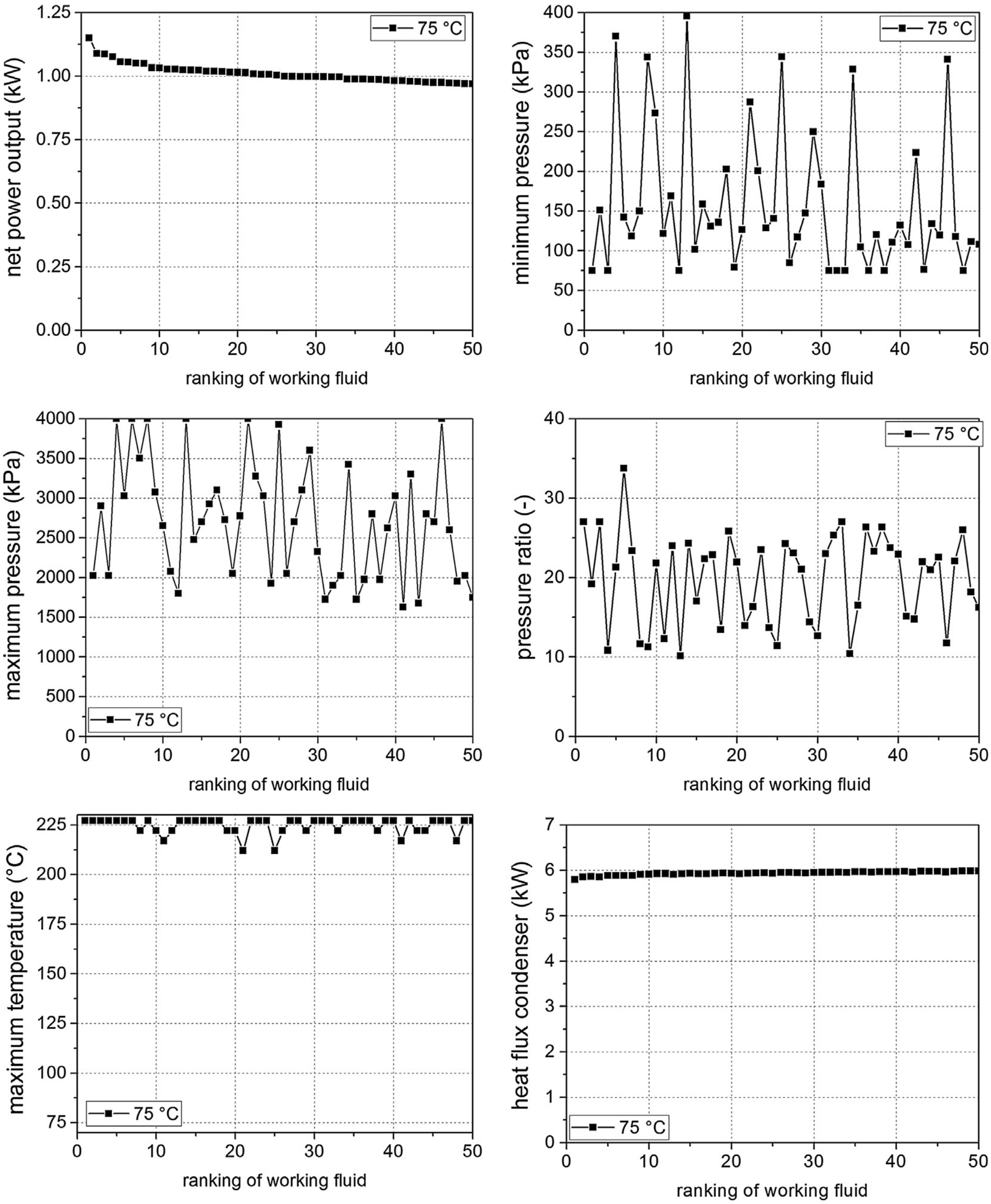

Fig. 6. Net power output (upper left) and five constructional parameters for the TOP 50 working fluids (application car, condensation temperature 75 °C).

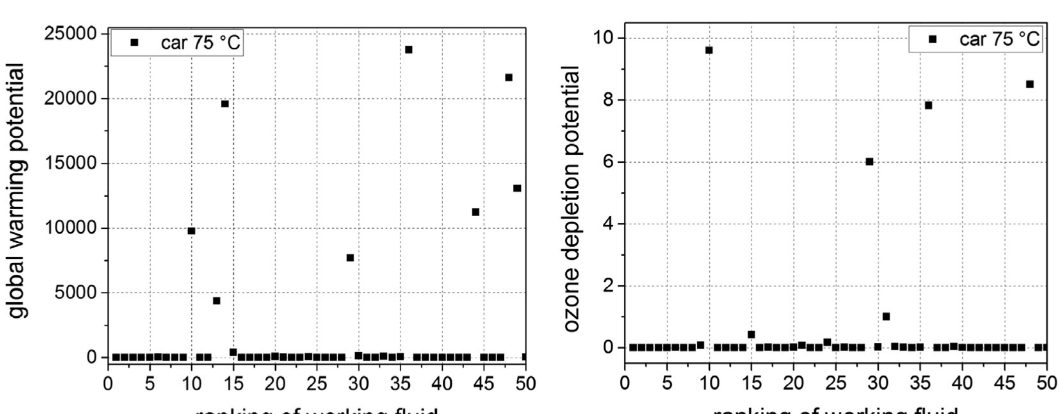

Fig. 7. Global warming potential (left) and ozone depletion potential (right) for the TOP 50 working fluids (application car, condensation temperature 75 °C).

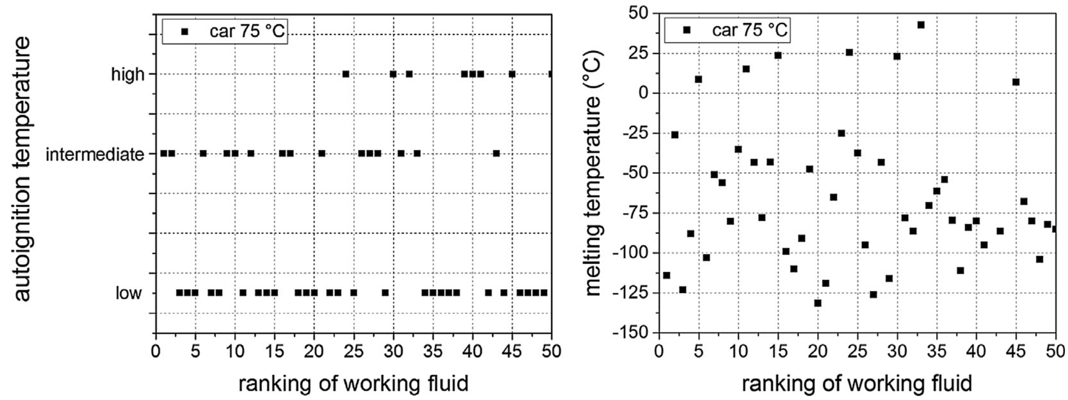

Fig. 8. Autoignition temperature (left) and melting point (right) for the TOP 50 working fluids (application car, condensation temperature 75 °C).

an optimal working fluid which is applicable in all applications and condensation temperatures and the investigated application car at 75 °C condensation temperature is just one of six cases.

Therefore, we must ask the following applied research question: How can we transform the gained knowledge about single parameters into an overall evaluation of all investigated working fluids in all applications and for all condensation temperatures? The main attributes of such an overall evaluation include:

1. The scoring system must be applicable to all working fluids.
2. The scoring system must consider all single criterions, however, with different weighting factors as some parameters are more important than others in real systems.
3. Single criteria must be evaluated based on relative (e.g. net power output is x% higher than the most efficient working fluid) or absolute values (e.g. minimum pressure is higher than ambient pressure).

The multi-criteria approach is a three-step process. First, 5.00 points are awarded for thermodynamic and constructional parameters. Second, 5.00 points are awarded for regulatory and safety issues. Third, exclusion criteria are defined for toxicological issues. Note that the evaluation parameters as well as their weighting have been discussed and selected together with an industrial advisory board in which about 15 companies (OEMs, suppliers, etc.) were involved. Together, we tried to make the evaluation process as applied to real applications as possible, still knowing that every multi-criteria evaluation based on weighting factors is always partly arbitrary. However, one of the strengths of our approach is the opportunity to adjust the evaluation criteria and their weighting to changing boundary conditions (e.g. in case of new legislative restrictions).

4.1. Multi-criteria approach

4.1.1. Thermodynamic and constructional parameters

Table A.1 summarizes the threshold values for the evaluation of thermodynamic and constructional parameters. Net power output is still the most important parameter in the evaluation, so the parameter is awarded with the highest score (2.00 points). Relative boundaries based on the median values of the TOP 200 working fluids in each case are chosen. Subsequently, five groups are formed. Working fluids exceeding the median net power output of the TOP 25 get 2.0 points. If net power output is higher than the TOP 50, TOP 100 and TOP 200, 1.5, 1.0 and 0.5 points are awarded, respectively. This example shows that highly efficient working fluids are of course advantageous compared to less efficient working fluids. However, even a working fluid which is ranked 225 and, therefore, gets 0.0 points for the criteria net power output, can still reach 8.25 points for all other parameters. Hence, it might still be considered as optimal working fluid. This example shows that the multi-criteria approach is a powerful tool for working fluid selection in ORC systems for vehicles. Subsequently, further thermodynamic and constructional parameters are briefly described. Details can be found in Table A.1. The minimum pressure is set as boundary condition to 75 kPa in Table 2. However, values above 100 kPa would increase the security of the system as air cannot get into the system during operation. Optimal pressure is set between 175 kPa to 250 kPa as even during standstill airflow into the system is hardly possible. Maximum pressure must be as low as possible concerning constructional costs due to necessary material strengths. The threshold values are based on the median values of the TOP 200 working fluids as this parameter must be evaluated relative from one working fluid to the other. As the temperature before the expansion unit is almost similar for all working fluids, just 0.25 points are awarded for this parameter. For the heat flux in the condenser, the scoring system is slightly different for the two applications. As the heat flux varies by more than 20% for the application truck, four groups are built which are awarded with 0.75 points, 0.50 points, 0.25 points, and 0.00 points, respectively. For the application car, the deviation in the heat flux is far less and, therefore, only two groups (0.25 points and 0.00 points) are formed. The scoring system for the expansion ratio is based on absolute values. Volumetric expanders like scroll and screw expanders reach high efficiencies with a pressure ratio between 3 and 10. Efficient mini-turbines have a pressure ratio lower than 30. Therefore, a pressure ratio between 3 and 10 is favorable as both, volumetric expanders and mini-turbines are applicable. Between 10 and 30 only mini-turbines can be considered. Values lower than 3 and higher than 30 are highly problematic for the construction of an expander and, therefore, awarded with 0.00 points.

4.1.2. Regulatory and safety parameters

A scoring system for regulatory criteria has been developed similar to thermodynamic and constructional parameters. Each compound can achieve a maximum score of five points for fulfilling all regulatory criteria. Most importantly, the molecular structures should be stable during operation. At the same time, the handling at the garage for inspection and repairs should be kept as easy as possible, so malodorant fluids such as sulfur-containing compounds are to be avoided. Compounds fulfilling the structural criteria are assigned 1.0 points. For each of the following criteria, a maximum score of 1.0 points can be achieved: the melting point is below −40 °C, the GWP is lower than 150, it has no ODP and the AIT is predicted to be high, above 400 °C. If the ODP is larger than zero, but lower than a threshold of 0.2 (based on the Class II ODP threshold value defined by the US EPA), then 0.5 points are assigned for the ODP criterion. Compounds with intermediate AIT values of at least 200 °C are assigned 0.5 points, otherwise zero.

4.1.3. Toxicological criteria and flammability

Toxicological and ecotoxicological assessment is desired for a holistic evaluation and the selection of the best possible ORC working fluid. Due to the biological complexity, toxicological assessment cannot be made in an automated way. Instead, toxicological information has to be aggregated separately for each potential working fluid. For a systematic toxicological evaluation, information collected by ECHA, the official regulatory authority of the European Union, is used for notified and registered substances; more specific, the ECHA Classification and Labeling Inventory, preferably based on harmonized classifications [58]. Additional sources of information are Material Safety Datasheets provided by chemical suppliers and the GESTIS database [59]. Fluids are not recommended as potential ORC working, if they exhibit one or more of the following criteria:

- carcinogenic (all classes)
- mutagenic (all classes)
- reproductive effects (all classes)
- highly flammable (classes Flam. Liq. 1 or Flam. Gas 1)
- acute toxic to humans (classes 1, 2, 3)
- toxicity to specific human organs (classes SE1, RE1, SE2, RE2)
- acute and chronic aquatic toxic (classes 1 or 2)
- knowingly damaging the ozone layer (class 1)

4.2. Discussion

The overall results reveal that a trade-off between optimal thermodynamic performance and safety issues occurs. Fluids with high net power output and low ODP are often highly flammable, well-performing non-flammable working fluids have drawbacks concerning environmental and toxicological issues. General considerations with respect to the different top-scoring compound classes are summarized in Table 4. Next, a list of the TOP 15 working fluids based on the averaged sum of all six cases is generated (Table 5). The results reveal that among the TOP 15 overall fluids, well-known as well as unconventional working fluids occur. Ethanol, hexamethyldisiloxane, and octamethyltrisiloxane are already used in mobile and stationary ORC-systems. 1-propanol and methanol have been investigated in numerous publications in the past. Benzene-derivates have also been discussed in the literature. However, mostly toluene, ethylbenzene and trimethylbenzene were investigated [60]. Furthermore, different chemical classes of working fluids are found among the TOP 15 (alcohols, siloxanes, refrigerants, benzenes, amines). Note that although regulatory parameters have been taken into account in Table 5, the toxicological evaluation has been carried out afterwards. Therefore, some fluids (like furan) are not applicable although scoring is well based on thermodynamic and regulatory parameters. A list of the TOP 100 working fluids is provided in the supplementary data.

Due to these constraints, Table 5 is investigated again including toxicological aspects as well as data from open literature. Furthermore, the specific application and condensation temperature are investigated in more detail. Thus, it is possible to select a set of diverse best-ranked fluids for further investigation. The ranking of those fluids in the different cases is shown in Table 6.

The overall best ranked fluid is ethanol. No special toxicological or ecotoxicological issues are associated with ethanol; especially, no acute or chronic toxicity, and likewise no toxicity to aquatic species, according to the harmonized CLP. It has no ODP, a non-significant GWP and a very low melting point. From a thermodynamic point of view, ethanol is universally applicable to all OPs under investigation. It ranks at least third for all cases (apart from application truck at a condensation temperature of 40 °C). For application car at a condensation temperature of 75 °C, ethanol is even the best performing ORC fluid.

The related fluid methanol provides a similar net power output as ethanol. For application truck at 40 °C, the thermodynamic efficiency of methanol is even 11% higher as compared to ethanol as ORC fluid. For higher condensation temperatures, 1-propanol (CAS 71-23-8) is suitable. It offers similar thermodynamic and regulatory properties as ethanol. At 100 °C, 1-propanol scores best for application car and second best for application truck OP. However, ethanol, 1-propanol and methanol are flammable liquids, so they must be handled with care and without contact to air-oxygen. Furthermore, note that methanol – but not ethanol or 1-propanol - is classified as toxic (acute toxicity and specific human target organ toxicity).

The working fluid hexamethyldisiloxane scores second in the overall ranking at higher condensation temperatures of 100 °C. It provides an alternative to the mentioned alcohols as ORC fluids. Recent experiments show that hexamethyldisiloxane can be operated at high temperatures and pressures without significant stability issues [61] and is, therefore suitable for high temperature ORCs [62]. The thermodynamic efficiency is in the same range of ethanol. Hexamethyldisiloxane does not have issues concerning GWP or ODP and is liquid at −40 °C. According to the lead dossier submitted to ECHA, no significant human health issues occur: it shows neither organ specific, acute or chronic

Table 4
Advantages and disadvantages of different compound classes for the use in mobile ORC applications.

Compound class	Advantages	Disadvantages
Alcohols	▪ High thermodynamic performance ▪ Good toxicological profile ▪ Low GWP, no ODP	▪ Flammable ▪ Not stable at high temperatures
Siloxanes	▪ High thermodynamic performance ▪ Not human toxic ▪ Low GWP, no ODP	▪ Flammable ▪ Environmental toxicology
Fluoroalkanes	▪ Generally high thermodynamic performance ▪ Perfluorated compounds very stable ▪ No ODP	▪ Potentially high GWP ▪ Release of hydrogen fluoride at high temperatures
Alkanes	▪ Reasonable toxicology ▪ Low GWP, no ODP	▪ Intermediate performance ▪ Flammable
Chloroalkanes	▪ Very high thermodynamic performance ▪ No or low flammability	▪ Toxicology of high concern ▪ Carcinogenicity ▪ ODP
Carbonyls and Carboxyls	▪ Very high thermodynamic performance (e.g., acetaldehyde, acetone, methyl formate) ▪ Good toxicological profile ▪ Low GWP, no ODP	▪ Flammable or highly flammable ▪ Unstable

Table 5
Overall ranking for all six cases.

PubChem-ID	name	score TD	score REG	score overall
702	Ethanol	3.25	4.50	7.75
24764	Hexamethyldisiloxane	2.46	5.00	7.46
8029	Furan	2.29	5.00	7.29
12223	1,2-Difluoroethane (R-152)	2.67	4.50	7.17
9741	1,3-Difluorobenzene	2.17	5.00	7.17
16910	1,2,3,5-Tetrafluorobenzene	2.08	5.00	7.08
57540913	*N*-2-Di(methyl)butan-1-amine	2.08	5.00	7.08
11084	1,2,3,4-Tetrafluorobenzene	2.04	5.00	7.04
9696	Pentafluorobenzene	2.00	5.00	7.00
1031	1-Propanol	2.42	4.50	6.92
24705	Octamethyldisiloxane	1.88	5.00	6.88
887	Methanol	2.33	4.50	6.83
6409	2,2,2-Trifluoroethanol	2.33	4.50	6.83
54221643	1,2-Difluoro-1-methoxyethane	2.21	4.50	6.71
11675	2,2,3,3-Tetramethylbutane	1.96	4.75	6.71

Table 6
Ranking of selected ORC working fluids for mobile applications.

Name	CID	Car				Truck				Rank	
		over-all	40 °C	75 °C	100 °C	over-all	40 °C	75 °C	100 °C	best	global
Best ranked fluids											
ethanol	702	1	3	1	2	2	24	1	3	1	1
hexamethyl-disiloxane	24764	3	14	19	3	1	61	3	1	1	2
R-152	12223	7	1	79	292	3	1	4	5	1	4
1,3-difluoro-benzene	9741	7	4	16	8	5	12	20	11	4	5
1-propanol	1031	2	182	4	1	87	2027	35	2	1	10
Good thermodynamic score											
methanol	887	41	22	222	26	10	21	7	13	7	12
R-30	6344	200	6	379	713	13	17	9	25	6	36
methyl formate	7865	353	591	213	288	97	124	95	69	69	172
Reference fluids											
Novec 649	2782408	510	786	181	954	756	923	302	1281	181	621
R-365mfc	67884	1004	1231	433	1351	674	665	270	1128	271	804
R-1336mzz(Z)	52991879	694	372	832	938	941	669	1148	1247	373	808
R-1233zd	2779022	1454	349	1410	2469	1504	465	1687	2244	350	1413
R-245fa	68030	1540	955	1728	2025	1576	865	1649	2049	866	1521

toxicity, nor carcinogenicity or mutagenicity. Regarding the disposal of this fluid, its environmental impact needs to be taken into account, as it is harmful to aquatic organisms.

The refrigerant R-152 (1,2-difluoroethane) is the best ranked fluid at lower condensation temperatures for both truck and car. It provides high net power output. It fulfils all regulatory criteria, as it has no reactive substructures, no ODP, low GWP (53) and a low melting point (calc. −93 °C). From a thermodynamic point of view, R-152 is a versatile fluid applicable to different cases. The refrigerant R-152 is not yet present in the ECHA C & L inventory, so full toxicological and safety assessment cannot be made for the time being. However, material safety datasheets (MSDS) indicate a highly toxic and flammable compound (outdated DSD hazard codes: “F” and “T”). When R-152 is heated to decomposition, it emits toxic vapors of hydrogen fluoride, forming hydrofluoric acid upon contact with skin or lung tissues.

R-30 (dichloromethane) is a similar well-performing compound. It provides the same net power output as R-152 for application car at 40 °C. It has an even lower GWP (8.7) and a low ODP (calc. 0.01). In contrast to R-152, this fluid is not flammable and does not emit toxic vapors of hydrogen fluoride. R-30 is the least toxic of the simple chlorohydrocarbons, however, there are some toxicological issues associated with R-30. Current research is not yet clear whether it may be carcinogenic, and since 2010, the fluid is banned in the European Union for consumers because of its acute inhalation hazards. In general, R-30 should only be applied in well-ventilated rooms by trained professionals.

1,3-Difluorobenzene is a working fluid that has not been investigated for ORC-systems so far. Although the efficiency is just average for all investigated fluids, it has an excellent behavior for the regulatory parameters which leads to a TOP 20 ranking in all six cases. It has a GWP of around 50, no ODP and a potentially high autoignition temperature. Furthermore, it has no relevant toxicological issues.

From a thermodynamic point of view, methyl formate provides a very high efficiency in the ORC, comparable to (or even outperforming) the refrigerants R-152 and R-30. At the same time, methyl formate is void of serious adverse health effects, and it has no significant impact on the environment (no aquatic toxicity, no significant GWP, no ODP). The downside of methyl formate is that it contains non-aromatic double bonds and is extremely flammable.

Despite their lower performance regarding mobile ORC applications, the physical and chemical properties of the defined reference fluids are well-investigated. Many of them are less toxic and potentially more stable than the ORC fluids discussed above. The modern fluids R-1336mzz(Z), R-1233zd and Novec 649 all have very low GWPs, in contrast to the classical fluids R-245fa and R-365mfc. Thus, it is worth looking at these reference fluids as well.

The common benchmark fluid R-245fa (pentafluoropropane; overall rank #1521) achieves a net power output up to 9.9 kW in the ORC simulations (truck, 40 °C: rank #865), thus a loss of 25% in performance, as compared to R-152. Even more, R-245fa has a GWP of 1030, which is, according to current EU regulations for the mobile sector, by a factor of seven too high.

The related refrigerant R-365mfc (1,1,1,3,3-pentafluorobutane; overall rank #804) performs best in the intermediate temperature range (truck, 75 °C: rank #270; car, 75 °C: rank #433). In comparison to ethanol, the thermodynamic efficiency is 20% lower for the application truck and even 33% lower for the application car. It is not toxic at room temperature, but it has the same flammability class as ethanol. As partially fluorinated compound, it might emit toxic vapors of hydrogen fluoride, when heated to decomposition. Similar to R-245fa, its GWP of 794 is far too high.

The comparison to other typical benchmark fluids reveals a similar loss in performance, e.g. R-1233zd (trans-1-chloro-3,3,3-trifluoropropene: between −27% and −59%; overall rank #1413) or Novec 649 (perfluoro-2-methyl-3-pentanone: even −40% to −59%; overall rank #621). However, these two benchmark fluids have no issues concerning the GWP (R-1233zd: GWP = 28; Novec 649: GWP = 1) and Novec 649 is stable up to 300 °C, according to the published material safety data sheet.

The benchmark fluid R-1336mzz (cis-1,1,1,4,4,4-hexafluorobut-2-ene; overall rank #804) has a similar thermodynamic performance as R-245fa or R-365mfc, but with a very low GWP of 4. R-1336mzz performs best at the low temperature range (car, 40 °C: rank #372; truck, 40 °C: rank #669). The thermodynamic efficiency higher than R-1233zd and Novec 649 over the full temperature range (loss in performance between −31% and −53%). According to recent research, it is stable at typical ORC conditions with an expected ASHRAE safety class of A1, according to information provided by the chemical supplier. At the same time, no toxicologically significant effects were observed; it is not mutagenic, teratogenic or carcinogenic.

5. Conclusion

Within the presented project, we screened about 72 million working fluids and - for the first time - evaluated such a number of substances based on a multi-criteria approach based on industrial boundary conditions and evaluation methods. Therefore, the study gives a contribution for ORCs in real dynamic applications (exhaust gas from heavy-duty truck and passenger cars). The main results can be summarized as follows:

- With the compound acetaldehyde, it was possible to identify a thermodynamically optimal working fluid which suits different ORC configurations and condenser concepts. However, acetaldehyde must be discarded due to safety issues.
- GWP, ODP and autoignition temperature were firstly applied as evaluation criteria in a large scale screening.
- A diverse set of promising candidates for real systems with ethanol being the most versatile working fluid can be identified. ORC configuration and condensing temperature are identified to have the highest influence on the overall ranking.
- Synthetic refrigerants which are discussed in the literature as benchmark fluids perform far worse under realistic boundary conditions than the given promising candidates.

To summarize, the results revealed that some theoretically ideal working fluids are not able to stand the high requirements in real systems. Hence, the work gives a contribution to future ORC research as we identified possible new working fluids and presented trade-offs which should be taken into account for applied fluid selection keeping real systems in mind. Therefore, the study tries to give knowledge about promising working fluids which should be investigated in more detail theoretically and within experimental setups in near future.

We intend to test the promising candidate hexamethyldisiloxane in our ORC test field to show its feasibility under real world conditions and to evaluate its behavior within different turbine configurations.

Acknowledgments

The project was funded by the FVV (German Research Association for Combustion Engines e.V./Project 1155/PG 1). Within the project several companies were active in the industrial advisory board. The authors highly appreciate the funding of the FVV and the valuable input of the advisory board.

Conflicts of interest

The authors declare the following competing financial interest(s). Markus Preißinger and Dieter Brüggemann declare no competing financial interests. Andreas Klamt is chief executive officer, and Johannes Schwöbel is an employee of COSMOlogic. COSMOlogic commercially distributes the COSMO*therm*, COSMO*quick*, and TURBOMOLE software used in this paper.

Appendix A

See Table A.1.

Table A.1
Evaluation parameters, threshold values and weighting factors for overall evaluation.

Application truck		Application car	
Net power output			
$P_{net} > P_{median\ 25}$	2.0 points	$P_{net} > P_{median\ 25}$	2.0 points
$P_{net} > P_{median\ 50}$	1.5 points	$P_{net} > P_{median\ 50}$	1.5 points
$P_{net} > P_{median\ 100}$	1.0 points	$P_{net} > P_{median\ 100}$	1.0 points
$P_{net} > P_{median\ 200}$	0.5 points	$P_{net} > P_{median\ 200}$	0.5 points
$P_{net} < P_{median\ 200}$	0.0 points	$P_{net} < P_{median\ 200}$	0.0 points
Minimum pressure values in kPa			
$175 < p_{min} < 250$	0.75 points	$175 < p_{min} < 250$	0.75 points
$100 < p_{min} < 175$	0.50 points	$100 < p_{min} < 175$	0.50 points
$p_{min} > 250$	0.25 points	$p_{min} > 250$	0.25 points
$p_{min} < 100$	0.00 points	$p_{min} < 100$	0.00 points
Maximum pressure			
$p_{max} < p_{max,\ median\ 200}$	0.75 points	$p_{max} < p_{max,\ median\ 200}$	0.75 points
$p_{max} < p_{max,\ median\ 50}$	0.50 points	$p_{max} < p_{max,\ median\ 50}$	0.50 points
$p_{max} < p_{max,\ median\ 25}$	0.25 points	$p_{max} < p_{max,\ median\ 25}$	0.25 points
$p_{max} > p_{max,\ median\ 25}$	0.00 points	$p_{max} > p_{max,\ median\ 25}$	0.00 points
Maximum temperature			
$T_{max} < T_{median\ 200}$	0.25 points	$T_{max} < 485$ K	0.25 points
$T_{max} < T_{median\ 200}$	0.00 points	$T_{max} > 485$ K	0.00 points
Heat flux condenser			
$\dot{Q}_{cond} < \frac{\dot{Q}_{cond,median200} + \dot{Q}_{cond,min200}}{2}$	0.75 points	$\dot{Q}_{cond} < \dot{Q}_{cond,\ median\ 200}$	0.25 points
$\frac{\dot{Q}_{cond,median200} + \dot{Q}_{cond,min200}}{2} < \dot{Q}_{cond} < \dot{Q}_{cond,\ median\ 200}$	0.50 points		
$\dot{Q}_{cond,\ median\ 200} < \dot{Q}_{cond} < \frac{\dot{Q}_{cond,median200} + \dot{Q}_{cond,max200}}{2}$	0.25 points		
$\dot{Q}_{cond} > \frac{\dot{Q}_{cond,median200} + \dot{Q}_{cond,max200}}{2}$	0.00 points	$\dot{Q}_{cond} > \dot{Q}_{cond,\ median\ 200}$	0.00 points
Pressure ratio			
$3 < p_{ratio} < 10$	0.75 points	$3 < p_{ratio} < 10$	0.75 points
$10 < p_{ratio} < 30$	0.50 points	$10 < p_{ratio} < 30$	0.50 points
$p_{ratio} < 3$ or $p_{ratio} > 30$	0.00 points	$p_{ratio} < 3$ or $p_{ratio} > 30$	0.00 points

Appendix B. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apenergy.2017.08.212.

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