Working fluid selection for the Organic Rankine Cycle (ORC) exhaust heat recovery of an internal combustion engine power plant

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Abstract. Organic Rankine cycle technology is capable to efficiently convert low-grade heat into useful mechanical power. In the present investigation such a cycle is used for the recovery of heat from the exhaust gases of a four stroke V18 MAN 51/60DF internal combustion engine power plant operating with natural gas. Design is focused on the selection of the appropriate working fluid of the Rankine cycle in terms of thermodynamic, environmental and safety criteria. 37 candidate fluids have been considered and all Rankine cycles examined were subcritical. The thermodynamic analysis of all fluids has been comparatively undertaken and the effect of key operation conditions such as the evaporation pressure and the superheating temperature was taken into account. By appropriately selecting the working fluid and the Rankine cycle operation conditions the overall plant efficiency was improved by 5.52% and fuel consumption was reduced by 12.69%.

1. Introduction
Increased fuel prices and environmental pollution concerns force research interest on the enhancement of the efficiency of existing power systems and the discovery of solutions leading to rational energy utilization. For a typical internal combustion engine (ICE), approximately 30% of the chemical energy of the fuel is brought into the environment by the exhaust gases. This energy can be usefully exploited by an appropriate waste heat recovery system leading in an overall efficiency improvement.

There are three typical approaches of ICE waste heat recovery including thermoelectric generation [1, 2], electrical or mechanical turbo compounding [3] and steam or organic Rankine cycles. The organic Rankine cycle (ORC) is a technology for low-grade heat to power conversion. It is similar to the conventional steam Rankine cycle used in power generation plants, but steam is replaced by an appropriate organic fluid. Hence, ORC is capable to realize more efficient expansion at low power and show better thermodynamic performance at low temperatures. Such cycles have been successfully applied in waste heat recovery, biomass energy plants and geothermal or solar energy applications [4-6].

Research on organic Rankine cycles for ICE waste heat recovery has started after the oil crisis of the ’70s. BMW, Honda and Cummins have installed ORC waste heat recovery systems in specific car or truck models and reported overall efficiency improvements in the range of 4-10% [6-8]. In these cases water, ethanol and R245fa have been selected as working fluids and heat was recovered from...
both exhaust gas and engine cooling systems. Similar results have been reported in numerous research studies [9-27] using a large variety of other organic fluids. Hung et al. [24] demonstrated that the major properties affecting the system performance included latent heat and specific heat of liquid and vapor. Chen et al. [25] and Maizza and Maizza [26] suggested that fluids with high latent heat and low specific heat are preferable while Yamamoto et al. [27] suggested that low latent heat fluids are preferable.

In the present investigation ORC exhaust heat recovery is applied in a large Diesel-natural gas dual fuel engine typically used for ship propulsion and power plant applications. This is the four stroke turbocharged V18 MAN 51/60 DF engine with maximum brake power of 17550 kW at 500 rpm [28, 29]. Exhaust combustion gases have been considered as the only heat source of the Rankine cycle and numerous candidate working fluids were compared upon thermodynamic, environmental and safety criteria.

2. Engine and fuel characteristics
Exhaust gas ORC heat recovery is considered in a V18 MAN 51/60DF engine, shown in Fig. 1. This is a natural gas-diesel dual fuel engine equipped with a MAN TCA77 (four stroke version) turbocharger. Engine and turbocharger characteristics are summarized in Table 1.

![Figure 1. The V18 MAN 51/60DF (dual fuel) engine.](image)

| Parameter                        | Value                        |
|----------------------------------|------------------------------|
| Number of cylinders              | 18                           |
| Cylinder bore                    | 510 mm                       |
| Piston stroke                    | 600 mm                       |
| Displacement per cylinder        | 122.5 lt                     |
| Compression ratio                | 13.3                         |
| Vee angle                        | $50^\circ$                   |
| Turbocharger type                | MAN TCA 77 (four stroke version) [23] |
| Turbocharger pressure ratio      | 5.5                          |
| Maximum engine speed             | 500 rpm                      |
| Maximum engine power             | 17550 kW at 500 rpm          |

Table 1. 18 cylinder MAN 51/60DF engine characteristics [28, 29]
The real cycle analysis of the engine has been conducted elsewhere [30] and operation conditions are summarized in Table 2. The engine is considered to steadily operate with either Diesel or natural gas fuel at the maximum speed of 500 rpm and at full load. Maximum temperature of the exhaust gases was estimated about 1128 K for natural gas mode. This value is about 30K higher than the maximum temperature of the Diesel cycle and for consistency natural gas operation will be considered. Exhaust gas temperature after the turbocharger is 633K as given by the MAN manufacturer [28]. Exhaust gas temperature is given in Table 3.

| Parameter | Diesel mode | NG mode |
|-----------|-------------|---------|
| Ambient temperature, $T_0$ (K) | 293 | |
| Ambient pressure, $p_0$ (MPa) | 0.1 | |
| Turbocharger outlet temperature, $T_C$ (K) | 517.63 | |
| Turbocharger outlet pressure, $p_C$ (MPa) | 0.55 | |
| Fuel mass flow rate, $\dot{m}_f$ (kg/h) | 4030.66 | 3412.82 |
| Air mass flow rate, $\dot{m}_a$ (kg/h) | 116332.9 | 116336.2 |
| Fraction of residual gases, $x_r$ | 0.0436 | 0.0425 |
| Temperature of residual gases, $T_r$ (K) | 825 | 848 |
| Temperature at the end of intake stroke, $T_1$ (K) | 535.83 | 536.47 |
| Pressure at the end of intake stroke, $p_1$ (MPa) | 0.522 | 0.522 |
| Temperature at the beginning of combustion, $T_2$ (K) | 1332.66 | 1334.09 |
| Pressure at the beginning of combustion, $p_2$ (MPa) | 17.29 | 17.29 |
| Temperature at the end of combustion, $T_3$ (K) | 2284.35 | 2430.93 |
| Pressure at the end of combustion, $p_3$ (MPa) | 25.93 | 26.82 |
| Temperature at the end of expansion, $T_4$ (K) | 1095.54 | 1128.05 |
| Pressure at the end of expansion, $p_4$ (MPa) | 1.09 | 1.10 |
| Exhaust gas temperature at the exit of the turbocharger, $T_I$ (K) | 653 | 653 |
| Brake (real) power, $P_b$ (kW) | 17473.91 | 17923.89 |
| Brake (real) thermal efficiency, $\eta_{th}$ (%) | 39.01 | 37.96 |

In the natural gas mode, the engine operates according to a lean-burn Otto combustion cycle. Natural gas is considered with an approximate composition of 95% mol CH$_4$, 4% mol C$_2$H$_6$, 1% mol C$_3$H$_8$ and with a lower heating value (LHV) of 49.8MJ/kg. Combustion typically takes place with lean fuel mixtures and the analysis was conducted assuming a lambda $\lambda$ ratio equal to 2 [30]. The pre-mixed lean gas–air mixture is ignited by the compression ignition of a small quantity of marine diesel pilot fuel injected into the main combustion space. A pilot injection of less than 1% of the normal liquid fuel quantity ensures very low NOx emissions in gas mode [31].
3. Rankine cycle analysis
In the present study, exhaust gas energy is exploited for power generation in a bottoming Rankine cycle. An ORC system consists of a working fluid pump, an evaporator, an organic turbine or expander and a condenser, as shown in Figure 2. Such a cycle consists of the following four steady state processes:

- Process 1-2: compression of liquid fluid in a pump.
- Process 2-3: isobaric heat addition to the fluid in an exhaust gas heat recovery exchanger.
- Process 3-4: expansion in a turbine or expander.
- Process 4-1: isobaric heat rejection in a condenser.

These four processes may form a simple Rankine cycle or a superheated Rankine cycle as shown in the T-s diagrams of the Figure 3. In the former case heat addition process 2-3 evaporates the fluid up to the condition of saturated vapor while in the latter case heat addition proceeds further to provide high temperature superheated vapor at 3'.

![Figure 2. Schematic diagram of the ORC exhaust heat recovery system.](image)

![Figure 3. T-s diagrams of a simple (1-2-3-4-1) and a superheated (1-2-3'-4'-1) Rankine cycle.](image)
Process 1-2 is carried out by a pump which receives the working fluid in the state of saturated liquid at the pressure of the condenser and compress it to the pressure of the isobaric heat recovery exchanger. Deviation from ideal isentropic compression is taken into account by the pump isentropic efficiency

\[ \eta_p = \frac{w_{ps}}{w_{pa}} = \frac{h_{2s} - h_1}{h_2 - h_1} \]

where \( w_{ps} \) is the ideal isentropic specific pump work, \( w_{pa} \) is the actual non-isentropic specific pump work, \( h_1 \) is the specific enthalpy of the saturated liquid at the inlet of the pump, \( h_2 \) is the specific enthalpy of the compressed liquid at the exit of the actual pump and \( h_{2s} \) is the specific enthalpy of the compressed liquid at the exit of the ideal isentropic pump. The pressure of the condenser has been considered 0.1MPa and the pressure of the heat exchanger has been considered in all base cases 3MPa. The isentropic pump efficiency was taken 80%.

Heat is recovered from the engine exhaust gases inside an insulated isobaric heat recovery exchanger. This results in the evaporation of the organic fluid which is taken at the saturation or superheated state 3. The rate of heat recovery by the exhaust gases is given by

\[ Q_r = \dot{m}_G (h_1 - h_{II}) \approx \dot{m}_G c_v T_I - \dot{m}_G c_v T_{II} \]

where \( \dot{m}_G \) is the mass flow rate of the combustion gases. Subscripts "I" and "II" correspond to the states of the exhaust gases before and after the heat recovery process, respectively. If sulfur is present in the fuel it transforms into sulfur dioxide during combustion and later into sulfur trioxide through further oxidation. Sulfur trioxide can then combine with steam vapor to form corrosive sulfuric acid if the temperature of the gas effluents is lower than the sulfuric acid dew point. Thus, \( T_{II} \) at the outlet of the heat recovery exchanger must be kept above the limiting value of 373.15K. In the present study, temperature \( T_I \) is considered 633K as suggested by the MAN manufacturer [28] and temperature \( T_{II} \) is assumed 378K. These values are kept invariable to set a constant temperature difference for all comparative fluid cases. Since the heat exchanger is insulated, heat losses are negligible and all heat recovered is absorbed by the organic fluid. That is,

\[ \dot{Q}_r = \dot{m}_F (h_3 - h_2) \]

where \( \dot{m}_F \) is the mass flow rate of the organic fluid.

The superheated organic fluid expands into a turbine to produce work. Expansion takes place in a single stage from the pressure of the recovery exchanger to the pressure of the condenser. Deviation from ideal isentropic expansion is taken into account by the turbine isentropic efficiency

\[ \eta_t = \frac{w_{ta}}{w_{ts}} = \frac{h_3 - h_4}{h_3 - h_{4s}} \]

where \( w_{ta} \) is the actual non-isentropic specific turbine work, \( w_{ts} \) is the ideal isentropic specific turbine work, \( h_3 \) is the specific enthalpy of the superheated fluid at the inlet of the turbine, \( h_4 \) is the specific enthalpy of the expanded fluid at the exit of the actual turbine and \( h_{4s} \) is the specific enthalpy of the expanded fluid at the exit of the ideal isentropic turbine. The turbine isentropic efficiency was considered 80%. The fluid leaving the turbine may be either superheated or a saturated gas-liquid mixture. In the latter case, the percentage of gas in the mixture is given by the mixture quality \( x \) as
where \( h_{fg} \) is the latent heat of evaporation at the pressure of the condenser. Quality \( x \) varies between 0 and 1. Finally, the expanded fluid returns at the initial state 1 by passing through the condenser. Heat rejected during condensation is given by

\[
\dot{Q}_{\text{out}} = \dot{m}_F (h_4 - h_1)
\]

The net power produced by the Rankine cycle is calculated as

\[
P_{\text{ORC}} = \dot{m}_F (w_{ta} - w_{pa}) = \dot{Q}_r - \dot{Q}_{\text{out}}
\]

and the thermal efficiency of the Rankine cycle is given as

\[
\eta_{\text{ORC}} = \frac{P_{\text{ORC}}}{\dot{Q}_r} = 1 - \frac{\dot{Q}_{\text{out}}}{\dot{Q}_r}
\]

The overall efficiency of the ICE-ORC power plant is then calculated as

\[
\eta = \frac{P_b + P_{\text{ORC}}}{\dot{m}_F \text{LHV}}
\]

where \( P_b \) is the brake power of the engine taken as 17923.89 kW, \( \dot{m}_F \) is the mass flow rate of natural gas calculated as 3412.82 kg/h and LHV = 49.8 MJ/kg is the lower heating value of natural gas. Efficiency improvement is finally given by

\[
\Delta \eta = \eta - \eta_e
\]

where \( \eta_e \) is the thermal efficiency of the engine which has been calculated 37.96% [30].

4. Working fluids

The working fluid selection is of key importance on the thermal performance of the ORC recovery system. Generally, the working fluids can be classified into the following three categories:

- wet fluids,
- dry fluids, and
- isentropic fluids.

This classification is based on the slope \( dT/ds \) of the saturation vapor curve of each fluid in a \( T-s \) diagram, as shown in Figure 3. The type of the working fluid can be determined through the following simplified equation [22]

\[
E = \frac{C_p}{T_H} \left[ \frac{n T_{rH}}{1 - T_{rH}} + 1 \right] \Delta H_{vap}
\]

where \( E \) is the reciprocal of the saturation vapor curve slope \( (ds/dT) \), \( C_p \) is the specific heat of the fluid at constant pressure, \( T_H \) is the evaporation temperature of the fluid, \( n \) is suggested to be 0.375 or 0.385 by Poling et. al. [32], \( T_{rH} \) is the reduced evaporation temperature \( (T_{rH} = T_H / T_{cr} \), where \( T_{cr} \) is the critical temperature), and \( \Delta H_{vap} \) is the latent heat of vaporization. Fluids having \( E > 0 \) have a
negative saturation vapor curve \((dT/\mathrm{ds} < 0)\) and are classified as wet fluids. Instead, fluids having \(E < 0\) have a positive saturation vapor curve \((dT/\mathrm{ds} > 0)\) and are classified as dry fluids. Finally, fluids having \(E \approx 0\) have an almost vertical saturation vapor curve and are classified as isentropic.

Conventional Rankine power plants usually employ water as working fluid. Water has a small molecular weight (18 kg/kmol), a high boiling point of 100°C at atmospheric pressure and a critical temperature of 347°C. It is chemically very stable, cheap, abundant, non-toxic and environmentally friendly but also has some disadvantages. Water is a typical wet fluid and when it is used in Rankine cycles requires high superheating to avoid condensation and erosion of the turbine blades due to the presence of liquid at the final stages of expansion. Steam turbines are also complex and expensive as they require to handle large steam volumes at the turbine exit. Due to these drawbacks water and other wet fluids are suitable only in high temperature applications like in plants for central power generation. In ORC recovery systems capturing heat from low-grade sources dry or isentropic organic fluids are suggested.

![Figure 4. Typical T-s diagrams of dry, wet and isentropic fluids. Classifications is based on the slope of the saturation vapor curve.](image)

**4.1. Thermodynamic selection criteria**

In terms of thermodynamics, appropriate fuels are usually those having high latent heats, high density and low specific heats [25, 26]. Higher latent heats are found to provide higher unit work output during expansion and higher densities are found to provide the same power outputs with smaller sized equipment. In the present study the thermodynamic comparison of 37 candidate fluids was conducted considering the same operation conditions of the V18 MAN 51/60DF exhaust heat recovery Rankine cycle described earlier. The most important thermodynamic properties of these fluids are summarized in Table 4. All selected fluids have critical pressure above 3MPa and therefore all Rankine cycles considered are subcritical.

**Table 4. Thermodynamic properties of various fluids [33-37].**

| ASHRAE Code | Substance Name | MW (kg/kmol) | Latent heat of evaporation | Critical temperature (K) | Critical pressure (MPa) | Type of fluid |
|-------------|----------------|--------------|---------------------------|--------------------------|-------------------------|---------------|

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| Substance                                      | at 0.1MPa (kJ/kg) | Phase  |
|-----------------------------------------------|-------------------|--------|
| R11  Trichloromonofluoromethane               | 137.37            |        |
| R12  Dichlorodifluoromethane                  | 120.91            |        |
| R13  Chlorotrifluoromethane                   | 104.46            |        |
| R14  Tetrafluoromethane                       | 88.01             |        |
| R21  Dichlorodifluoromethane                  | 102.92            |        |
| R22  Chlorodifluoromethane                    | 86.46             |        |
| R23  Trifluoromethane                         | 70.01             |        |
| R32  Difluoromethane                          | 52.02             |        |
| R41  Fluoromethane                            | 34.03             |        |
| R113 1,1,2-Trichloro-1,2,2-Trifluoroethane    | 187.38            | Dry    |
| R114 1,2-Dichloro-1,1,2-Tetrafluoroethane     | 170.92            | Dry    |
| R115  Chloropentafluoroethane                 | 154.47            |        |
| R116  Hexafluoroethane                        | 138.02            |        |
| R123  2,2-Dichloro-1,1,1-Trifluoroethane      | 152.93            | Dry    |
| R124  1-Chloro-1,2,2,2-Tetrafluoroethane      | 136.5             |        |
| R125  Pentfluoroethane                        | 120               |        |
| R134a 1,1,1,2-Tetrafluoroethane               | 102.03            |        |
| R141b 1,1-Dichloro-1-Fluoroethene             | 116.9             |        |
| R142b 1-Chloro-1,1-Fluoroethene               | 100.5             |        |
| R143a 1,1,1-Trifluoroethane                   | 84.04             |        |
| R152a 1,1-Difluoroethane                      | 66.05             |        |
| R236ea 1,1,1,2,3,3-Hexafluoropropane           | 152               | Dry    |
| R236fa 1,1,1,3,3-Hexafluoropropane            | 152               | Dry    |
| R245ca 1,1,2,2,3-Pentafluoropropane           | 134               | Dry    |
| R245fa 1,1,1,3,3-Pentafluoropropane           | 134               | Dry    |
| R417a 46.6% R125, 50% R134a, 3.4% R600 (by weight) | 106.75          |        |
| R422a 85.1% R125, 11.5% R134a, 3.4% R600a (by weight) | 113.6           |        |
| R422d 65.1% R125, 31.5% R134a, 3.4% R600a (by weight) | 109.94          |        |
| R423a 52.5% R134a, 47.5% R227ea (by weight)  | 125.96            |        |
| R170  Ethane                                  | 30.07             |        |
| R290  Propane                                 | 44.09             |        |
| R600  Butane                                  | 58.12             |        |
| R601  Pentane                                 | 72.1              |        |
| R717  Ammonia                                 | 17.02             |        |

**Notes:**
- **Isentropic:** Indicates isentropic behavior.
- **Dry:** Indicates dry conditions.
- **Wet:** Indicates wet conditions.
4.2. Environmental and safety selection criteria

Organic fluids may also be classified according to their chemical structure into the following groups:

- **CFCs**: Chlorofluorocarbons (CFCs) are organic compounds that contain only carbon, chlorine, and fluorine. They are also known by the DuPont brand name "Freon". Such organic fluids are R11, R12, R13, R113, R114, and R115.

- **HCFCs**: Hydrochlorofluorocarbons (HCFCs) contain carbon, chlorine, fluorine, and hydrogen atoms. Such organic fluids are R21, R22, R123, and R124.

- **HFCs**: Hydrofluorocarbons (HFCs) contain carbon, fluorine, and hydrogen atoms. Such organic fluids are R23, R32, R41, R125, R134a, R143a, R152a, R236ea, R236fa, R245ca, R245fa, R417a, R422a, R422d, and R423a.

- **PFCs**: Perfluorocarbons (PFCs) or just fluorocarbons contain only atoms of carbon and fluorine. Such organic fluids are R14 and R116.

- **HCs**: Hydrocarbons (HCs) are known substances containing only carbon and hydrogen atoms. Such fluids are R170 (ethane), R290 (propane), R600 (butane), R601 (pentane), cyclohexane, benzene, and toluene.

In addition to the criteria for thermodynamic performance, selection criteria must also be considered on the effect of the fluids to the natural environment and on the safety during handling and operation. Environmental criteria are of major importance and focus on the effect of each fluid on ozone layer depletion and global warming. Quantification of these effects takes place using the indices of Ozone Depletion Potential (ODP) and Global Warming Potential (GWP). The ODP is a relative measure of the degradation effect of each fluid on the ozone layer on the assumption that the ODP value for R11 is equal to 1. The GWP is a relative measure of how much heat the fluid gases trap in the atmosphere compared to the heat absorbed by an equal amount of carbon dioxide. It is usually calculated over the time interval of 100 years. Based on these definitions, the higher the value of ODP or GWP, the more detrimental is the effect of the fluid on the ozone layer and global warming, respectively. ODP values are considered medium below about 0.1 and high above 0.1. GWP values are considered low below 150, medium between 150-2500, and high above 2500. ODP and GWP values are summarized for the majority of the candidate fluids in Table 5.

An indication of the dangerousness of a fluid during handling and operation is provided by the ASHRAE 34 safety classification standard. Accordingly, fluids are classified into two health effect groups A and B as well as into three flammability groups 1, 2, and 3. Class A rating indicates no evidence of toxicity below 400 ppm while Class B indicates evidence of toxicity below this concentration limit. On the other hand, class 1 indicates a fluid which does not propagate a flame in open air under normal conditions, class 2 indicates a fluid that may propagate a flame in open air under certain conditions, and class 3 indicates a fluid of high flammability. Toxicity and flammability classifications are jointly providing a fluid index which can be either A1, A2, A3, B1, B2, and B3. Recently two new safety classes A2L and B2L have been added for fluids that are mildly flammable. For the majority of the candidate fluids of the present investigation ASHRAE 34 classification is given also in Table 5.

| ASHRAE Code | Substance Name                        | Ozone depletion potential | Global warming potential - 100 yr | ASHRAE 34 Safety Group |
|-------------|--------------------------------------|---------------------------|----------------------------------|------------------------|
| R11         | Trichloromonofluoromethane            | 1                         | 4750                             | A1                     |
| R12         | Dichlorodifluoromethane               | 1                         | 10900                            | A1                     |
| R13         | Chlorotrifluoromethane                | 1.7                       | 14400                            | A1                     |
| R14         | Tetrafluoromethane                    | 0                         | 7390                             | A1                     |
| R21         | Dichlorofluoromethane                 | 0.04                      | 151                              | B1                     |
| Fluid        | Name                                      | Density | Molecular Weight | Phase Out Plan |
|-------------|-------------------------------------------|---------|------------------|----------------|
| R22         | Chlorodifluoromethane                      | 0.05    | 1810             | A1             |
| R23         | Trifluoromethane                          | 0       | 14800            | A1             |
| R32         | Difluoromethane                           | 0       | 675              | A2L            |
| R41         | Fluoromethane                              | 0       |                  |                |
| R113        | 1,1,2-Trichloro-1,2,2-Trifluoroethane      | 1       | 6130             | A1             |
| R114        | 1,2-Dichloro-1,1,2,2-Tetrafluoroethane     | 1       | 10000            | A1             |
| R115        | Chloropentafluoroethane                    | 0.44    | 7370             | A1             |
| R116        | Hexafluoroethane                          | 0       | 12200            | A1             |
| R123        | 2,2-Dichloro-1,1,1-Trifluoroethane         | 0.02    | 77               | B1             |
| R124        | 1-Chloro-1,2,2,2-Tetrafluoroethane         | 0.022   | 609              | A1             |
| R125        | Pentafluoroethane                         | 0       | 3500             | A1             |
| R134a       | 1,1,1,2-Tetrafluoroethane                 | 0.055   | 1430             | A1             |
| R141b       | 1,1-Dichloro-1-Fluoroethane               | 0.12    | 725              | A2             |
| R142b       | 1-Chloro-1,1-Difluoroethane               | 0.12    | 2310             | A2             |
| R143a       | 1,1,1-Trifluoroethane                     | 0       | 4470             | A2L            |
| R152a       | 1,1-Difluoroethane                        | 0       | 124              | A2             |
| R236ea      | 1,1,1,2,3,3-Hexafluoropropane              | 0       | 1370             |                |
| R236fa      | 1,1,1,3,3,3-Hexafluoropropane              | 0       | 9810             | A1             |
| R245ca      | 1,1,2,2,3-Pentafluoropropane               | 0       | 693              |                |
| R245fa      | 1,1,1,3,3-Pentafluoropropane               | 0       | 1030             | B1             |
| R417a       | 46.6% R125, 50% R134a, 3.4% R600 (by weight) | 0       | 2346             | A1             |
| R422a       | 85.1% R125, 11.5 R134a, 3.4% R600a (by weight) | 0       | 3143             | A1             |
| R422d       | 65.1% R125, 31.5% R134a, 3.4% R600a (by weight) | 0       | 2729             | A1             |
| R423a       | 52.5% R134a, 47.5% R227ca (by weight)      | 0       | 2280             | A1             |
| R170        | Ethane                                    | 0       | 5.5              | A3             |
| R290        | Propane                                   | 0       | 3.3              | A3             |
| R600        | Butane                                    | 0       | 4                | A3             |
| R601        | Pentane                                   | 0       | 4                | A3             |
|             | Cyclohexane                               |        |                  |                |
|             | Benzene                                   |        |                  | B2             |
|             | Toluene                                   |        |                  | A3             |
| R717        | Ammonia                                   | 0       | 0                | B2L            |

CFCs and later HCFCs have been used extensively as refrigerants during the first part of the last century. These compounds were found to be relatively safe for handling and operation but their environmental effect was not addressed until the mid ’70s. At the time, the severe consequences of the continuous utilization of the CFCs became obvious and this led to the international phase out treaty of 1987 which is known as the Montreal Protocol. Under this treaty CFCs are currently banned. Replacement has taken place mainly by HCFCs which were equally safe but their widespread utilization eventually became a major global warming source. In view of this threat HCFCs fall also into phase out plans aiming at a gradual step down of their utilization after 2016. In this category, R22 was the most applicable fluid in residential and commercial air conditioning and refrigeration. It has
been already phased out in most developed countries but it is still used as a refrigerant in many other
developing. DuPont suggests R22 substitution by HFC refrigerant blends of similar physical properties
such as R417a, R422a and R422d [34-36]. HFCs are currently adopted in preference to HCFCs since
they don't contain chlorine and they don't harm the ozone layer. However, as can be observed in Table
5, they form greenhouse gases with a high GWP. Due to this effect international discussions are open
on the future reduction of HFCs also. PFCs, finally, were also used as replacement fluids of CFCs.
They are generally very inert and non-toxic but have high GWP values between 6000 and 10000.

To replace the substances mentioned above there exist some interesting hydrocarbon choices.
Propane (R290), butane (R600) and pentane (R601) are commonly used as refrigerants or in ORCs.
They are also mixed in hydrocarbon blends containing also ethane (R170). They have excellent
thermodynamic properties, and in this respect they are as good as or better than HCFs or HCFCs in
most applications. They are environmentally friendly with zero ODP and extremely low GWP values.
However, they are highly flammable and must be handled with care. In order to ensure safety,
hydrocarbon applications are governed by various international, regional and national standards and
regulations. They may pose an explosion risk if the concentration is between the lower and upper
flammability limits but following the safety standards the concentration of any leaked hydrocarbon
will not increase even in extreme situations.

The list of the selected fuels concludes with ammonia (R717), the only non-organic fluid candidate.
Ammonia is renowned for its favorable thermodynamic properties, it has zero ODP and zero GWP.
However, it has a number of disadvantages that have so far prevented its use in commercial
applications, e.g. material compatibility, toxicity, and flammability. Even under strict safety
regulations there is pressure on ammonia installations to reduce charge levels, especially when situated
in populated areas.

5. Results and discussion
All 37 selected fluids have been comparatively examined for the ORC exhaust heat recovery of the
V18 MAN 51/60 natural gas engine. Initially, ORC operation conditions were kept similar in all cases
with the pressure of the condenser constant at 0.1MPa and the pressure of the evaporator constant at
3MPa. Since all fluids have critical pressures above 3MPa every Rankine cycle examined was
subcritical. Considering simple non-superheated operation the comparative characteristics of all fluids
are summarized in Table 6. As shown, under these conditions exhaust heat recovery was found
capable to increase power plant efficiency by 3.61-4.93%. These terms are translated into additional
power outputs of 1700-2325kW just by exploiting the otherwise wasted engine gases, and also mean
fuel consumption improvements by 8.68-11.45%. Higher efficiency improvements are taken for R22
(4.93%), ethane (4.82%), R143a (4.71%), R41 (4.64%), R14 (4.53%), propane (4.5%), R13 (4.48%),
R32 (4.42%), ammonia (4.41%), R23 (4.40%), R12 (4.40%), R11 (4.32%), R21 (4.28%), R152a
(4.25%).

Table 6. Comparative characteristics of the simple (non-superheated) exhaust heat recovery
Rankine cycle and overall plant efficiency improvement for all candidate fluids.

| ASHRAE Code | Fluid mass flow (kg/s) | Pump power (kW) | Turbine power (kWe/kg) | Maximum cycle temperature (K) | Expanded fluid quality | ORC Power (kW) | ORC efficiency (%) | Power plant efficiency (%) | Δη (%) |
|-------------|------------------------|-----------------|------------------------|-------------------------------|------------------------|-----------------|-------------------|--------------------------|--------|
| R11         | 44.18                  | 108.19          | 2146.99                | 445.07                        | Superheated            | 2038.80         | 19.65             | 42.28                    | 4.32   |
| R12         | 51.21                  | 124.77          | 2199.50                | 376.25                        | 0.9748                 | 2074.73         | 19.99             | 42.36                    | 4.40   |
| R13         | 61.64                  | 146.76          | 2257.97                | 290.67                        | 0.8972                 | 2111.21         | 20.35             | 42.44                    | 4.48   |
| R14         | 75.31                  | 170.18          | 2306.90                | 219.98                        | 0.8133                 | 2136.72         | 20.59             | 42.49                    | 4.53   |
| R21         | 36.72                  | 94.66           | 2158.96                | 417.06                        | 0.9446                 | 2064.30         | 19.89             | 42.34                    | 4.38   |
| R22         | 39.94                  | 102.68          | 2428.86                | 343.19                        | 0.8962                 | 2326.18         | 22.42             | 42.89                    | 4.93   |

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R23 41.95 105.13 2179.91 280.11 0.8262 2074.78 19.99 42.36 4.40
R32 26.52 79.21 2163.85 321.17 0.8182 2084.64 20.09 42.38 4.42
R41 21.11 86.82 2272.56 287.94 0.7931 2185.74 21.06 42.60 4.64
R113 47.57 114.26 1921.25 478.88 Superheated 1806.99 17.41 41.79 3.83
R114 53.70 128.14 1963.65 414.01 Superheated 1835.51 17.69 41.85 3.89
R115 65.26 151.71 2003.06 350.69 Superheated 1851.35 17.84 41.89 3.93
R116 76.28 172.18 2018.98 292.4 0.955 1846.79 17.80 41.88 3.92
R123 44.64 111.01 1981.46 444.45 Superheated 1870.45 18.03 41.93 3.97
R124 48.39 118.97 2003.16 385.26 Superheated 1884.19 18.16 41.96 4.00
R125 52.21 124.97 2015.99 330.64 0.9895 1891.02 18.22 41.97 4.01
R134a 40.02 105.32 2007.00 359.35 0.9751 1901.68 18.33 41.99 4.03
R141b 34.14 101.38 2083.23 454.73 Superheated 1981.85 19.10 42.16 4.20
R142b 36.58 111.13 2100.45 393.07 Superheated 1989.32 19.17 42.18 4.22
R143a 35.67 110.79 2334.01 359.35 Superheated 2223.22 21.42 42.67 4.71
R152a 27.44 98.31 2102.53 365.22 0.9241 2004.22 19.31 42.21 4.25
R236ea 43.90 107.26 1856.37 405.98 Superheated 1749.10 16.86 41.67 3.71
R236fa 49.16 123.26 1826.30 394.75 Superheated 1703.04 16.41 41.57 3.61
R245ca 36.50 95.41 1862.00 432.09 Superheated 1766.58 17.02 41.71 3.75
R245fa 38.37 101.78 1876.49 416.57 Superheated 1774.70 17.10 41.72 3.76
R417a 44.29 112.39 2040.08 346.87 0.9801 1927.69 18.58 42.05 4.09
R422a 49.27 125.03 2036.64 334.97 0.9854 1911.60 18.42 42.01 4.05
R422d 46.74 118.59 2047.83 341.07 0.9804 1929.24 18.59 42.05 4.09
R423a 47.13 119.59 1961.77 364.09 Superheated 1842.18 17.75 41.87 3.91
Ethane 19.26 128.30 2401.82 282.89 0.8589 2273.52 21.91 42.78 4.82
Propane 19.78 123.35 2246.60 350.84 0.979 2123.25 20.46 42.46 4.50
Butane 19.08 114.98 2092.89 410.85 Superheated 1977.92 19.06 42.16 4.20
Pentane 18.61 110.60 1902.99 462.13 Superheated 1792.39 17.27 41.76 3.80
Cyclohexane 17.10 86.11 1837.94 529.43 Superheated 1751.82 16.88 41.68 3.72
Benzen 17.66 78.63 2014.62 523.55 0.1294 1935.99 18.66 42.07 4.11
Toluene 17.43 81.07 1826.40 566.22 Superheated 1745.33 16.82 41.66 3.70
Ammonia 7.24 38.45 2118.90 338.87 0.8366 2080.44 20.05 42.37 4.41

The list of thermodynamically favorable fluids which was selected in the previous discussion may be greatly narrowed on the basis of their environmental footprint. Among these choices R22, R14, R13, R12 and R11 have already been prohibited as CFCs. R143a is an HFC used mainly as a blend component in refrigerants. It has zero ODP, high GWP at 4470 and is mildly flammable at the A2L class. R41 is also an HFC used mainly in semiconductor manufacturing but with unknown GWP and safety behavior. It may be considered for further evaluation but it can't be selected until further research. R14 is a PFC with a high GWP value of 7390. Instead, R32 presents a good performance with medium to low GWP at 675. R23 is an HFC with a very high GWP at 14800. R21 is an HCFC with medium ODP and is under phase out. R152a is a promising and environmentally friendly choice with good performance. Finally the list above includes ethane and propane, two well known HCs, and ammonia, the only non organic candidate. These fluids have a low environmental impact but are highly flammable and need special attention and safety measures. Ammonia is also dangerously toxic.
Based on this discussion the list of selected fluids narrows only to ethane, R41 (under lack of data), propane, R32, ammonia and R152a.

![Graph](image)

**Figure 5.** Effect of the ORC evaporation pressure on the overall efficiency improvement of the V18 MAN 51/60 DF natural gas power plant for selected working fluids. Condenser pressure is 0.1MPa in all cases and Rankine cycles are simple without superheating.

The effect of the ORC evaporation pressure on the efficiency improvement of the power plant may be shown for selected fuels in Figure 5. Results are given for subcritical pressures and simple non-superheated cycles in all cases. Given the Montreal Protocol prohibition CFCs are not considered any further and Figure 5 contains only R22 for comparison. As shown, an increase of the evaporation
pressure is always beneficial leading to better plant efficiencies for all fluids. It can be seen that the effect of the evaporation pressure is more dramatic at low pressures. As the evaporation pressure increases the slope of the curve of the efficiency improvement $\Delta \eta$ reduces and even negative improvement values can be taken when attaining the critical pressure of a fluid. In this respect one can set a limiting upper evaporation pressure at about 85-95% of the critical pressure value of each fluid. The optimum evaporation pressure for a fluid is therefore dictated by its critical pressure and fluids with higher critical pressures have greater potential for efficiency enhancement. Accordingly, ethane, R41, R32 and ammonia may further improve their performance at elevated pressures. Maximum pressure is set for ethane at 4.5MPa, for R41 at 5MPa and for R32 at 5MPa. Ammonia has an extremely high critical pressure of 11.333 MPa but results show that above 5MPa further improvement of about 1% is only possible. To avoid risk of leakages and increased costs for special safety measures the maximum pressure for ammonia was set also at 5MPa. Finally, propane is found to maximize performance at 3.5MPa and R152a at 4MPa.

![Figure 6. Effect of the ORC superheating temperature on the overall efficiency improvement of the V18 MAN 51/60 DF natural gas power plant for selected working fluids.](image)

Except propane which is an isentropic fluid, all other fluids selected so far are wet. For a wet fluid and a simple non-superheating Rankine cycle an increase of the evaporation pressure results in a reduction of the quality of the saturated gas-liquid mixture taken after expansion. This means an increase of the percentage of liquid state at the final stages of turbine expansion and a danger for turbine blade erosion and wear. In all these cases simple Rankine cycle is inappropriate and superheating of the fluid vapor above the saturation temperature must be followed. The effect of the superheating temperature on the efficiency improvement of the power plant is illustrated for the cases of ethane, R41, propane, R32, ammonia and R152a at Figure 6. Each fluid is assumed at its optimum pressure mentioned before and superheating temperature is increased so that after expansion the fluid to be slightly superheated. As can be seen, an increase of the superheating temperature always leads to an overall efficiency improvement. Maximum efficiencies are attained at about 360K for ethane, 400K for R41, 375K for propane, 435K for R32, 480K for ammonia and 410K for R152a. The
characteristics of these optimum ORC cycles are summarized at Table 7. Among the selected fluids the ORC cycle of R32 is selected as the most appropriate due to high thermodynamic performance, low environmental impact and low flammability-toxicity. Such a cycle may provide an overall efficiency improvement of the order of 5.52%, as shown in Table 7. This improvement is also translated into a reduction of the fuel consumption by 12.69%.

| ASHRAE Code | Fluid mass flow (kg/s) | Pump power (kW) | Turbine power (kJ/kg) | Maximum cycle temperature (K) | Evaporation pressure (MPa) | ORC Power (kW) | ORC efficiency (%) | Power plant efficiency (%) | Δη (%) |
|-------------|------------------------|----------------|--------------------|-----------------------------|--------------------------|--------------|------------------|------------------------|-------|
| Ethane      | 14.72                  | 148.72         | 284.99             | 360                         | 4.5                      | 2696.27      | 25.98            | 43.68                  | 5.71  |
| R41         | 15.63                  | 108.58         | 2838.96            | 400                         | 5.0                      | 2730.38      | 26.31            | 43.75                  | 5.79  |
| Propane     | 17.85                  | 130.51         | 2386.34            | 375                         | 3.5                      | 2255.83      | 21.74            | 42.74                  | 4.78  |
| R32         | 19.6                   | 8              | 99.32              | 2703.64                     | 5.0                      | 2604.32      | 25.10            | 43.48                  | 5.52  |
| Ammonia     | 5.69                   | 51.04          | 2623.21            | 480                         | 5.0                      | 2572.14      | 24.79            | 43.41                  | 5.45  |
| R152a       | 23.40                  | 112.73         | 2343.77            | 410                         | 4.0                      | 2231.04      | 21.50            | 42.69                  | 4.73  |

Conclusions
In the present work the ORC exhaust heat recovery of a V18 MAN 51/60DF internal combustion engine power plant was examined. The plant was assumed to operate with natural gas at 500rpm and design focused on the selection of an appropriate ORC working fluid on the basis of thermodynamic, environmental and safety criteria. The study was undertaken for 37 working fluids under subcritical Rankine cycle conditions and examined the effect of key operation conditions such as evaporation pressure and superheating temperature. After an appropriate selection of these operation conditions for each candidate substance, R32 was selected as the most appropriate working fluid given its high thermodynamic performance, its low environmental impact and its low flammability-toxicity characteristics. Analysis has shown that R32 may provide an overall efficiency improvement of the power plant by 5.52% and a reduction of fuel consumption by 12.69%. Given the high power rating of the V18 MAN 51/60DF engine at about 18000kW, these improvements are translated into enormous cost savings during operation. The methodology employed in the present study may also serve as a guideline for future optimization of other energy systems.

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