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New fluid for high temperature applications

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ABSTRACT

As a result of the worldwide increased consumption of energy, energy saving measures come more and more in the focus of commercial acting.
Besides the efficiency enhancement of energy consuming systems the utilization of waste heat is an additional possibility of saving energy.
Areas where this might be feasible are geothermal power plants, local combined heat and power plants, solar-thermal-systems and high temperature heat pumps (HTHP).
All these applications need a transfer fluid which secures the transport of the energy from it's source to the place where it is needed at high temperatures.
The paper will start with a description or overview of promising energy sources and their utilization. The thermo physical properties of an azeotropic binary mixture of HFC-365mfc and a per-fluoro-poly-ether (PFPE) which fulfils the requirements on a high temperature working fluid are introduced in the second part of the paper.
First results and practical experiences in an ORC process are shown in this context followed by an estimation regarding the saved energy or the improved efficiency respectively for other applications.
The paper will end with a brief outlook on possible new applications e.g. autarkic systems or immersion cooling of electrical parts.

1. INTRODUCTION

As a result of the increasing consumption of fossil fuels throughout the world efficient use of these energy transfer media has increasingly become a focus of energy policies. The CO2 emissions associated with the consumption of fossil fuels must also be minimized due to their contribution towards the greenhouse effect.
One contribution towards the economical/ecological use of energy is to utilize the waste heat from many different processes. One key component in waste heat utilization is the working fluid which enables the economic conversion of heat into work or electricity.
Cooling of electrical components operates in a similar temperature range. Here, too, efficient cooling is the key to further improving the performance of these components.
In the following the thermo-physical properties of a fluid, which is particularly suitable for these applications will be presented. An application which has already proved successful will also be presented as well as future applications for which this fluid is especially suitable.

2. Utilizing waste heat

As a general rule heat flows below 400°C are regarded as unsuitable for water-based energy conversion systems (water-steam processes). Due to the low density of steam very large systems are needed for the traditional steam process. This makes the economic use of smaller heat flows – also with higher temperatures - impossible. Organic Rankine Cycles (ORC), which enable economic utilization of smaller heat flow at temperatures below 400°C with an organic working fluid, fill this gap.

The economically utilizable minimum heat flow depends on many different parameters, such as the type of expansion machine or the remuneration rates for electricity fed into the grid, but also on such factors as the investment costs for connection to energy grids with decentralized, automatic operation of machines. In the conversion of waste heat a 6-10% efficiency level can be assumed – depending on the temperature level.

The upper temperature in the working range of the fluid presented here, comprising 65% by weight R365mfc and 35 % by weight a perfluoropolyether, is 225°C. Promising heat sources for utilizing these blends as a working fluid for heat conversion processes are listed below.

2.1. Thermal solar energy

The average energy input depends on the geographical location. The solar constant of 1370Wm^{-2} is the ideal heat quantity which radiates on to the Earth vertically to the sun's rays at the sun's average distance from the Earth with no atmosphere. The actual value depends on the time of year, atmospheric turbidity and cloud cover. For Frankfurt / Germany on a clear day in July with low atmospheric turbidity the max. radiation energy is 1000 Wm^{-2}.

In many cases it is not possible to use the sun 's energy directly as a source of heat, as in times of intensive solar radiation only small heat flow are required, as heating for example. One possibility of utilizing solar energy in solar collectors is to convert the energy into work or electricity, although the solar-thermal generation of electrical current is practical only if this is more efficient than direct electricity generation via photovoltaic technology. Typical efficiencies for photovoltaic cells are in the range of 10-25% of the radiated solar energy. One disadvantage of photovoltaic technology is that the efficiency decreases as the temperature rises.

Examples of solar energy utilization are systems to generate electricity and decentralized, automatic machines.

2.2 Geothermal systems

The earth is increasingly warmer the deeper one goes. For Central Europe the temperature rises on average by 3K per 100m. At some points of the Earth's surface, such as Iceland, temperatures of up to 1000°C exist just several metres from the surface. Various processes to use this energy exist depending on the different geothermal sources. In volcanic regions it is often possible to use hot water or steam deposits directly. In other areas warm, water permeable layers of the Earth – so-called aquifers- can be tapped in a similar manner. In the hot dry rock process energy is extracted from the hot rock formation by circulating water through them.

In Germany geothermal systems are the largest source of waste heat generation at 63GWth (Lund *et al*., 1999). In most cases geothermal systems are operated to supply heat. A disadvantage of this form of utilization is the seasonal needs for heat. In Germany heating stations reach a maximum of 2000 to 3000 full load hours per year. The heat distribution also requires an extensive hot water network (Schallenberg *et al.*, 1999).

Geothermal systems which use the heat to generate electricity reach 7000 full load hours per year and are thus suitable for servicing the electricity base load (Lund *et al*., 1999). At the same time there is no need to provide a cost- intensive district heating network.

2.3. Biogas systems

In the energetic utilization of biogas organic material is fermented. The methane gas that is produced is cleaned and fed to an internal combustion engine which generates electricity via a generator. Agricultural facilities are a promising market for biogas systems. The organic material can be plant biomass as well as faecal matter from animal production. Here, too, we are faced with the issue of whether the waste heat from the internal combustion engine can be used practically. Direct utilization of the waste heat is possible only with seasonal limitation and requires considerable investments in terms of distribution.

As in the above examples the additional conversion of the waste heat from the internal combustion engine offers a promising approach to improved utilization of bioenergy. Figure 1 contains a diagram of a promising system.

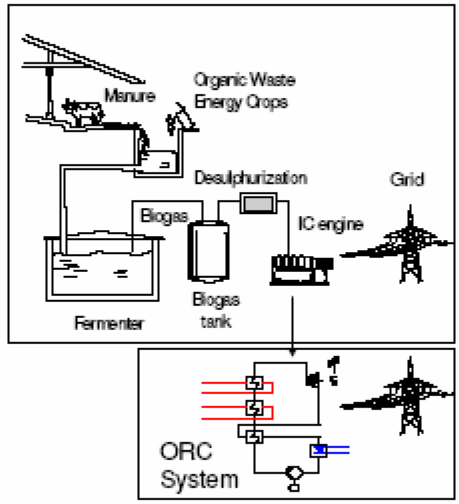

Figure 1. Diagram of decentralized utilization of biogas

2.4 Combined heat and power generation and engine-based cogeneration systems

These systems are also decentralized systems that provided electricity and waste heat. These systems are operated with an IC engine. As with the operation of biogas incineration systems the problem is again the economic, seasonally related utilization of the waste heat flow. Here, too, additional conversion of the waste heat to electricity is one option for efficient operation.

2.5 Waste heat from industrial processes

In Germany alone the waste heat from industrial processes is estimated at 6.7GWth per year. If this were all to be converted to electricity around 400MWel could be generated in this area. In addition to converting waste heat from industrial processes the operation of heat pumps for thermal utilization of the waste heat flow is another interesting option, if the heat can be used, for example in a networked production location.

3. Thermo-physical properties of the working fluid

As mentioned above, the working fluid is a key component in the utilization of the above-mentioned waste heat sources. The demands placed on a suitable working fluid are similar to those placed on refrigerants. The most important properties are non-flammability, low toxicity, chemical stability, suitable thermo-physical properties, economic availability and no ODP and a low GWP.

Existing refrigerants which combine these properties often have low critical temperatures and too high boiling pressures. The fluid described below is a non-flammable, binary mixture with azeotropic properties. The components of the mixture are R365mfc and Galden® HT55, a perfluoropolyether (PFPE) with a Normal Boiling Point (NBP) of 55°C. The mixing ratio is 65/35 %by weight. The molecular weight is 184.53 kg/kmol. In the following this mixture is described as SES36 because of its NBP of 35.6°C.

3.1Thermodynamic data

Within the scope of measuring the thermo-physical variables at Erlangen University the saturated vapour pressure, saturated densities, sonic speed, kinematic viscosity, thermometric conductivity and surface tension were measured (Fröba *et al*., 2005).

The critical temperature was determined by measuring thermal conductivity. The critical pressure was determined via extrapolating the Wagner equation formed with the critical temperature. The critical density was determined theoretically via the measured boiling densities and the acentric factor according to Reid *et al.* (1987). The table below shows the critical values with some other characterizing values.

Table1: Critical and other physical properties of SES36

Physical Property	Unit	Value
Molecular mass	g mol^{-1}	184.53
NBP	°C	35.64
$T_{crit.}$	°C	177.55 ± 0.5
$p_{crit.}$	bar	28.49 ± 0.24
crit. density	kg m^{-3}	538
liq. density @ NBP	kg m^{-3}	1339.25
vap. density @ NBP	kg m^{-3}	6.95
cp' @ NBP	J kg^{-1} K^{-1}	1167.2
cp'' @ NBP	J kg^{-1} K^{-}	641.9
cp''/cv'' @ NBP	-	1.01
heat of vaporisation	kJ kg^{-1}	152.94

3.2. Thermal and caloric properties of state in the wet vapour range

Figure 2 shows the heat capacity in the ideal gas state (cp_0). These values, together with a Martin-Hou equation, which was adjusted to measured pvT-values from the super heated area, were used to calculate enthalpies and entropies on the condensation curve. Recalculation of the values on the boiling curve was done with the Clausius-Clapeyron equation. The reference points for enthalpy and entropy were chosen according to the IIR proposal with an enthalpy of 200kJ/kg and an entropy of 1.0 kJ/(kg k) for the boiling curve at 0°C. Table 2 shows the enthalpies and entropies in a state of saturation via temperature, pressure and density.

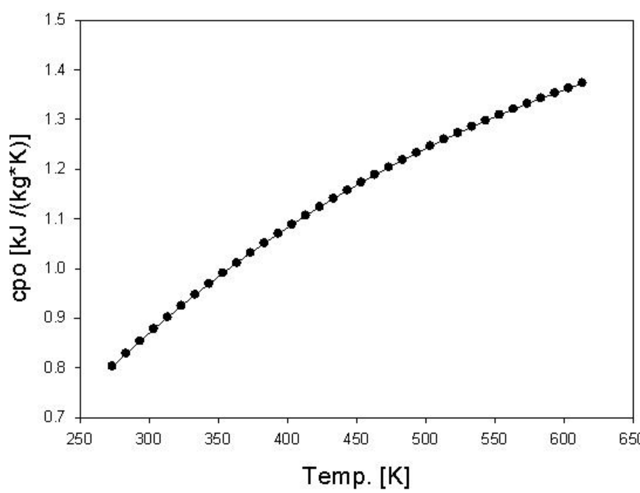

Figure2: Ideal isobaric heat capacities vs. temperature

Table 2: Saturated Pressure / Density /Enthalpy and Entropy values of SES36

Temprature [K]	Pressure [bar]	Liq. Density [kg/m³]	Vap. Density [kg/m³]	Liq. Enthalpy [kJ/kg]	Vap. Enthalpy [kJ/kg]	Liq. Entropy [kJ/(kg K)]	Vap. Entropy [kJ/(kg K)]
273.15	0.263	1422.04	2.00	200.00	349.88	1.000	1.549
283.15	0.395	1400.14	2.89	207.26	359.64	1.026	1.564
293.15	0.579	1377.21	4.12	215.92	369.63	1.056	1.580
303.15	0.833	1353.24	5.77	226.05	379.70	1.090	1.597
313.15	1.174	1328.22	8.00	237.62	389.66	1.127	1.613
323.15	1.622	1302.16	10.97	250.50	399.25	1.168	1.628
333.15	2.200	1275.04	14.90	264.36	408.23	1.210	1.642
343.15	2.932	1246.85	20.08	278.74	416.31	1.252	1.653
353.15	3.845	1217.59	26.82	293.04	423.29	1.293	1.662
363.15	4.964	1187.26	35.45	306.69	429.05	1.331	1.668
373.15	6.316	1155.82	46.31	319.35	433.67	1.365	1.671
383.15	7.929	1123.24	59.79	331.04	437.38	1.396	1.673
393.15	9.831	1089.48	76.45	342.12	440.51	1.424	1.674
403.15	12.055	1054.38	97.20	353.16	443.37	1.451	1.675
413.15	14.636	1017.66	123.68	364.78	446.20	1.479	1.676
423.15	17.622	978.55	158.94	377.61	449.10	1.509	1.678
433.15	21.072	934.72	209.17	392.33	451.93	1.542	1.680
443.15	25.067	875.19	289.01	410.03	454.18	1.582	1.681

4. Example of application with SES36

4.1 Generating electricity from a geothermal system via ORC

In principle ORC is identical to the steam process based on water as the working fluid. There can be various reasons for choosing an organic working fluid. Organic working fluids allow, for example, lower condensation temperatures to be used, which would not be economically possible if water were used as a working fluid due to the low density of the steam (Angelino *et al.*, 1999). Another important reason for using SES36 in the ORC system described below is the possibility of utilizing energy at a relatively low temperature.

Table3: Key figures of an European geothermal project

Data Geothermal System	
Depth of the production well	2306 m
Depth of the injection well	2165 m
Temperature of the thermal water	106°C
Production volume	100 dm³/s
Length of the heating network	~14.5 km
Number of consumers of the district heating network	~650
Data ORC System	
Type of expansion machine	Turbine
Manufacturer of the machine	Turboden, Italy
Rotation speed	1500 min^{-1}
Nominal electrical capacity	1000 kW
Yearly working Hours	~ 7500
Supplied electrical power since 4/2001	2 mio kWh
Mass flow thermal water	seasonal
Mass flow coolant	seasonal
Temperatures thermal water inlet / outlet	106°C / 50-70°C
Temperatures coolant inlet / outlet	seasonal

The system described is a geothermal system in Europe. The system is based on the aquifer principle. The first development phase has been operating since 1990 and since then has been feeding a district heating network, which was originally planned for 500 households. Due to the increasing demand the system, which was originally operated on the artesian principle, was extended with a second well in 1997/1998. The second well is used for the thermal water return. This allowed the production quantity to be increased to 100 l/s.
The most important key figures of the geothermal system are listed below in Table 3:
In the second development stage an ORC system was put into operation to generate electricity. Figure 3 shows the principle of the geothermal system.

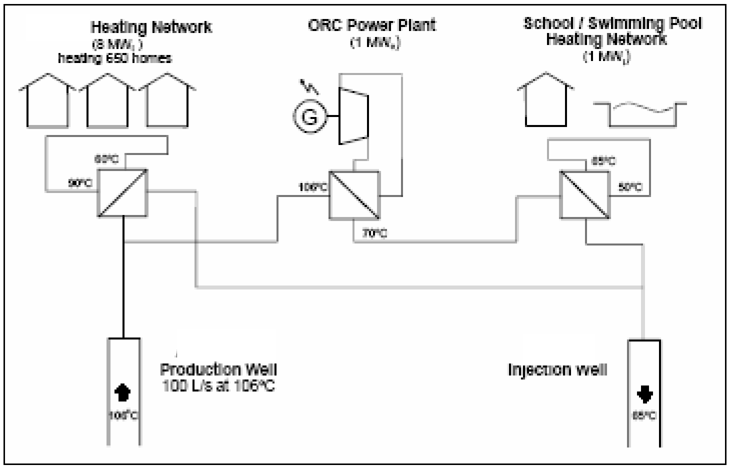

Figure 3: European Geothermal Plant [7]

Within the scope of an inspection in May 2005 the losses of the existing working fluid had to be balanced. Due to availability problems of the existing working fluid, it was replaced completely by SES36. The fluid change was possible without any changes on the existing ORC system. Only minor measures were taken on the leak tightness of the system.
With the change of the working fluid the efficiency of the system was increased. Figure 4 shows the relation between supplied electrical power and used thermal power of the thermal water. The values were measured empiric. A significant increase of the efficiency was measured. In average the efficiency increased from 4.9% to 6.9 % which corresponds to a relative increase of ~40%.

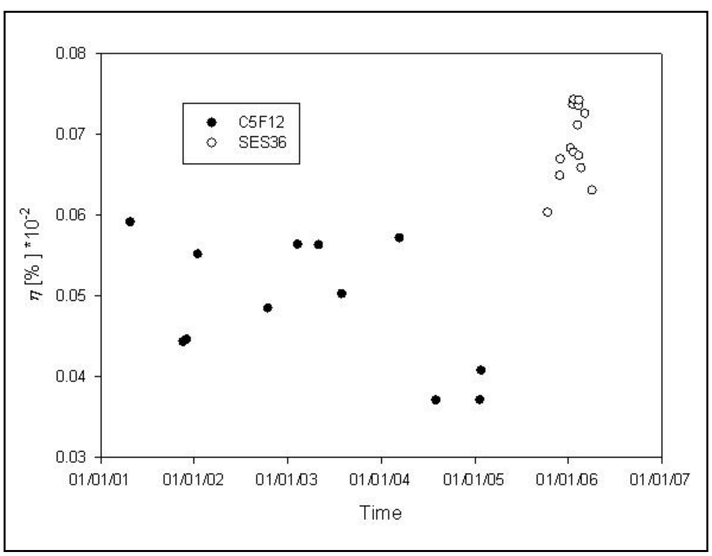

Figure 4: Measured efficiency as $P_{el.}/W_{th.}$ vs. Time

According to the operators statement the increase is related to the improved heat transfer behaviour on the thermal water side as well as on the coolant side. This improvement was measured by the temperature difference between thermal water / working fluid / coolant.
With

$$\dot{S}_{irr} = k \cdot A \cdot \frac{(T_A - T_B)^2}{T_A \cdot T_B} \tag{1}$$

a direct decrease of the irreversible entropy flow during the heat transfer can be deducted. This is equal to a decrease of losses of the heat flow (Baehr, 2000).

4.2. Cooling electrical components

In addition to its use as a thermal transfer medium for ORC or other machines SES36 is also suitable for cooling electrical components. Typical electrical components that have to be cooled include CPUs, IGBT (Insulated Gate Bipolar Transistors) of inverters or all electrical components with a high power density and a high clock rate respectively. In principle two different types of cooling have proven to be advantageous.
The first cooling method is via a separate, self-contained system, which is in contact with the electrical component. The heat can be removed via the evaporating fluid within a thermosyphon system which condenses and flows back to the system at the other end releasing heat. The advantage of this is the low pressure in combination with relatively high enthalpy differences. The low pressure enables systems to be operated with thin walls, which in turn minimizes heat transfer resistance and component costs.
A second possibility of cooling electronic components is to cool the component directly in liquid SES36. SES36 has non-conductive properties, which are shown in Figure 5. The lamp shown there is completely submerged in liquid SES36.

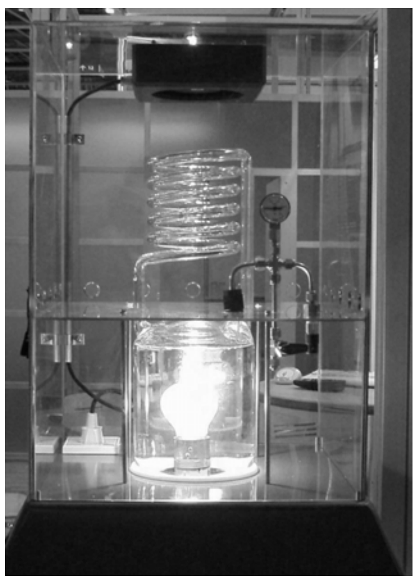

Figure 5: Electric lamp cooled with liquid SES36

The electrical properties of SES36 are listed in Table 4.
In direct immersion cooling the heat is released directly to the fluid. The heat can also be removed in a thermosyphon system. The advantage of immersion cooling is the optimum heat transfer and thus the possibility of further increasing the power density of electrical components.

Table 4: Electrical properties of SES36

Dielectric Strength (kV; 0.1" gap)	35.5
Dielectric Constant (1kHz)	6.9
Volume Resistivity (Ω cm)	5 e^8

5 Conclusion & Outlook

The future scarcity of our current main energy carriers will increasingly lead to the use of regenerative energy sources. The greatest potential for substituting conventional energy carriers are wind energy, geothermal system and the use of biomass (Gramlich, 2005). At the same time solar energy will play an important part in the energy mix in warmer regions of the world. Energy-efficient heat transfer media and working fluids play a significant role in the utilization of geothermal systems, biomass and solar energy.
Cooling of electrical components enables the power density to be increased further. Optimum results have been achieved with immersion cooling.
SES36 is a suitable working fluid for both areas of application.
In addition to the example of using low temperature heat flows for power generation and cooling electrical components there are other interesting areas of application such as operation of decentralized, automatic machines based on solar energy.

6 REFERENCES

Angelino G., Invernizzi C., Molteni G., 1999, The potential role of organic bottoming Rankine Cycles in steam power stations, Proc Instn Mech Engrs Vol 213 Part A, p. 75

Baehr, H.D.; Thermodynamik, Springer, Berlin 2000, p. 108 - 115

Fröba A. et al., 2005, Thermophysikalische Eigenschaften eines Kältemittelgemisches aus R365mfc (1,1,1,3,3-Pentafluorbutan) und Galden® HT 55 (Perfluorpolyether), DKV Conference 2005, Würzburg

Gramlich K.; Entwicklungstendenzen in der Energieversorgung, Dresdener Kolloquium der Kältetechnik, Dreden Germany, 2005

Lund, J.W. Boyd, T., 1999, Small Geothermal Power Project Examples, Geo-Heat Center Quarterly Bulletin, 20: 9-26

Reid R.C., Prausnitz J.M., Poling B.E., The Properties of Gases and Liquids, McGraw-Hill, New York, 1977 and 1987

Schallenberg, K., et.al., 1999, Geothermisches Heizkraftwerk Neustadt-Glewe: Zustands- und Stoffparameter, Prozessmodellierungn, Betriebserfahrungen und Emissionsbilanzen, STR99/04, Geoforschungszentrum Potsdam

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