FLUID STABILITY IN LARGE SCALE ORCS USING SILOXANES - LONG-TERM EXPERIENCES AND FLUID RECYCLING

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ABSTRACT

The results in this work show the influence of long-term operation on the decomposition of working fluids in eight different power plants (both heat-led and electricity-led) in a range of 900 kW_{el} to 2 MW_{el}. All case study plants are using Octamethyltrisiloxane (MDM) as a working fluid. The case study plants are between six to 12 years old. On one system detailed analyses, including the fluid distribution throughout the cycle, have been conducted. All fluid samples have been analysed via Head Space Gas Chromatography Mass Spectrometry (HS-GC-MS). Besides the siloxane composition, the influence of contaminants such as mineral oil based lubricants (and its components) has been examined. In most cases the original main working fluid has degraded to fractions of siloxanes with a lower boiling point (low-boilers) and fractions with a higher boiling point (high-boilers). As a consequence of the analyses, a new fluid management system has been designed and tested in one case study plant (case study number 8). The measures include fluid separation, cleansing and recycling.

Pre-post comparisons of fluid samples have proved the effectiveness of the methods. The results show that the recovery of used working fluid offers an alternative to the purchase of fresh fluid, since operating costs can be significantly reduced. For large facilities the prices for new fluid range from € 15 per litre (in 2006) to € 22 per litre (in 2013), which is a large reinvestment, especially in the light of filling volumes of 4000 litres to 7000 litres per cycle. With the above mentioned method a price of € 8 per litre of recovered MDM can be achieved.

1. INTRODUCTION

Over the recent years a large number of ORCs (over 200) based on siloxanes as a working fluids have been taken into operation all across Europe. Siloxanes are advertised as uncomplicated and long lasting working fluids. Many siloxanes are classified as inflammable, and they are more stable than their carbo-organic equivalents. The bond energy of a siloxy group is significantly higher than the bond energy of a carbon chain (Zhou et al., 2006). There are only a few sources in literature describing the decomposition of siloxanes in high-temperature applications (250°C to 350°C) in detail, such as Grassie and Macfarlane (1978). Most studies are related to the use of poly-siloxanes as solids under oxygen and nitrogen atmospheres (Zhou et al., 2006). The Siloxy-bonds in siloxanes are very strong (809 kJ/mol), but compared to the methyl-silane group they are the weaker link. The methyl-silane decomposition takes place above 400 °C. In general, siloxanes have a tendency to polymerise or oligomerise above 300 °C. The equilibrium of the polymerisation and the product configuration depend on pressure and educt configuration. Formic acid may be produced during thermal decomposition. In thermal conversion siloxanes react to SiO_2, CO_2 and hydrocarbon residues (Dow Corning, 2013). Over longer periods of operation, cycle fluids degrade through decomposition or contamination. Strong oxidants, catalytic alloys or sulphur can trigger or accelerate the decomposition processes. Contaminants and decomposition products of cycle fluids can lead to severe disturbances of the process. High-boilers, which are still liquid while the main working fluid is fully evaporated, can damage the turbine or heat exchangers by droplet impingement. Vaporous low-boilers can lead to cavitation in the feed-pump, galloping in the pre-heater, excessive super-heating in the evaporator and low heat transfer coefficients. The volume distribution across the cycle can significantly differ from the original design. As a consequence lower electric efficiencies and higher maintenance costs have to be expected.

2. METHODOLOGY

The authors have analysed the data of seven power plants across Europe. The focus was set on the following points:

- Operational mode: heat-led or electricity-led
- Total hours of operation and up-time per year
- Fluid quality: contaminations, degree of degradation, low-boilers, high-boilers
- Source temperature and degree of super-heating

Based on the above mentioned points a correlation between the cycle operation and the final working fluid composition was searched for. Besides the cause of the fluid decomposition and the contaminations, the removal of contaminations and the recycling of the working fluid was tested on one case study (number 8). Furthermore, the sequestration of fluid fractions across the cycle has been observed in this case study. The power plant for the recycling analysis is located in the city quarter Scharnhauser Park near Stuttgart. Since the year 2004 the power plant covers the demand of an area with an estimated population of 7000. The combined heat and power unit (CHP) is biomass driven and heat-led. A $7\,\mathrm{MW_{th}}$ furnace converts landscape preservation residues and wood chips into heat. The ORC is connected via a thermal oil cycle to the furnace. The system is controlled according to ambient temperature. The sink temperature levels are 60 °C/80 °C. The source temperature (thermal oil) of the OR-cycle is limited to 290 °C.

For all case studies fluid samples have been taken and analysed using the Head Space Gas Chromatography Mass Spectrometry (HS-GC-MS) method. In order to test the separation of contaminated working fluid mixtures distilling experiments have been conducted on various samples of case study number 8. For each distilling experiment the original working fluid sample (base fluid) and the products of the processes have been analysed.

3. RESULTS

3.1 Analysis of working fluids from seven power plants

The following table shows an overview on the conditions under which the seven case study plants are working. For the sake of completeness the case study number 8 is listed as well. An operation time cannot be defined for case study 8, as major parts of the cycle have been replaced and the working fluid has been fully substituted.

Table 1: Boundary conditions for seven case study ORCs

case	$\vartheta_{source,max}$	age	op.-time	P_{max}	operation mode, description
-	[°C]	[Y]	[h]	[kVA]	-
1	300	10.5	52500	1200	heat-led, district heating
2	300	12	90000	1280	electricity-led
3	313	5.5	45100	2000	heat-led, district heating
4	300	10.5	75600	1000	both, district heating
5	315	6	49200	1000	heat-led, district heating
6	310	7	57400	1000	both, district heating
7	308	7	38500	1000	heat-led, district heating
8	290	10	-	950	heat-led, district heating

In figures 1 and 2 the composition of the fluid samples from the seven different power plants are depicted. In figure 1 the lubricant fraction is included, in figure 2 only the siloxane fractions are depicted. The degree of degradation of the working fluid samples varies across a wide range (between 5% and 55%, respectively 5% to 34%).

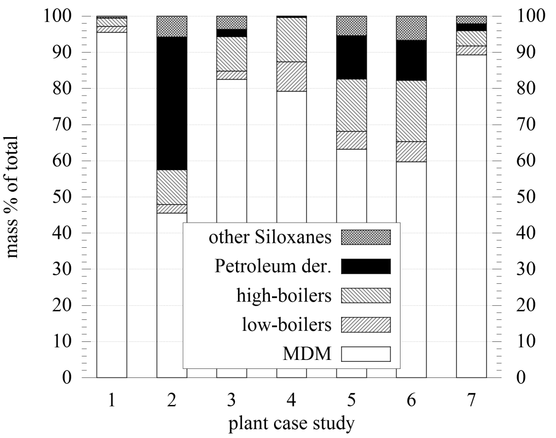

Figure 1: Composition of case study fluids including contamination

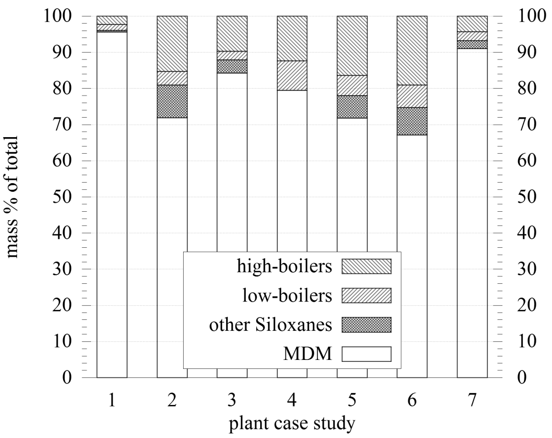

Figure 2: Composition of case study fluids, siloxane fractions only

The following figure 3 depicts the total degradation of the original working fluid MDM for all case studies versus the operating time. As time is one of the main factors in chemical reactions a rough trend can be seen. However, the dispersion is very large.

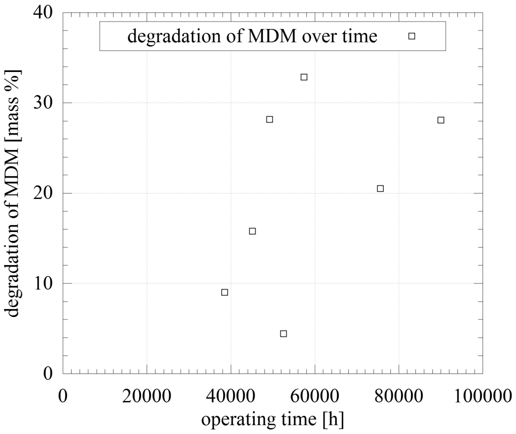

Figure 3: Degradation of working fluid vs. up-time

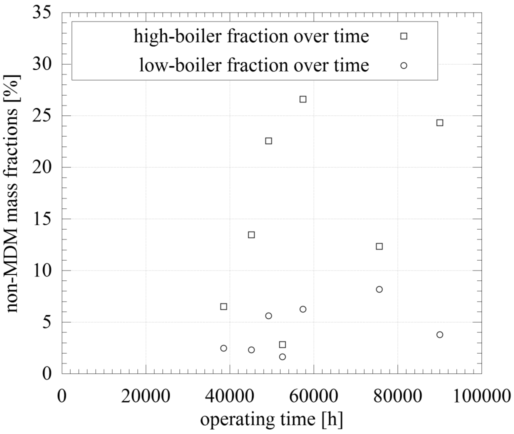

Figure 4: High- and low-boiler fraction in fluid samples vs. up-time

In figure 4 the development of the two categories of reaction products versus the operating time of the cycle is shown. The amount of high-boilers is significantely higher compared to the low-boilers. Besides the siloxane compounds in the working fluid, the samples were contaminated with varying fractions of petroleum derivates. These contaminations usually come from a leakages located at the turbine shaft sealing. A certain leakage rate cannot be avoided, but some of the samples show massive contaminations (case 2, 5 and 6 in figure 1).

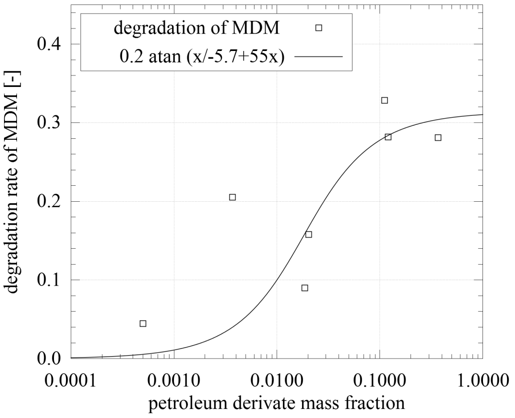

Figure 5: Degradation rate of MDM vs. petrol derivate fraction in cycle fluid

The data in figure 5 depict the degradation ratio of the original cycle fluid versus the measured fraction of lubricant residues on a logarithmic scale. The trend depicted in the diagram shows a correlation between the amount of hydrocarbon contaminants and the degradation of the original working fluid.

3.2 Fluid distribution within the cycle (case study 8)

In case of fluid degradation, the fluid composition throughout a cycle is not equal. Depending on the local thermodynamic state, the equilibrium of compounds shifts. This distribution of compounds across the cycle has been tested on power plant case study number eight. The following HS-GC-MS analyses in table 2 to table 5 show the results of various fluid samples taken from different points of the cycle. The first fluid sample (table 2) has been tapped from the pre-heater after a full stop of the cycle:

Table 2: HS-GC-MS analysis of cycle fluid (pre-heater after full-stop) (Erhart, 2015)

compound -	abbr. -	CAS -	mass fraction [%]
Octamethyltrisiloxane	L3 / MDM	107-51-7	79.2
Hexamethyldisiloxane	L2 / MM	107-46-0	7.55
Hexamethylcyclotrisiloxane	D3	107-52-8	0.592
Octamethylcyclotetrasiloxane	D4	556-67-2	4.93
Decamethyltetrasiloxane	L4 / MD2M	141-62-8	5.12
Decamethylcyclopentasiloxane	D5	541-02-6	0.535
Dodecanethylpentasiloxane	L5 / MD3M	141-63-9	1.7
Trimethylsilanol	MOH	1066-40-6	-

The second used fluid sample (table 3) has been taken from the reservoir of the vacuum pump (see figure 10). The large fraction of MM is very obvious. As the condensables in the condenser are fed back into the cycle and take part in the overall process, the low-boiling MM collects as vapour in the condenser shell. Consequently the vacuum pump takes the MM from there.

Table 3: HS-GC-MS analysis of cycle fluid (vacuum pump) (Erhart, 2015)

compound -	abbr. -	CAS -	mass fraction [%]
Octamethyltrisiloxane	L3 / MDM	107-51-7	50.9
Hexamethyldisiloxane	L2 / MM	107-46-0	45.5
Hexamethylcyclotrisiloxane	D3	107-52-8	0.898
Octamethylcyclotetrasiloxane	D4	556-67-2	1.4
Decamethyltetrasiloxane	L4 / MD2M	141-62-8	0.816
Decamethylcyclopentasiloxane	D5	541-02-6	0.099
Dodecanethylpentasiloxane	L5 / MD3M	141-63-9	0.238
Trimethylsilanol	MOH	1066-40-6	-
other poly-siloxanes	-	-	0.116

After a full stop of the cycle the sample presented in table 4 has been taken from the bottom of the recuperator (under liquid line). The analysis shows a large amount of high-boilers (MD2M and MD3M). After the turbine, the expanded vapour is transported through the recuperator. Meanwhile the saturation pressure of the high-boilers is reached. Furthermore, the flow of the vapour decelerates. Therefore, the high-boilers precipitate inside the recuperator shell. The high-boilers that are not evaporated before the turbine can damage the turbine blades.

Table 4: HS-GC-MS analysis of cycle fluid (recuperator reservoir) (Erhart, 2015)

compound -	abbr. -	CAS -	mass fraction [%]
Octamethyltrisiloxane	L3 / MDM	107-51-7	65.50
Hexamethyldisiloxane	L2 / MM	107-46-0	5.09
Hexamethylcyclotrisiloxane	D3	107-52-8	0.50
Octamethylcyclotetrasiloxane	D4	556-67-2	4.97
Decamethyltetrasiloxane	L4 / MD2M	141-62-8	11.00
Decamethylcyclopentasiloxane	D5	541-02-6	1.30
Dodecanethylpentasiloxane	L5 / MD3M	141-63-9	7.05
Trimethylsilanol	MOH	1066-40-6	-
other poly-siloxanes	-	-	4.56

The last sample (table 5) has been taken from the feed pump. It is the most representative for the fluid mixture involved in the overall thermodynamic process. Less than 80% of the original working fluid is left.

Table 5: HS-GC-MS analysis of cycle fluid (feed pump) (Erhart, 2015)

compound -	abbr. -	CAS -	mass fraction [%]
Octamethyltrisiloxane	L3 / MDM	107-51-7	78.3
Hexamethyldisiloxane	L2 / MM	107-46-0	3.6
Hexamethylcyclotrisiloxane	D3	107-52-8	0.543
Octamethylcyclotetrasiloxane	D4	556-67-2	4.04
Decamethyltetrasiloxane	L4 / MD2M	141-62-8	6.55
Decamethylcyclopentasiloxane	D5	541-02-6	0.92
Dodecanethylpentasiloxane	L5 / MD3M	141-63-9	3.96
Trimethylsilanol	MOH	1066-40-6	0.001
other poly-siloxanes	-	-	1.852

3.3 Distilling under laboratory conditions

In order to prove the feasibility of a working fluid separation, a laboratory test was conducted. The liquid educt samples was taken from the recuperator reservoir (liquid line).

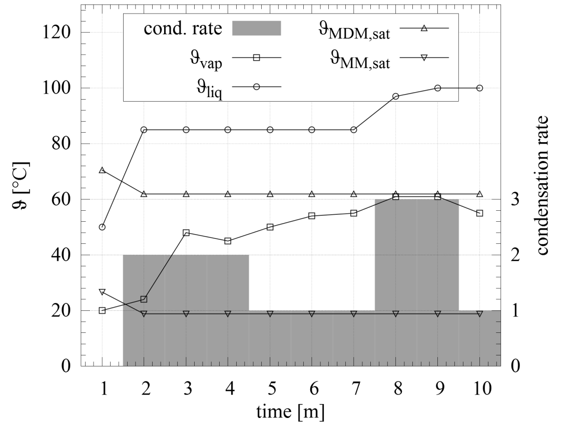

Figure 6: Distilling process of sample 1

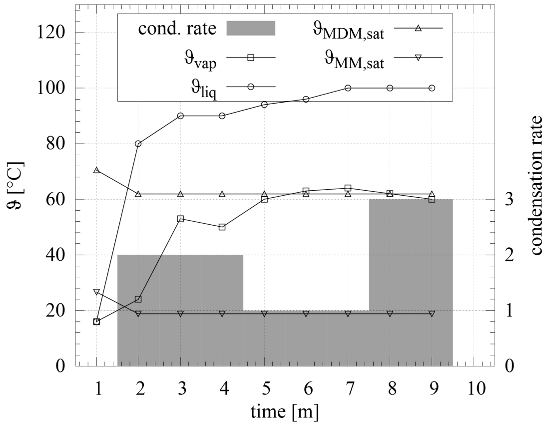

Figure 7: Distilling process of sample 2

Under a pressure of 40 mbar two fluid samples are evaporated and condensed, the results of the two experiments are shown in the figures 6 and 7. In the diagrams the saturation temperature of MDM and MM are given according to the measured pressure in the flask. The temperature of MM represents itself and all other low-boilers that evaporate below MDM. Furthermore, the temperatures of the boiling fluid mixture and the vapour are shown. The condensation rate is categorized (0-none, 1-low, 2-medium, 3-high) by observation. In experiment 1 the base fluid reservoir was first heated to a set-point of 85 °C and to 85 °C. In the second experiment the first temperature set-point was set to 90 °C. If the liquid temperature exceeds the saturation temperatures, evaporation occurs. If the measured vapour temperature is above or near to the saturation temperature condensation occurs. During the time steps 2,3 and 4 the condensation rate rises in both experiments; in that period the first distillates are taken. The first distillate usually contains the largest share of low-boilers. The second distillate, containing mainly MDM, is extracted during the time steps 8 and 9.

In the experiment number one, 54.2% of MDM could be recovered (figure 6) from the base fluid. In experiment number two 64.2% of the MDM could be recovered from the base fluid.

A detailed analysis of the distilling products of experiment number 2 (figure 7) showed: The first distillate contained 62.3% of MDM, 15.8% of MM, 19.92% of Petroleum derivates and minor fractions of other siloxanes. The second distillate from the fluid sample contained 95.2% of MDM, and 2.4% of D4. The rest of the product was a mixture of various siloxanes (less than 1% each). The residue of the base fluid contained 25.5% MDM, 8.5% L4 and 18.4% L5. The lubricant was removed successfully from the original sample and no lubricant was in the product sample. Based on the experiences from the laboratory tests the condensation was tested in real scale.

3.4 Distilling and fluid treatment under field conditions

Unlike the laboratory set-up, under real conditions the base samples for fluid treatment can be of different origin. In this case study the main fluid source is the reservoir of the recuperator. As the distillation experiments in the last section show, this source contains a high fraction of high-boilers and lubricant. For the recovery of MDM and the elimination of lubricant fractions from the working fluid it is the perfect source. The distilling apparatus (1) built for the condensation of MDM from fluid mixtures with a high fraction of high-boilers, is depicted in figure 8. It is mounted on top of the multi-cyclone (2) and heated by the hot exhaust gases of the biomass furnace. A water cooled coil (3) is used for condensation.

Usually power plants of that type have a vacuum system removing inert gases and low-boilers. In the original layout of this power plant, the vacuum pump (claw type) extracts working fluid vapour, containing a high fraction of low-boilers and inert gas, from the condenser. The extracted fluid is usually released to the ambient. By doing so, the MDM in the extracted fluid is lost and the working fluid exhaust pollutes the environment. In order to avoid this, a reservoir has been added to the cycle. The extracted mixture is collected in a vessel outside the turbine house ((1) in figure 9). In order to separate the low-boilers and inert gases from the mixture in the vessel, a second vacuum pump (membrane type) has been added. It can provide a lower pressure than the original pump ((2) in figure 9). The membrane pump and the external vessel are depicted on the very right margin of figure 10.

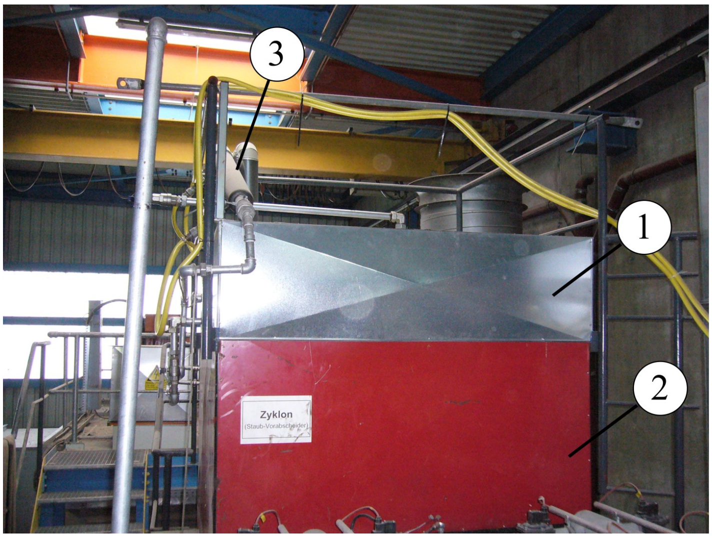

Figure 8: Distilling apparatus on top of multi-cyclone/ exhaust gas duct

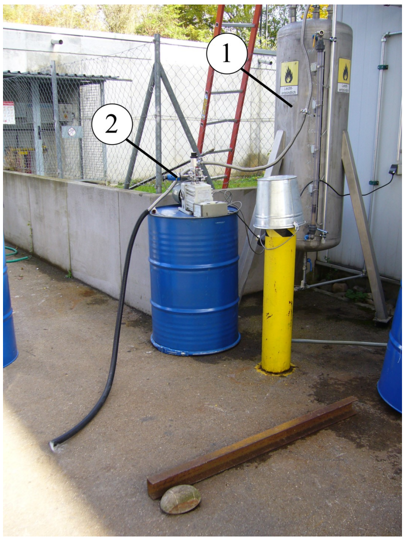

Figure 9: New vacuum pump fluid reservoir and membrane pump

3.5 Cycle modifications

The modifications that were made in order to conduct the recycling procedures are depicted in figure 10. Besides the original vacuum pump, a membrane pump was installed (figure 10, right margin). Vapour from the condenser vessel is collected in a reservoir outside the turbine house where it partially condenses (figure 9). As the tests show (table 3), the fluid mixture from the vacuum pump contains a great share of MM. In order to remove the MM from the mixture, a pressure between 10 mbar and 43 mbar is necessary (ambient temperature in a range of 0 °C to 20 °C). This system is operated batch-wise, as soon as the capacity of the vessel is reached (200 litres) the membrane pump is started. After the end of the procedure, the remaining MDM is returned to the cycle.

The removal of working fluid with a high fraction of high-boilers is done via a drain in the recuperator vessel. With the original design of the cycle this was not possible. The liquid from this tap is evaporated in the distilling apparatus depicted in figure 8. Up to now there are no long-term operational experiences with this system. Although, with the modifications of the cycle, the costs for the recovery of one litre of MDM, with a purity of more than 95%, are estimated to € 8.

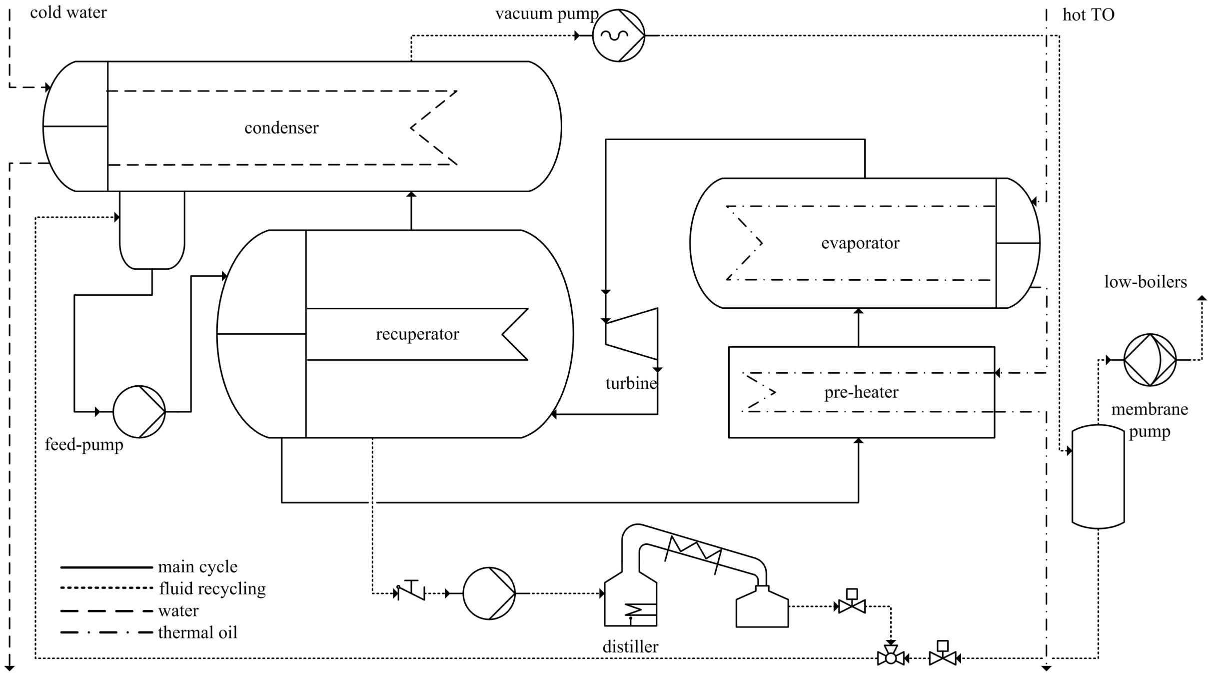

Figure 10: Cycle including all modifications Erhart (2015)

4. CONCLUSIONS

The following conclusions can be drawn from the observations in this paper:

- The degradation of MDM in ORCs is related with the amount of petroleum based lubricants. If this is related to the main component of the lubricant, to its additives or to the decomposition products of the lubricant is not clear.
- The decomposition process under the observed conditions, leads to a large amount of high-boilers in the working fluid.
- The fluid composition throughout the cycle differs significantly. A large fraction of high-boilers precipitate after the turbine. This offers the opportunity to remove these high-boilers from the system if the recuperator has a closed reservoir.
- Low-boilers can be removed from the cycle with the vacuum system by adding an additional membrane pump.
- The distilling of highly contaminated working fluid delivers 95% of pure MDM after the first treatment. Lubricants can be removed from the fluid reliably under laboratory conditions.
- The laboratory distilling tests have shown, that up to 64% of the MDM from the original fluid can be recovered.
- The economical effort of distilling contaminated fluid is far below the effort of a reinvestment in new working fluid. The costs for the distillation for one litre of pure working fluid are around € 8. Over the last years, the price for new working fluid ranged between € 15 and € 22.

Even though the number of analysed power plants is rather low, the data show the necessity for further investigation. The detailed chemical processes, especially the interaction of Hydrocarbons from the lubricant oil with MDM, could not be analysed in detail. A chemical analysis, under laboratory conditions, is necessary to determine the reaction kinetics of this complex process.

NOMENCLATURE

MM	Hexamethyldisiloxan	
MDM	Octamethyltrisiloxane	
D3	Hexamethylcyclotrisiloxane	
D4	Octamethylcyclotetrasiloxane	
MD2M/L4	Decamethyltetrasiloxane	
D5	Decamethylcyclopentasiloxane	
MD3M/L5	Dodecanethylpentasiloxane	
MOH	Trimethylsilanol	
CHP	Combined Heat and Power	
CAS	Chemical Abstract Service registry number	
HS-GC-MS	Head Space Gas Chromatography Mass Spectrometry	
TO	Thermal Oil, here Therminol66	
$\vartheta_{source,max}$	Temperature [°C]	-

Subscript

cond	condensing
max	maximum

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