Testing of pyrolysis oil emulsions in small scale boiler pumps: preliminary results

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ABSTRACT: The use of Pyrolysis Oil (PO, also called Bio Crude Oil) in small scale domestic oil boilers represents a very interesting potential market. However, it is well known that the corrosive and aggressive characteristics of PO (compared to those of Light Fuel Oil, LFO) makes very difficult its use, expecially in small scale systems. Metallic components are subject to fast erosion and corrosion, which cause rapid decrease in performances, increase of maintenance and substitution costs, and even prevent from long term use. The substitution of conventional components with corrosion resistant ones, such as stainless steel components, is technically feasible but often unacceptable from a cost point of view.
The production and use of Pyrolysis Oil / Light Fuel Oil emulsions is a possible alternative, which aims at avoiding expensive component modifications. The objective of this work is to investigate PO-LFO emulsion use in typical gear pumps used in small scale boilers. In order to verify the response of critical plant components to PO-LFO emulsions, a test rig has been designed. Emulsions (10 % w/w LFO in PO) have been produced using two different Pyrolysis Oils, analysed under optical microscope and FOQELS (Fiber Optic Quasi Elastic Light Scattering) techniques, and used for the pump test. The surface of the gears and other critical elements after use with emulsions have been investigated by means of optical microscope. The effect of selected emulsions on the spray angle of the injection nozzle has also been preliminary investigated. The result of the work is that emulsions seem not compatible with standard low-cost gear pumps, the main problem being the poor lubrication properties of the PO. Surface treatments have to be used to protect the components.

INTRODUCTION

Biomass pyrolysis is a thermochemical process that is used to convert solid biomass into a liquid biofuel, which gives the advantages typical of a liquid fuel compared to a solid one. However, from the end-user point of view, pyrolysis oil (PO) use represents a serious challenge, as it is corrosive, erosive, tends to deposit, and has poor lubrication properties.

Corrosion characteristics of biomass pyrolysis oils as well as PO material compatibility have already been extensively studied by various authors [1; 2; 3; 4; 5; 6; 7;]. Standard construction steels (mild steel), aluminium, and - to a lesser extent - copper, are not compatible with pyrolysis oil even at low temperatures: stainless steel, cobalt-based materials, brass, and various plastics are to be used for manufacturing components which are in contact with PO. Corrosion rates increase when surface deposits are continuously removed by fast and unsteady flows.
In general, two basically different approaches can be adopted to use Pyrolysis Oil: on one hand, standard components can be substituted with ones made of materials compatible with this viscous, tarry and corrosive liquid; on the other hand, the fuel can be upgraded (by means of various methods) to a more friendly one. Among this second option, emulsification is one of the most promising solution, expecially for small scale systems. The properties and characteristics of emulsions become closer to those of LFO as the amount of emulsified PO is reduced.
The possibility of producing Light Fuel Oil (LFO) / Pyrolysis Oil (PO) emulsions have already been demonstrated by various authors [8; 9]. Surfactants are to be added to obtain stable emulsions. Emulsions have been tested in Diesel engines [10] with promising results, even if long term tests are still needed. Limited information are instead available on pyrolysis / Light Fuel Oil emulsions for heating, which represents one of the most interesting market for this fuel.
Small scale heating systems usually adopt gear pumps to feed the fuel to the burner (operating pressure around 9-12 bars). It make sense to investigate if PO-LFO emulsion can be used in standard domestic boiler, i.e. if the LFO can act as a protective coating on the surface of the most affected pump components, increasing component lifetime.

MATERIALS AND METHODS

DESCRIPTION OF LFO-PO EMULSIONS

LFO based emulsions with two different oils were formulated: a forestry residue liquid (bottom phase) prepared by VTT (Espoo, Finland) and a pine sawdust liquid prepared by Fortum (Porvoo, Finland). The main physico-chemical properties of both these oils are reported in table 1.

Table 1 Main characteristics of PO used for emulsions

	Pyrolysis Oil	
	VTT	**FORTUM**
H_2O content (% w/w)[a]	25.8	26.1
Viscosity at 40°C	17 cSt	25 cSt
Insoluble Solid Content[b] (%w/w)	0.17	0.20
Ash Weigth (%w/w)	0.099	0.035
Density at 20°C	1.12 kg/dm^3	1.22 kg/dm^3
pH	2.5-3	2.5-3
Elemental Analysis *wet basis*		
Carbon content (% w/w)	45.07	49.55
Hydrogen content (% w/w)	0.41	0.06
Nitrogen content (% w/w)	6.41	7.03
Oxygen content (% w/w)	48.11	43.36

a. Obtained by Karl-Fischer method.
b. Determined as insoluble residue in methanol-dichloromethane mixture.
c. Oxygen percentage was calculated as difference.

As regards viscosity, the following values have been measured:

Table 2 Viscosity of LFO, PO and emulsions (30 % w/w PO in LFO)

Ligh Fuel Oil *(cSt @ 20 °C)*	**Emulsion (30 % w/w)** *(cSt @ 20 °C)*		**Pyrolysis Oil** *(cSt @ 40 °C)*	
	VTT	**FORTUM**	**VTT**	**FORTUM**
1.64	1.58	1.61	17	25

Both emulsions were elaborated by testing several classes of surfactants and various emulsification methodologies. Emulsions were characterized by means of optical microscopy and FOQELS (Fiber Optic Quasi Elastic Light Scattering) analysis.

Various PO/LFO weight ratios were investigated (30/70, 25/75,20/80, 15/85, 10/90, 5/95). During the process for obtaining a stable emulsion, approximately one hundred different surfactants have been tested. Emulsions were prepared both by solving the surfactant in the PO and in the LFO. As dispersing methodology, magnetic agitation and micronization by means of an Ultra-Turrex Disperser were investigated. Influence of temperature on emulsions' stability was investigated as well.
As regards the Lower Heating Value and the viscosity of the emulsions, this issue has already been investigated in previous works by several authors [8; 9]. Heating value of emulsions is directly proportional to the amount of biofuel emulsified with the fossil fuel. Viscosity of emulsions is instead significantly greater than the starting oil, and relative viscosity tends to become constant irrespective of temperature [8; 9]. Corrosion tests results also showed that corrosiveness of emulsions is about half that of pure PO, and it does not depend on PO concentration (at least in case of low PO in LFO emulsions) [4].
After having identified the proper dispersion methodology and surfactant type, the surfactant amount was reduced as much as possible in order to minimize costs.
Emulsions were then characterized by optical microscopy and FOQELS analysis. Microscopy images were collected by means of a Nikon optical microscope: a drop of the emulsion was placed in between two microscopy glass slides and pictures were taken by a Nikon digital camera. Two images of an emulsion obtained by using the FORTUM PO are reported in figure 1: the variation of the droplet size distribution between the fresh emulsion (on the left) and the 20 days aged emulsion (on the right) is pretty small, accounting for the stability of the emulsion obtained.

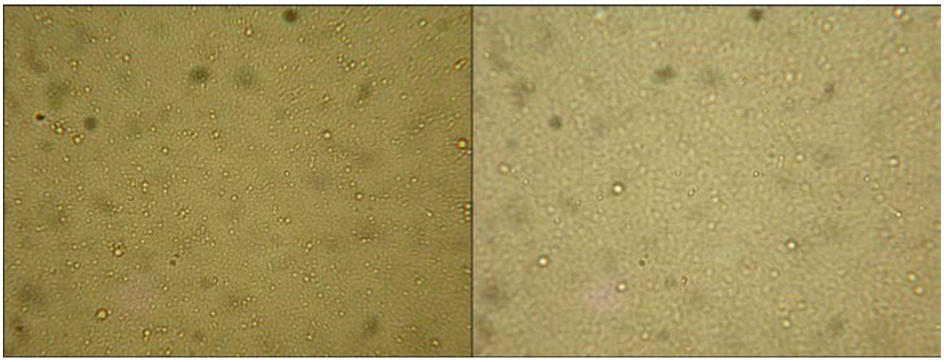

Fig. 1 Fresh emulsion (left) and 20 days aged (right) emulsion obtained by micronization of FORTUM PO (30% w/w) and LFO (70% w/w). Average diameter of the droplets is about 2 μm.

A similar analysis has then been carried out on VTT oil emulsions, which showed a lower stability after 20 days aging. In this case, phase separation at microscopic level has been detected.
Emulsions were also characterized by means of Fiber Optic Quasi Elastic Light Scattering (FOQELS) analysis. The result of this technique is the so called auto-correlation function. This function accounts for the size distribution of the scattering objects that are present in the sample. In the case of the emulsions, the auto-correlation function is directly related to the size distribution of the droplets.

So, using both optical microscopy and FOQELS, the droplet size distribution and its behaviour as a function of time was obtained. It is worthwhile to remark that these techniques investigate to different size ranges: >1 μm in the first case, from 2 nm to 2 μm in the second one. This means that, by combining these two techniques, the size and the growth of the droplets can be investigated.
Results obtained from the characterization using FOQELS show that the emulsions constituted by FORTUM oil are more stable than those based on the VTT oil. In this latter case a bottom phase appears in the samples after about 10 days.

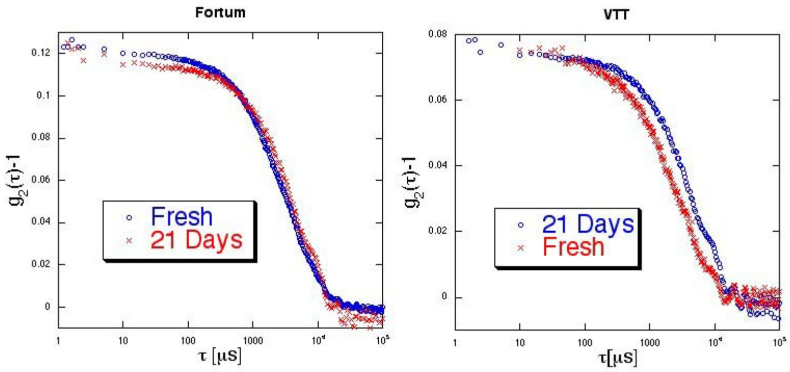

Fig. 2 Fresh emulsion (red) and 21 days aged (blue) emulsion obtained by micronization at 70ºC of Fortum (left) and VTT (right) POs (30%) and Diesel Oil (70%). X axis: τ [μs] is the delay time; Y axis: $g_2(\tau)$-1 is the autocorrelation function of the scattering intensity. In the Fortum case, the aged curve is almost identical to the fresh one

Owing to the higher stability, FORTUM oil was selected for pump tests in the test rig. In order to easily evaluate the effects of the emulsion on the mechanical parts, the selected PO/LFO ratio was 10 % w/w.

DESCRIPTION OF THE TEST RIG

A test rig has been designed and constructed with the specific purpose of performing long term test runs on small boiler pumps fed with LFO-PO emulsions. The main components of the test rig are the following:

- The gear pump
- The electrical motor
- The spray nozzle
- A transparent storage tank
- A pressure transducer (PT)
- A pressure indicator (PI)
- A pressure switch (PS)
- A temperature transducer (T)
- The data logger
- The control board

The layout of the pump test rig is given in the next figure.

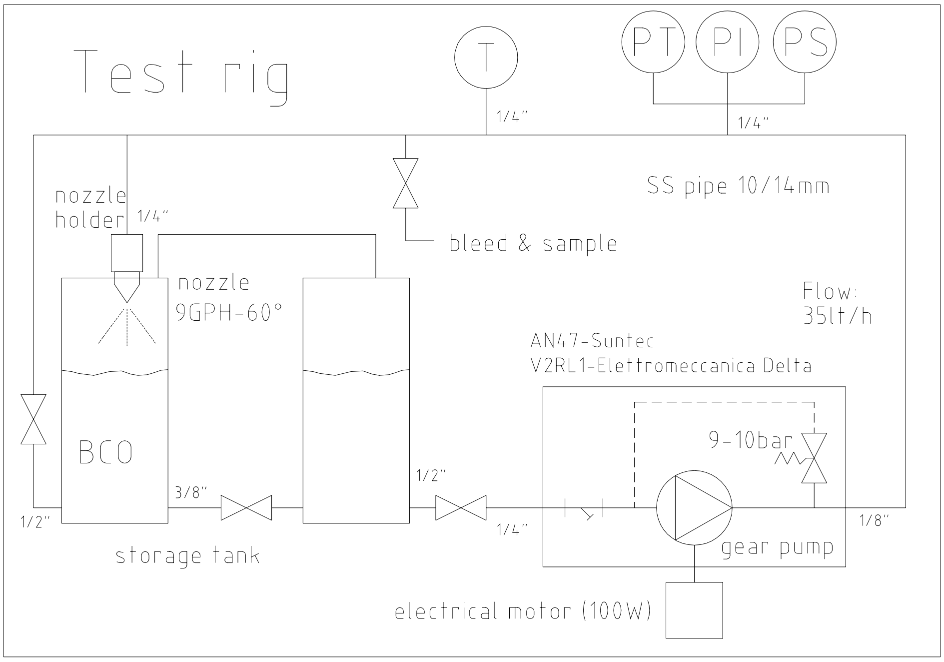

Fig. 3 Layout of the pump test rig.

A regards the selection of the pump type for the tests, two main options have been considered: the Elettromeccanica Delta pump and the Suntec pump. Both of them are gear pumps, with similar operating conditions. The pumping gear mechanism is slightly different between the two pumps, as shown in the following figure. The Suntec pump has an additional element (not present in the Delta pump) moving on the top of the cogs, which could potentially further increase or accelerate the erosion-corrosion phenomena when using unconventional liquids as PO or emulsions. The Delta pump has finally been selected for the tests, also taking into account its capability of working with low quality (i.e. dirty) liquids, as installers report.

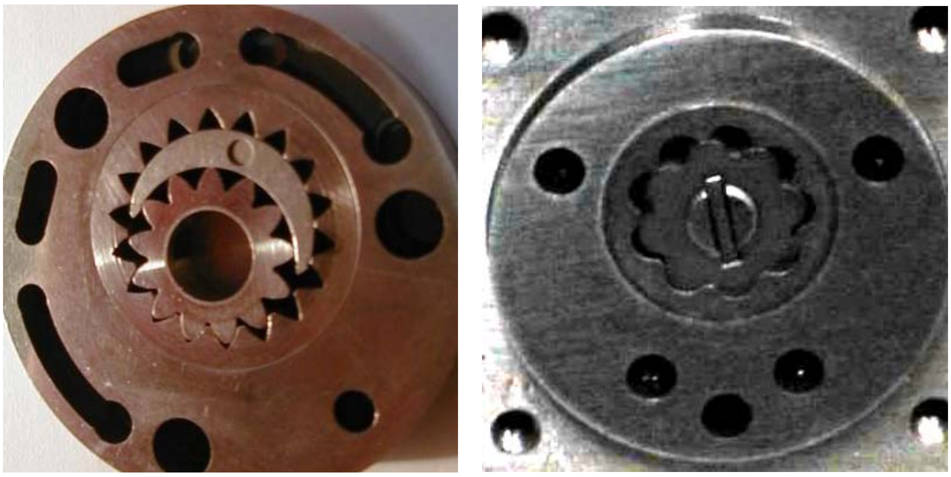

Fig. 4 Gears of the Suntec pump (left) and Delta pump (right).

The selected Delta gear pump operates at nominal working pressure conditions of 9 bar, delivering 42 l/h and requiring 45W (reference conditions: viscosity 5 cSt at ambient temperature 2850 rpm). The pump is equipped with a pressure regulating valve (7-14 bar) which is needed to adjust and keep constant the delivered pressure.
As regards nozzles, a wide range of nozzle types exist, each specific for a certain fuel or boiler type. There are 3 main types of commercial nozzles, which generate different spray angles. The most common one produces a 60° spray angle, while the other 40° and 80° angles respectively. The needs for larger or narrower spray angles depends on the combustion chamber geometry, as well as other aspects which we will not discuss here.
Even if the pump tests were carried out without using the spray nozzle (in order not to modify the pumped fluid by vaporization), short term tests have been carried out to observe the spray angle when using PO-LFO emulsions. A transparent tank was installed on the pump test rig with the exact purpose of visualizing the spray angle. During normal test operation, the nozzle has instead been excluded by the circuit and its pressure drop simulated by means of a regulated pressure valve immersed in the fuel. As said above, this is necessary in order not to modify the PO when passing through the nozzle and being sprayed in open air many times.
The circuit is therefore completely closed: it contains a maximum of 5 lt of liquid. The measure of the liquid flow is performed by means of two transparent tanks: the pumps takes the liquid from one tank and deliver it to the other. The two tanks are connected by a valve which is always open: the flow can be measured by closing this valve (i.e. disconnecting the tanks), and observing the height difference in the tanks during a defined amount of time. This is a rather simple, even if not very accurate, system to measure flows of liquids as PO.
The system is equipped with a control board and a data logger. The control board is able to repeat long-term on-off or continuous cycles and protect the electrical components, while the data logger store the data transmitted (pressure, temperature) by the measuring instruments installed on the test rig. A photo of the test rig is given in the next figure.

Fig. 5 Picture of the pump test rig.

TEST PROCEDURE

Test were always started with LFO for one hour: this procedure allows for a complete check of the system before each run with LFO-PO emulsions, as well as to lubricate the pump with a thin film of LFO before switching to emulsions.
As already mentioned, pressure and temperature are measured and recorded during the test. The pressure indicator (PI) and transducer (PT) show the changes in pump delivered pressure, and it is a mean to understand when pump performances falls below minimum acceptable performances. If, during the test, the pressure falls below

7.2 bar, the experiment is automatically interrupted, as the spray quality and angle would not be sufficient to assure good combustion conditions. This action is done by the pressure switch (PS).
The measure of the temperature (T) at pump outlet is mainly used to control the thermal stress of the fuel. Ambient temperature is also measured and recorded.
A Delta pump has also been operated for 72 hours with pure LFO as control.
Pictures with a standard camera and with optical microscope were taken of the most critical pump component operated with pure LFO and LFO-PO emulsions.
A test form has been elaborated to collect the most important results, as those obtained from visual and microscope inspection of pump components, the quality of the emulsions after the tests, and further test details.

RESULTS

The test started at 12:06, after having completed the preliminary operation with pure LFO according to the planned test procedure. At the beginning of the test, pictures of the spray angle were taken for both the pure LFO and 10 % w/w emulsion. The temperature of the pump (external body) as well as the emulsion and the ambient temperatures, were recorded. Similarly, pressure at pump outlet was also registered. These are given in the next two figures.
The two sudden decreases in the temperature value are due to a factor (opening of the test rig cover by the operator) not related to the experiment itself. It is instead worth to observe that the pump temperature rapidly increased to values around 28-29 °C, while the ambient temperature was around 14-13 °C). During the last period of the test, this temperature was even greater, above 29 °C. The emulsion temperature was most of the time above 31 °C, up to 31.7 °C: differently from the pump temperature, the fuel temperature decreased before the test stop.

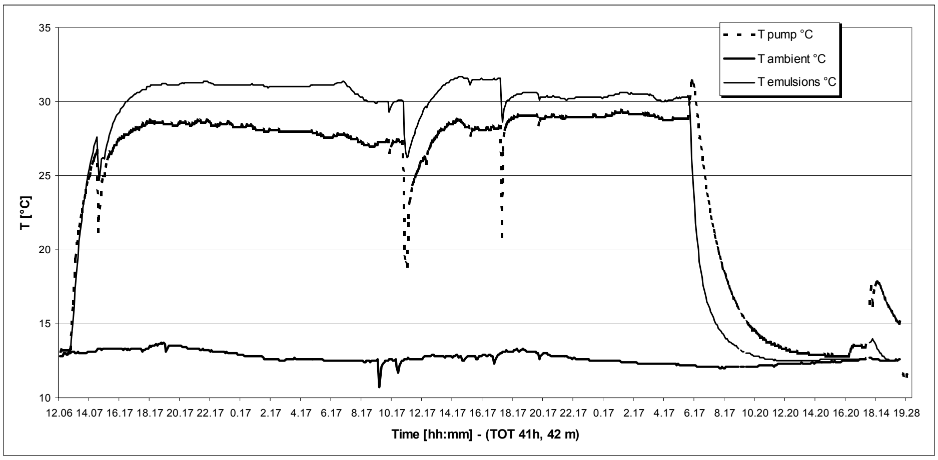

Fig.6 Temperatures during the PO-LFO pump test

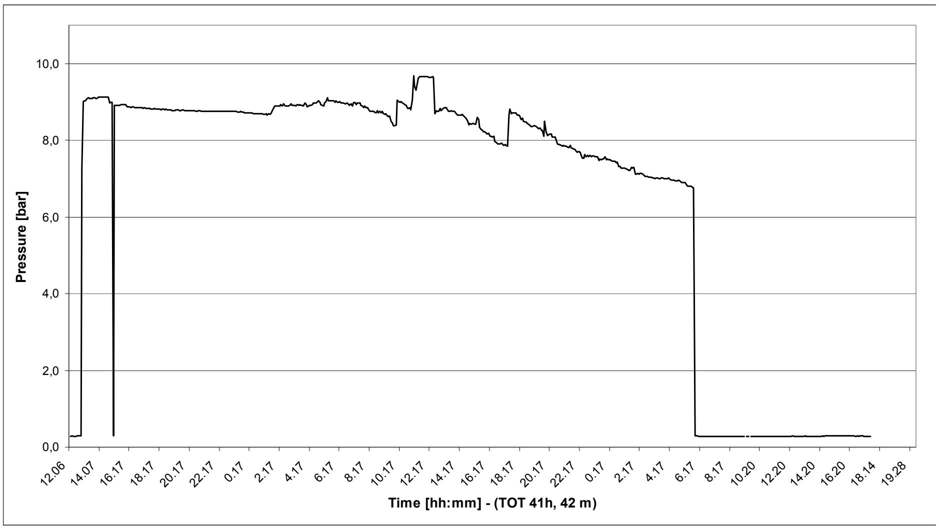

Fig.7 Pressure at pump outlet during the PO-LFO pump test

The pressure indicator, initially very stable, showed more and more severe oscillations after 12 hours from the beginning of the tests. After 20 hours the pressure became very unstable, varying from approximately 8 to 11 bar. When pressure dropped below 7 bar, the pressure switch (PS) stopped the pump and the test was interrupted. It happened after 41 hours and 42 minutes from the test start.

Both the shaft (which drives the pump gears) as well as the pressure regulating valve were stuck.

Several items were investigated by visual inspection and through optical microscope (lens 8x and 11x) and photographs taken by a Nikon Coolpix 2 M digital camera.

Components were cleaned before the inspection by the following procedure: 5 hours bath in ethanol, 1 hour ultrasonic bath in pure ethanol (repeated 3 times), and 1 hour ultrasonic bath in a water acetone mixture. The components under investigation are shown in the following figure.

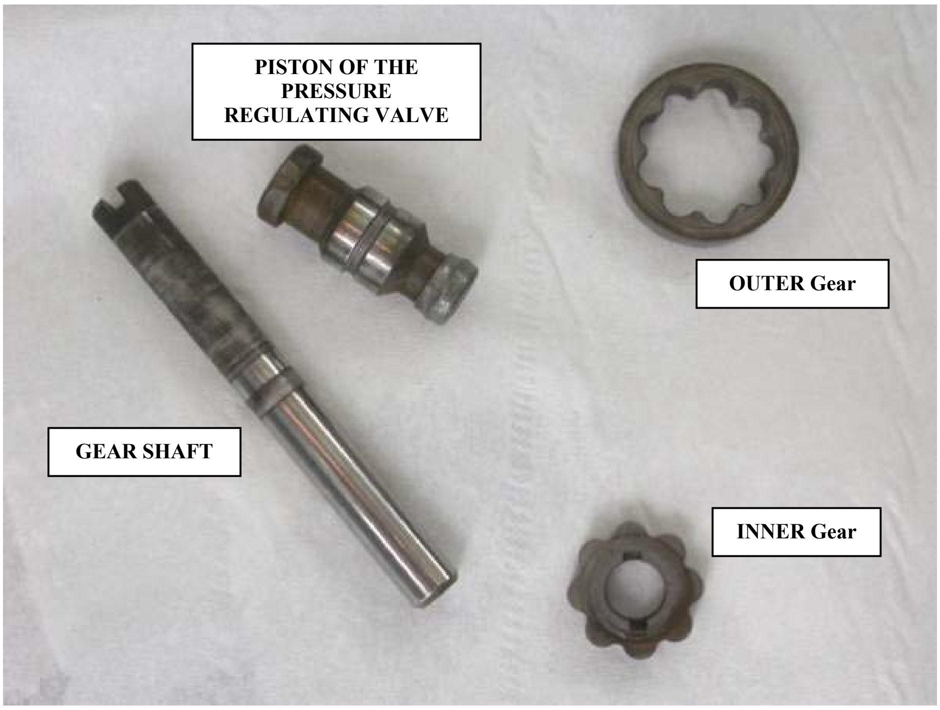

Fig. 8 Pump components under investigation

The inner gear cog surface was clearly affected by the emulsion use, as indicated in the next figure, while the lateral parts of the gears did not suffer significantly. Similar results can be observed on the surface of the external gear as well as on the sliding parts of the pressure regulating valve piston.

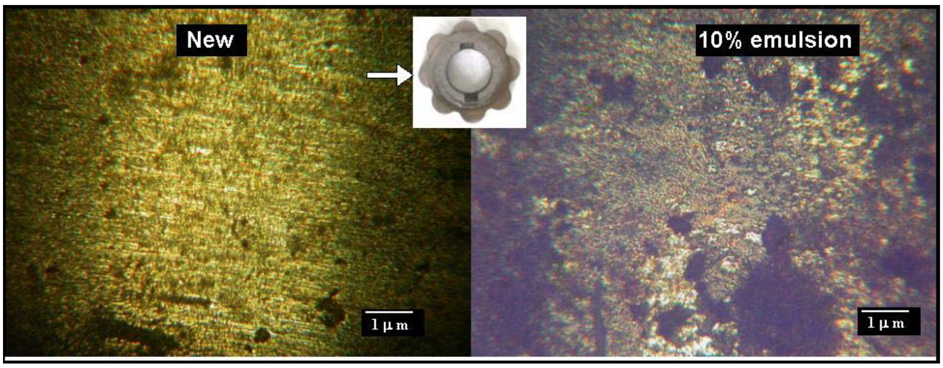

Fig. 9 Cog surface after pump test

The impact of LFO-PO emulsion on the gear shaft surface can be easily seen in the next figure, which shows different parts of the shaft after its use. While the part which is not in contact with the emulsion looks shiny and smooth, those parts having been in contact with the emulsion show significant surface damages and corrosion.

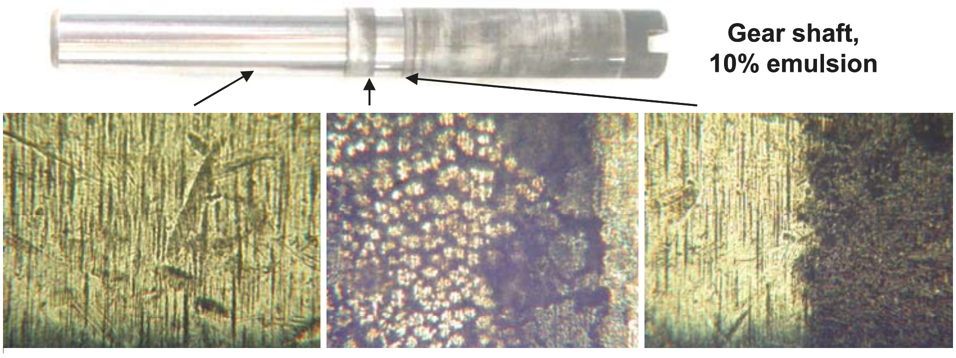

Fig. 10 Shaft gear surface after pump test

Finally, as planned the spray angle was also preliminary observed with the two different fuels by taking photographs and movies. This work is currently ongoing: laser techniques will be applied in the remaining part of the research work to obtain a precise understanding of this aspect. As it can be seen in the next two figures, the spray angle seems not to change significantly (from approximately 63° to 61°) when using emulsions, compared to pure LFO (p=9 bar). No investigation was performed as regards material compatibility and long-term performances of the injector.

Fig. 11 Spray angles using 10 % w/w PO-LFO emulsion (right).

DISCUSSION AND CONCLUSIONS

The severe pressure oscillations recorded after 20 hours from the beginning of the test were due to the bad functioning of the built-in pressure regulating valve, which after that time was not able to operate correctly anymore with emulsions. This was a first indication that the emulsion was affecting the movement of the piston. At the end of the test, the shaft was blocked and the electrical motor was not able to start the pump anymore: the intervention of the operator, which manually moved the shaft into its seat, made possible to start the pump again.

This result, which need a deeper investigation, lead to the preliminary conclusion that shaft lubrication is probably the main problem. Lubrication, which is normally done by the LFO itself during “standard” operation with this fuel, becomes very critical when PO (or emulsions) is pumped, even when low percentage PO-in-LFO emulsion are investigated. PO has lower lubrication properties compared to LFO, as well as greater corrosiveness. Despite the fact that a small amount of PO is emulsified in a continuous phase of LFO, the thin LFO film lubricating the moving parts (which is developed during the initial phase of the test when only pure LFO is pumped) seems not sufficient to protect them. By a combination of physical and chemical processes, PO droplets probably attack the metal in different ways: the emulsion could be broken by the high speed motion and vibrations within the small *meatus* between the shaft and its seat, then corrosion of the shaft and its seat occur, and PO starts to deposit on the surface. The process is a typical degenerative one: the *meatus* locally reduces, and PO quickly build-up on the surfaces, eventually blocking the moving parts.

These preliminary results suggest that the use of PO, even if emulsified at low percentages in LFO, is critical when small-scale low-cost technologies are considered, as it is the case of common small boilers for domestic heating, where common construction steel is often used. Further work is necessary to better understand the behaviour of PO-LFO emulsions under pressure conditions.

These preliminary results seems in rather good agreement with those of a previous project, in which emulsions where produced by CANMET using VTT oil, and tested by Neste Oy [11].

As regards the possibility of substituting the gear pump with different types of pumps, or applying surface treatments to the most critical parts of gear pump components, not only technical issues but also cost aspects have to be carefully considered. This work is currently on going.

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