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FIELD EXPERIENCE AND LABORATORY ANALYSIS OF OXIDATION CATALYST ON DUAL FUEL ENGINES

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ABSTRACT

A DCL oxidation catalyst for exhaust-gas cleaning has been field tested on a Wärtsilä 50 series dual-fuel engine during 5000 hours of continuous operation in an end-user power plant application. The engine has been designed for continuous operation on natural gas (NG), light fuel oil (LFO) as well as heavy fuel oil (HFO), thus giving the consumer a wide variety of fuelling options. All three fuels were used at some point during the 5000 hours field trial. These fuels have different properties such as differing levels of sulphur and ash contents that affect the abatement efficiencies of the oxidation catalyst.

A detailed study was performed to understand the effect of different fuels, lube oil poisoning and long running hours on the abatement performance of the oxidation catalyst. The oxidation catalyst was equipped with sample cores that were exchanged during scheduled engine maintenance periods. This allowed parallel field and laboratory evaluation of the emissions abatement and the quantity of lube oil deposits on the catalyst at successive intervals of engine running hours. We will show that the combination of the dual fuel engine and the oxidation catalyst is very robust, even for the different fuels, and it gives low emissions.

INTRODUCTION

Power plants with the facility to operate on different fuels, such as gas, light fuel oil and heavy fuel oil, have become a popular alternative to mono-fuel installations. Being able to change from gas to liquid fuel and back to gas, while continuously operating the plant, allows a very reliable and flexible operation on occasions when the gas supply is temporarily interrupted or uncertain.

The prime mover suitable for these multi-fuel applications is an engine that normally uses gas as its main fuel and light fuel oil is used as a pilot fuel for igniting the mixture of gas and air. In other words, the engine operates according to the Otto principle with a very high air to fuel ratio. The performance and emissions of this dual fuel engine are similar to a spark-ignited lean-burn gas engine. When the dual fuel engine is operated on liquid fuels alone, it operates as a diesel engine and its performance and emissions resemble those of a pure diesel engine. In marine applications the dual fuel engine is often used as a prime mover for liquid natural gas carriers. In this application, the engine uses the boil off gas as its fuel when the vessel carries liquid natural gas (LNG). When returning to the gas field for reloading, the vessel makes use of the ability to run on heavy fuel oil. In power plants, the ability to run the plant on both gas and oil has been welcomed in special niche applications where high flexibility is important under circumstances of unreliable gas supply. Examples of such applications are airports and hospitals where reliable electricity is an ultimate necessity. The major operation mode for the dual fuel power plants is under gas operation. This paper focuses in particular on power plant emissions under gas operation with LFO pilot fuel and the risk of catalyst deactivation when running the dual fuel engine on LFO or HFO only.

Local and/or national regulation on the emission of pollutants determines the allowed emission levels in power plant applications. However, at locations with no emission legislation, the World Bank Group guidelines are frequently applied. The "Thermal Power" guidelines set limits for the emissions of nitrogen oxides, sulphur dioxide, and particulate matter [1]. Wärtsilä gas, dual fuel, and diesel engines can fulfil these guidelines without a secondary emission control with moderate quality fuels.

Many industrialised countries have found it necessary to set technology specific guidelines for lean burn gas engines. The

German TA Luft 2002 [2] has limits for the emission of sulphur, nitrogen oxides, carbon monoxide, and formaldehyde. This requires the installation of an oxidation catalyst on the Wärtsilä dual-fuel engines. In addition to the components listed in TA-Luft 2002 the catalyst will also lead to the minimization of potentially ozone-forming photoactive volatile organic compounds. The EU directive on integrated pollution prevention and control [3] together with the reference documents on best available techniques (BREF's) for large combustion plants limit the hydrocarbons with the help of an oxidation catalyst that reduces CO [4]. Formaldehyde emissions should be below 23 mg/Nm³ and CO below 100 mg/Nm³ (15% O₂). NO_x emissions abatement is considered to be best available technology (BAT). For gas fired engine plants, there are no limits or specific emission cleaning techniques assigned to particulate and SO₂ emissions, as these are considered insignificant when using natural gas.

A similar approach, to the legislation in EU and Germany, is found in the United States of America where the Environmental Protection Agency sets rules for the "maximum achievable control technology" of hazardous pollutants [5]. Here an oxidation catalyst with strong carbon monoxide abatement can be used for controlling the emissions of hazardous air pollutants. The obligation to continuously monitor the emissions of formaldehyde can be avoided using this type of catalyst. Turkey [6] uses this modern approach with technology specific legislation and emission regulations that include carbon monoxide abatement and legislation with efficiency bonuses. Some legislation in European countries is unluckily inappropriate for lean burn gas engines, besides regulating nitrogen oxides and carbon monoxide they also limit the emissions of non-methane hydrocarbons. This legislation limits the use of the commercial natural-gas resources since the ethane concentration in the fuel gas is reflected in the composition of the hydrocarbon emissions of the engine. This fact excludes the use of gases with high ethane content such as North Sea, Algerian, and Iranian gases. Russian gas has low ethane content and consequently low non-methane hydrocarbon emissions.

The environmental legislation for carbon monoxide and hydrocarbon species has lead to the installation of oxidation catalysts on gas-fired lean-burn stationary engines in many countries. Besides gas applications, oxidation catalysts are used for smaller diesel applications where the running hours can be kept low and the liquid fuels are of a good quality with low sulphur content. However, power plants driven by large engines commonly use fuels with higher sulphur contents. This limits the use of oxidation catalysts since the catalyst further oxidizes the sulphur in the flue gases. The installation of an oxidation catalyst in dual fuel applications is therefore a challenge with respect to durability and efficacy. The oxidation catalyst must withstand the sulphur together with the ash components of the liquid fuels and lubricating oils. The lube oil composition used for natural gas operation is different than that used for sulphur – containing fuel oils.

In this study we tested the durability of an oxidation catalyst on a dual fuel application running on gas, light fuel oil, and heavy fuel oil. Full-scale emission tests are compared to bench

scale experiments with one catalyst formulation. We aged two catalyst formulations during full-scale operation and tested the performance using a bench scale model gas reactor.

NOMENCLATURE

HFO- Heavy Fuel Oil
LFO- Light fuel Oil
MGR – Model Gas reactor
FTIR – Fourier transform Infrared Spectroscopy
NMHC – Non-methane hydrocarbons
NMNEHC- Non- methane, non-ethane hydrocarbons
THC- Total Hydrocarbons
DF – Dual Fuel

ROBUST FIELD TEST AND DETAILED LABORATORY STUDIES PROCEDURE

POWER PLANT AND ENGINE DESCRIPTION

The full-scale tests of this study were conducted at the Bermeo power plant in Northern Spain. The installation serves two purposes: one as a power supplier for the electrical grid and second as an engine test laboratory for Wärtsilä. A new 6 MWe Wärtsilä 6L50DF engine was installed in the power plant during April 2004. After an initial tuning of the engine and installation of the oxidation catalyst the plant has been running as a base load plant. The plants daily operating profile starts in the morning at approximately 08:00 and stops at around 22:00 in the evening.

Wärtsilä 50DF engines are built on the Wärtsilä 46 diesel engine design platform. For power plant applications, the engine is produced with 18 cylinders. Table 1 lists technical data of a dual fuel engine running on gas and used in a power plant application.

The dual fuel engine operates on the lean-burn principle with an excess of air in the cylinder. Lean combustion reduces peak temperatures and therefore NO_x emissions. Moreover, the efficiency is increased and higher power is reached while knocking can be avoided. In the dual fuel engine the combustion of the lean air-fuel mixture is initiated by the injection of a small amount of liquid fuel (pilot fuel) into the cylinder. To obtain the best efficiency and lowest emissions, every cylinder is individually controlled to ensure operation at the correct air-fuel ratio and with the correct amount and timing of pilot fuel injection.

The fuel system of the Wärtsilä 50DF is divided into two parts: one for gas and the other for diesel oil. In gas mode each cylinder has an individual feed pipe to the gas admission valve on the cylinder head. The fuel oil supply on the engine is divided into two systems: one for the pilot fuel and the other for backup fuel. The pilot fuel is elevated to the required pressure by a pump unit. The high-pressure pilot fuel is then distributed through a common-rail pipe to the injection valves at each cylinder. The pilot fuel amounts to less than 1% of fuel at full-load when running the engine in gas mode. Pilot fuel injection is electronically controlled and the main diesel injection is hydro-mechanically controlled. The individually controlled

solenoid valve allows optimum timing and duration of pilot fuel injection into every cylinder when the engine is running in gas mode.

Table 1: Technical data of the dual fuel engine

Technical data 50 Hz	Unit	18V50DF
Power, electrical	kW	16638
Heat rate	kJ/kWh	7608
Electrical efficiency	%	47.3
Engine speed	rpm	500
Length	mm	18404
Width	mm	5140
Height	mm	6277
Weight	tonne	379

Heat rate and electrical efficiency at generator terminals, including engine-driven pumps, ISO 3046 conditions and LHV. Tolerance 5%. Power factor 0.8. Gas Methane Number >80. Dimensions and weight (generating set with liquids and 150 mm high spring elements)

TEST MODES AND FUEL TYPES

The long-term catalyst test involved running the 6L50DF power plant under two different scenarios. In the first part of the test (scenario 1) the installation was run mainly in gas mode (gas plus 1% pilot LFO) and only occasionally in diesel mode (LFO only). The fuels used were natural gas and a light fuel oil with a sulphur content of 0.2% as a pilot fuel. This scenario simulates the dual fuel engine as it is run in normal power plant applications. In the second part of the test (scenario 2) the engine was simulating the operation profile and fuels of a marine vessel shipping liquid natural gas. Besides the gas mode (gas +pilot HFO) the engine was run for extensive periods on heavy fuel oil only with a sulphur content of 1%. Figure 1 shows the running hours and the operation profile of the test.

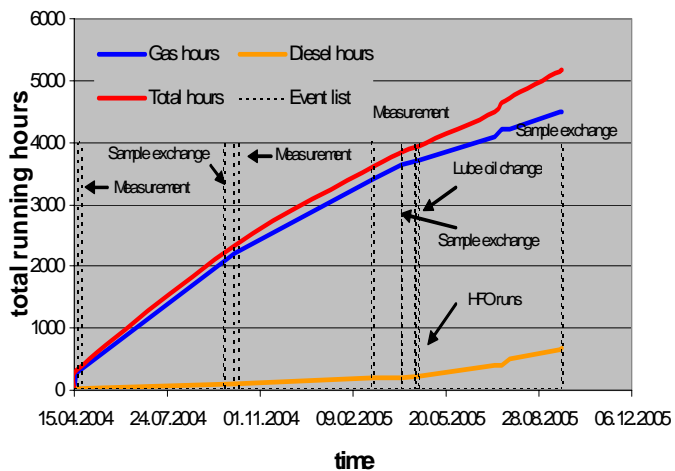


Figure 1: Running profile of the test

Table 2 show analysis of the natural gas and Table 3 the amount of ash and inorganic constituents in the liquid fuels that were used in the Wärtsilä 6L50DF power plant.

Table 2: Natural gas composition

Component	%
CH ₄	90.06
C ₂ H ₆	5.97
C ₃ H ₈	1.61
i-C ₄ H ₁₀	0.27
n-C ₄ H ₁₀	0.30
i-C ₅ H ₁₂	0.06
n-C ₅ H ₁₂	0.04
C ₆ H ₁₄	0.01
N ₂	1.08
CO ₂	0.60
S	Not measured

Table 3: Light fuel oil and heavy fuel oil analysis of Bermeo power plant

Components	Unit	LFO	HFO
Sulphur	% m/m	0.19	1
Ash	% m/m	0.01	
Aluminium	mg/kg	< 1	22
Calcium	mg/kg	< 1	9
Iron	mg/kg	< 1	42
Nickel	mg/kg	< 1	27
Phosphorus	mg/kg	< 1	1
Silicon	mg/kg	< 1	23
Sodium	mg/kg	< 1	32
Vanadium	mg/kg	< 1	35
Zinc	mg/kg	< 1	< 1

m/m denotes mass/mass

During the HFO operation the lube oil is changed to a higher base number to prevent corrosion in the engine. The higher base number oil has a higher calcium concentration

CATALYST INFO

A DCL QUICK-LID™ housing containing a 4AC9 oxidation catalyst was installed at the Bermeo power plant. The catalyst was sized to fit the tight space requirements and meet backpressure requirements. The catalyst was sized at a space velocity of 250,000h⁻¹ @ STP with a cell density of 200 cpsi. Catalyst specifications can be found in Table 4.

The catalyst is designed to allow exchange of sample cores during scheduled maintenance periods of the engine. The catalyst has 16 cores distributed radially across the substrate body (Figures 2, 3). The use of cores allows the exchange of the samples at varying operating hours and the ability to field-test different catalyst formulations. The substrate is installed into a DCL QUICK-LID™ housing (Figure 4) that allows for easy removal of the catalyst element for maintenance and sample exchange. The catalyst element can be easily removed by unbolting the top cover plate and using a hoist or crane. The housing is designed to bolt easily between the expansion

bellows. The housing was equipped with sample ports for backpressure and exhaust measurements.

For this study, two catalyst formulations will be discussed. One of the formulas was applied to the main body of the catalyst and the sample cores. One formula consists of 1g Pt per litre of substrate (1gPt/lsub) dispersed on a proprietary washcoat material (Pt-based) and was coated on sample cores and the main body of the catalyst. A second formula (Pd-based) using the same washcoat was used for NMHC reduction. It was coated only on sample cores

Table 4: Catalyst Specifications

Part	Main Catalyst	Sample core
Volume (l)	99.5	0.045
Dimensions:	47.24" O.D. x 3.5", 1/8" SS ring	1" O.D. x 3.5", 1/8" SS ring
Cell Density (cps)	200	200
Formulas:		
Pt - based	1gPt/lsub	1g Pt/lsub
Pd-based		7g/l Pd-based



Figure 4: DCL QUICK-LID™ catalyst reactor housing

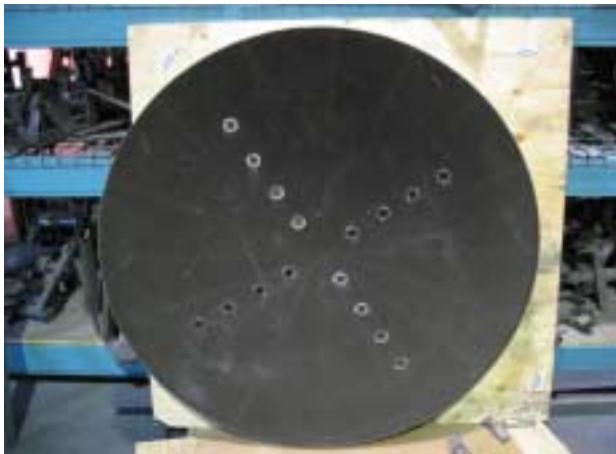


Figure 2: Image of Catalyst substrate with sample cores installed



Figure 3: Close-up image of one sample core

CORE SAMPLE EXCHANGE

Sample cores were exchanged after approximately 2000 and 3500 engine operating hours of gas/LFO operation. The third exchange was done when the catalyst had been aged about 1200 hours of gas/HFO fuel operation of which 425 on HFO operation alone. Only four samples were exchanged at each exchange time. One set of the four samples was run for the entire duration of the test. At the submission time of this paper the catalyst was still in operation. Figure 1 and Table 5 describes the number of hours that the sample cores were exposed before each exchange. The first two exchanges were performed after the second and third field test campaigns. We attempted to keep field exchange and field-testing times close. Discrepancies of a few hundred hours are a result of coordinating maintenance and testing campaigns. Sample core exchange occurred during scheduled engine maintenance.

The samples were returned to DCL after field aging for laboratory testing. The samples were tested for lube oil contaminants and evaluated under controlled laboratory conditions using a model gas reactor.

Table 5: Sample Exchange Schedule

	Exchange 1	Exchange 2	Exchange 3 (HFO)
Catalyst Gas Hours	1797	3343	874
Catalyst LFO Hours	70	174	0
Catalyst HFO Hours	0	0	425

BENCH SCALE CATALYST TESTING

Returned sample cores were evaluated on the bench scale model gas reactor (MGR) [7]. The MGR consists of mass flow meters, and a heated line for introducing water to the air stream via a peristaltic pump. Reactant gases are preheated before being reacted on the catalyst. Product gases are analyzed by a Varian 3800 Gas chromatograph, these include CO, hydrocarbons and CO₂.

The gas composition used is similar to the natural gas mode of the dual fuel engine (Table 6). Due to the limitations of the MGR, a space velocity of 90,000h⁻¹ was tested. This space velocity is about 2.7 times lower than the field catalyst space velocity. This will translate into higher conversions of the exhaust components on the MGR tests when compared to the field tests.

The data collected on the MGR allows a direct comparison of the sample cores under known controlled conditions.

Table 6: Gas Composition data Space velocity = 90,000 h⁻¹

<i>Component</i>	<i>Concentration</i>
Methane	1000 ppm
Ethane	170 ppm
CO	1000 ppm
H ₂ O	6 %
O ₂	10 %
SO ₂	3 ppm
Ethylene	100 ppm
Propane	50 ppm

Chemical poisons deposited on the catalyst core samples were determined by elemental analysis using PIXE (proton induced x-ray emission). Due to the destructive nature of collecting the sample from the substrate cores, elemental analysis measurements were only performed after bench scale reactor testing.

FIELD TESTING

Emission field-testing was conducted on 3 occasions during the 5000h test period. The first emission test was conducted to establish a baseline when the catalyst was new and the engine had been running only a few hours. The second test was conducted after 2219 engine hours and the catalyst had then been aged about 1900 hours in gas operation and about 80 hours on LFO. The engine running hours after the third emission test were 3600 hours and the catalyst had by that time been exposed to 3100 hours in gas mode operation and 170 hours of LFO operation. All of these tests were conducted before the switch to HFO. As all the emission tests show similar results to the third one we will only report the results from the third measurement campaign. The flue gas temperature was about 410°C when running on gas.

Emissions of NO, NO₂, CO, and hydrocarbons were tested using the US EPA 320 method. A Gasmet Fourier Transform Infrared analyzer was used for the analysis. N₂ was used as zero

gas. The uncertainty of the FTIR analysis was estimated to approximately +/- 30% for the hydrocarbons and aldehydes. The uncertainty for NO, NO₂ and CO was estimated to be 15%. The two sampling points were located in a horizontal duct, one closely before the catalyst and one closely downstream of the catalyst. The sampling points did not fulfil the requirements for approved sampling. However, as the FTIR enabled online measurement of the emissions components, we were able to quantify whether there were any concentration gradients as the sampling lance location was moved in a radial direction with respect to the duct. No concentration gradients were determined during this test. Special attention was paid to sample line heating to avoid condensation in the sampling system.

RESULTS/DISCUSSION

FIELD RESULTS

Emission field tests were performed at three occasions. As the result of the measurement campaigns showed similar result and since we found no activity decline of the catalyst activity we will only report the results of the third measurement campaign. Figure 5 shows the emission abatement efficiency of the catalyst for carbon monoxide, methane, ethane, propane, formaldehyde, and ethene when running the 6L50DF at full steady power. The results indicate that the platinum based catalyst we used at this installation is effective at reducing CO greater than and CH₂O up to 80% using natural gas as the main fuel. The abatement of alkanes is significantly lower than the abatement of formaldehyde and ethene. For the alkanes, the abatement efficiency increases as the numbers of carbon atoms in the emission component increases. Throughout the entire 5000-hour field test we found no deterioration or problems associated to the catalyst. The backpressure over the catalytic converter was within the design values and no significant increase of pressure could be detected even after HFO operation.

At the end of a 75-hour continuous HFO run, the catalyst was removed from the engine and examined. Figure 6 shows a typical HFO ash deposit over the inlet face of the catalyst.

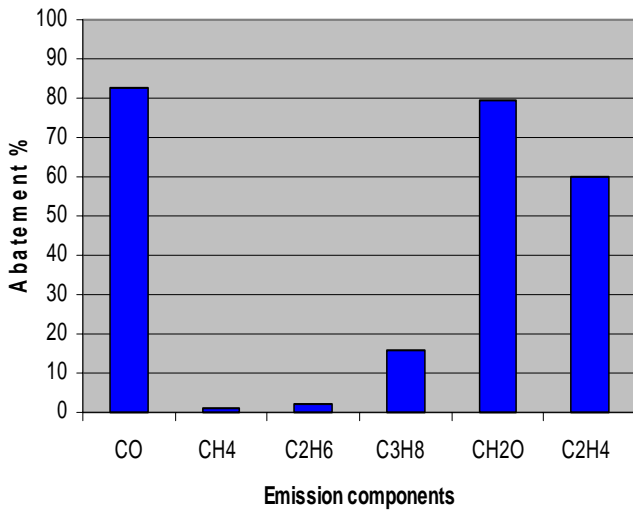


Figure 5: Full scale field test run data and abatement efficiencies [mole %] as measured with the FTIR

CATALYST DEPOSIT ANALYSIS

The aged catalyst samples were analyzed and the main deposits (or inorganic constituents) that accumulated on the catalyst are reported below (Table 7). As expected, the elements deposited on the catalyst are directly related to elements present in the lube oil and fuel. Sulphur is a direct result of the fuel and more specifically from the LFO or HFO fuels. The contribution of sulphur from the lube oil and natural gas is considered negligible. Higher accumulations are observed with more S in the fuel as per the HFO fuel. Vanadium is present only in the HFO fuel and is present on the catalyst during the HFO operation. Lube oil components such as Ca, P and Zn show high accumulation in a short operating time. Higher amounts of sulphur on the HFO sample are a direct result of higher concentrations in the HFO lube oil and fuel.

Table 7: Catalyst deposits on Pt-based Catalyst

	Exchange 1	Exchange 2	Exchange 3
Phosphorus (%)	1.99	2.68	0.05
Sulphur (%)	2.39	2.80	5.02
Calcium (%)	1.28	2.40	1.16
Titanium (%)	0.13	0.12	0.12
V (%)	< 0.006	< 0.006	1.52
Chromium (%)	0.56	0.20	0.15
Manganese (ppm)	411	< 25	< 25
Iron (%)	1.47	0.53	0.75
Co (ppm)	< 25	< 25	194
Nickel (%)	0.24	0.07	0.39
Copper (ppm)	396	< 20	< 20
Zinc (%)	0.41	0.70	0.08
As (ppm)	< 20	113	312



Figure 6: Typical HFO ash deposited on the catalyst

BENCH SCALE CATALYST TESTING

Lights off curves for the catalyst formula on the main part of the catalyst are plotted for the end of the second exchange (i.e. end of scenario 1; gas/LFO mode operation). Only the light off curves for CO, ethane, and propane are shown. Vertical hatched lines have been added to the plots to indicate the upper and lower temperature-operating window of the dual fuel engine.

Figures 7-9 for Pt-based, CO, ethane and propane shows that with increasing time on stream that the catalyst is slowly deactivated. In the gas mode during the difference between 2000 hrs and 4000 hours is negligible, indicating very little deactivation. A more pronounced change in conversion efficiency is observed in the fuel change to HFO. This shift is likely due to high sulphur content in the HFO compared to the gas (~4000 times higher) resulting in sulphur poisoning of the catalyst.

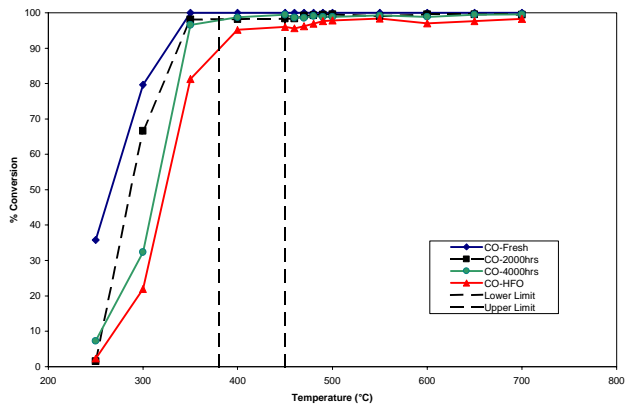


Figure 7: CO oxidation on Pt-based, 90,000 h⁻¹ - MGR

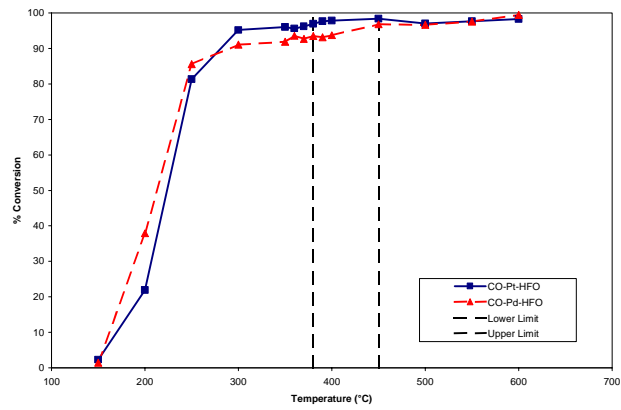


Figure 10: Pt, Pd Formula Comparison – CO- MGR

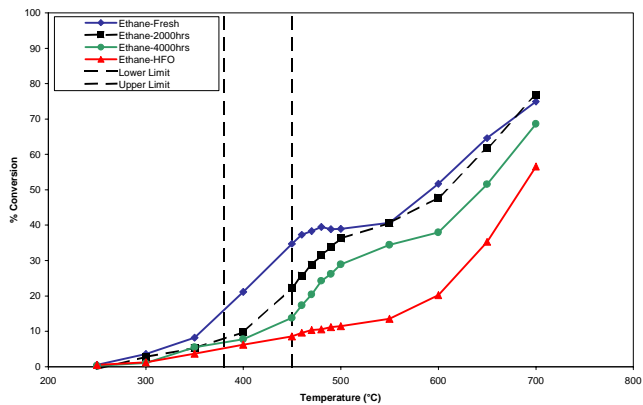


Figure 8: Ethane oxidation on Pt-based, 90,000 h⁻¹-MGR

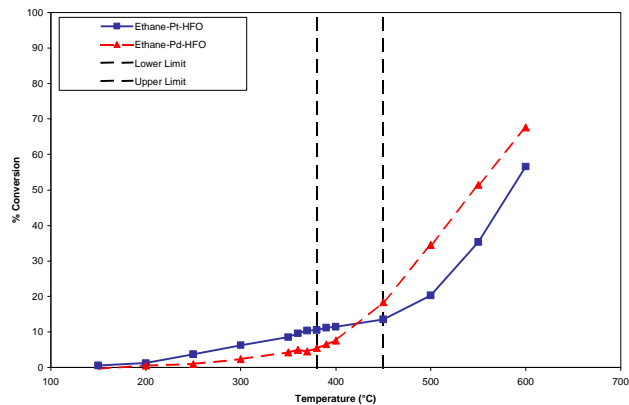


Figure 11: Pt, Pd Formula Comparison – Ethane-MGR

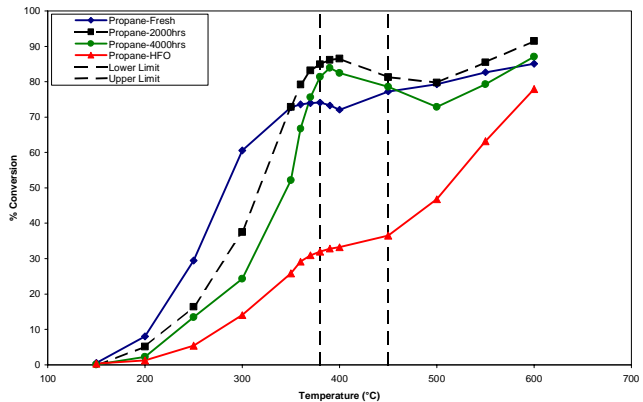


Figure 9: Propane oxidation on Pt-based, 90,000 h⁻¹-MGR

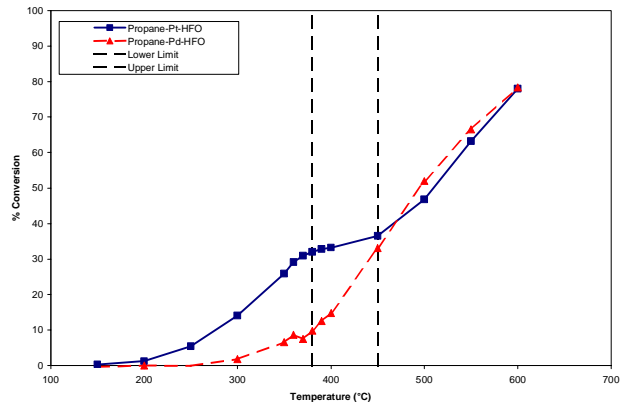


Figure 12: Pt, Pd Formula Comparison – Propane-MGR

A comparison of the different catalyst formulations (Pt versus Pd-based) evaluated during the lab test of the exchanged samples is made for CO, ethane and propane conversion after the HFO operation (Figures 10-12). The HFO operation mirrors the observations made of the catalyst under gas/LFO operation. It is seen that the two catalyst formulas have similar ethane conversion efficiency within the temperature window of the engine. If this engine was to only operate with natural gas then it would be expected that the Pd based catalyst might be slightly superior to Pt based catalyst. This is not the case for the dual fuel engine using the LFO for a pilot. The sulphur present in the LFO is enough to deactivate the Pd based catalyst and make the ethane conversion similar to that of the Pt-based catalyst. The combination of sulphur poisoning on Pd catalysts and gas quality issues could greatly compromise the reliability of gas only ethane conversion on the Pd catalyst. Propane conversion is improved with less Pd on the oxidation catalyst (Figure 12). This follows the trend seen by other researchers for sulphur promoted Pt- based propane oxidation [8-9].

Pd based catalysts are reported to be sulphur poisoned with minimum levels of sulphur present in the exhaust stream [10-13]. But, in this temperature window the advantage of a Pd based catalyst is negligible for THC or NMHC conversion. Sulphur poisoning does not fully explain the deterioration since the surface layer of the Pd metal should have been fully saturated [10-13]. Further study is needed to know how much of a role the high concentration of Ca or V may have played in the Pd catalyst deactivation. Elemental analysis of this specific catalyst will have to be done to gain further insight.

A Pt based formula is better suited for dual fuel applications. Excellent CO and fairly good alkane conversions are observed with a compact sized catalyst. Methane and ethane have better removal with the Pd based formulas but not at temperatures of operation of efficient lean-burn Otto engines. Operating temperature window and fuel/lube oil deposits have a strong effect on the performance of the catalyst. The catalyst must be tolerant to the number of deposits found in the different fuels and lubricating oils used on the dual fuel engine. For this particular dual fuel engine the choice of a robust, compact sized, Pt based catalyst is the preferred choice with regards to CO and hydrocarbon oxidation.

SUMMARY AND CONCLUSIONS

Modern emission legislation for lean-burn gas engine driven power plants has its main focus on limiting the emissions of carbon monoxide and formaldehyde. For new power plants, this involves the installation of an oxidation catalyst that oxidizes CO and formaldehyde efficiently and removes potentially ozone forming photoactive volatile organic compounds.

The results of this paper show that an efficient pilot ignited lean burn dual-fuel engine meet with these requirements for low emission with no severe catalyst deterioration provided that the plant is running mainly on gas and provided that the pilot fuel is of good quality. The use of low-grade fuels, with higher sulphur content, and longer diesel mode operation has the

potential to poison the catalyst. A thorough review of the fuels and the operating profile between gas and diesel is essential in applying oxidation catalysts to dual fuel applications. This is possible by a close cooperation between the end users, catalyst, and engine manufacturers to develop the best available technology.

The bench scale tests of this study show that LFO/HFO operation had only a small impact on the catalyst efficiency for CO abatement. On the contrary, the HFO operation reduced the abatement efficiency for alkanes significantly. The decrease in the activities is more severe for the catalyst with a Pd based formula as compared to the catalyst with the Pt based formula. This leads to the conclusion that a Pt based catalyst is more suitable for the dual fuel engine from the catalyst poisoning point of view. The effect of catalyst poisoning is more severe for emissions of NMNE hydrocarbons or even NM hydrocarbons since the abatement efficiency for propane and ethane decrease more drastically. With good quality fuels and operation with gas alone there is still a challenge due to the fact that the flue gas temperature of a lean burn gas engine is too low for an efficient abatement of ethane and propane.

In summary the dual fuel engine proved a fuel flexible, energy efficient solution and when combined with an oxidation catalyst it also has low emissions once operated on appropriate fuels.

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