

1 INTRODUCTION

Renewable energy production will account for an increasing amount of future energy systems. Due to the intermittent nature of electricity production of these new wind and photovoltaic plants, more attention must be focused on peaking power so that electricity grids remain stable. Hydro power is a good way to adjust the electricity supply so that the frequency and voltage of the electricity network remain at the required level.

However, if sufficient hydro power is not available then combustion-based power should be adopted for grid-balancing. Gas-driven engines are particularly suitable for peaking power plants because they are able to start quickly and can handle full load within a few minutes. They can also be stopped in only one minute. [1]

Hydrocarbon emissions can increase during very rapid transient load conditions and at low loads. [2] Since natural gas (NG) is composed mainly of methane (CH₄), it is methane emissions that could be expected to escape from the combustion process. CH₄ is a significant greenhouse gas, proven to have a stronger impact on global atmosphere warming than carbon dioxide (CO₂) at equivalent emission rates [3]. Therefore, novel solutions have to be adopted to ensure that gas-engine power-plants used for peaking power in future systems also satisfy the most stringent incoming emissions legislation. In addition to other pollutants that give rise to global warming, CO₂ and nitrogen oxides (NO_x), future regulations will also limit methane emissions. Hydrocarbon (HC) or CH₄ emissions from power plants are not yet regulated in the European Union but some countries like Portugal, Denmark and Netherlands have already introduced their own domestic regulations. With growing use of natural and biogas it is likely that HC or CH₄ limits for power-plants will be widely adopted elsewhere.

An oxidation catalyst oxidizes HC and carbon monoxide (CO) by using the oxygen present in the exhaust gas flow, converting them to CO₂ and water vapour. The catalyst is activated at a certain temperature, with longer hydrocarbons in the exhaust starting to oxidize at lower temperatures. For example, ethane in the NG helps to oxidize methane. Therefore, catalyst performance is dependent on both exhaust gas temperature and exhaust content of longer hydrocarbons. The performance increases linearly with the exhaust temperature until the temperature level is high enough. [4]

Supported palladium (Pd) catalysts have shown to have good CH₄ conversion activity. Catalysts based on platinum (Pt) are commonly used for

elimination of non-methane hydrocarbons (NMHC) but are not reported to have strong activity for oxidizing CH₄. Palladium oxide (PdO) is recognised as the active species for CH₄ conversion but Pt/Pd mixtures are also used. Alumina has been reported to be the most active catalyst support for CH₄ combustion, although it is not very durable.[3],[5],[6]

Catalyst activity decreases over time if exposed to thermal ageing or sulphur poisoning. (Lee et al. 1995) Palladium-based catalysts are particularly sensitive to sulphur poisoning and their CH₄ oxidation activity deteriorates quickly if sulphur dioxide (SO₂) or sulphur trioxide (SO₃) is present. As little as 1 ppm SO₂ present in the exhaust has already been found to inhibit oxidation of methane. (e.g. [7],[8]) The exhaust of gas engines contains 1-5 ppm sulphur. This may originate from the NG itself, it may have been added to gas as an odorant for safety reasons or it can come from the engine's lubricating oil. [9]

Hoyos et al. have identified the poisoning species to be sulphate groups which have been adsorbed on the Pd particles [10]. According to Leprince et al. the deactivation occurs through adsorption of SO₂ onto Pd particles. When it happens, sulphur spills over onto the alumina support. [9] The mechanisms causing deactivation in the presence of SO₂ are more related to operating temperatures than to the composition of the gas, so the rate of deactivation is a function of exhaust temperature. At low temperatures, approximately 240 °C to 400 °C, the adsorption rate of SO₂ and SO₃ is at its maximum and so deactivation of the catalyst is rapid. At 500 °C, deactivation is much weaker because SO₂ adsorption on the Pd particles is lower and SO₂ adsorbed into alumina wash coat begins to desorb. Temperatures below 500 °C are reported to be impractical for catalyst regeneration. The regeneration process should be performed periodically, often and rapidly. [9] However, Kinnunen et al. have proposed a new hypothesis suggesting that sulphur itself does not poison the methane oxidation catalyst but it makes the catalyst more sensitive to water-vapour poisoning. Their laboratory experiments studied the effect of water vapour on CH₄ conversion, finding that a catalyst poisoned by SO₂ was more active at low temperature when the exhaust did not contain water vapour. Conversion decreased notably when water was added to the exhaust. [11] Sulphur poisoning is claimed to reduce oxygen mobility and prevents water desorption.

Results from various studies indicate that H₂ gas recovers the catalyst activity by removing the sulphite and sulphate groups. [6],[9],[10],[12]-[16] Consequently, this work concentrated on