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DECARBONISATION OF INDUSTRIAL POWER GENERATION GAS TURBINES WITH BIO-ALCOHOLS

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ABSTRACT

The intermittency of renewable power generation means that dispatchable power sources are required to meet global energy demands. Gas turbines firing low carbon fuels, such as bio- and e-alcohols, offer flexible dispatchable power generation.

Despite previous work highlighting the suitability of ethanol in lean-premixed gas turbines, the present study shows that in practice evaporated ethanol is less attractive than previously suggested due to higher than anticipated NO_X *emissions and higher evaporation temperatures if the fuel has significant water content.*

This paper introduces a "dual phase" burner concept where methanol may be fired either as a liquid or evaporated as a gas. Liquid methanol could be fired in a normal dual fuel distillate-natural gas burner with little or no modification to the liquid fuel paths/nozzles. Evaporated methanol could be fired with relatively minor modifications to the fuel gas path and nozzle. The gas turbine could be started on liquid methanol until sufficient exhaust heat was available to evaporate the methanol. Switching to evaporated methanol firing would result in an estimated 5-6% reduction in fuel consumption compared to liquid firing because of the exhaust waste heat recovery.

Whilst this study demonstrates the suitability of evaporated alcohols in a particular lean-premixed gas turbine combustion system, each different combustion system must be individually evaluated.

Keywords: Gas turbine, combustion, novel fuels, evaporated fuels, ethanol, methanol, emissions.

NOMENCLATURE

ADT	Autoignition Delay Time [ms]
CFD	Computational Fluid Dynamics
FTF	Flame Transfer Function
HMRC	His Majesty's Revenue and Customs (UK)
HVO	Hydrotreated Vegetable Oil
LHV	Lower Heating Value [MJ/kg]
OCGT	Open Cycle Gas Turbine
SCC	Stress Corrosion Cracking
A/F	Mass based Air/Fuel ratio [-]
C_i	Mass fraction of fuel in cell I [-]
M_i	Mass flow through cell i [kg/s]
P	Pressure [bar], [atm]
S	Unmixedness parameter given by equation 1 [-]
S_0	Unmixedness of a fully unmixed binary fluid given by equation 3 [-]
S_N	Normalised unmixedness given by equation 2 [-]
SST	Shear Stress Transport

1. INTRODUCTION

Despite the worldwide ambition for a low-carbon economy, the intermittency of renewable energy generation means that dispatchable power sources are required to meet global energy demands. Gas turbines offer flexible power generation but traditionally burn carbon-based fossil fuels. Whilst zero-carbon fuels such as hydrogen and ammonia show promise as future green fuels, carbon-based biodiesels, bio-alcohols and e-alcohols can also offer significant carbon dioxide reduction benefits. Uniper has already demonstrated the suitability of hydrotreated vegetable oil (HVO) to replace diesel in liquid-fired gas turbines [1].

A previous study [2] investigated the possibility of firing evaporated alcohols in lean premixed gas turbine combustors that had been designed for use with natural gas. The study used Uniper's Killingholme plant as an example.

Killingholme Power Station entered operation in 1992, built as a 900MW combined cycle gas turbine plant made up of two units each incorporating two SGT5-2000E gas turbines firing natural gas with lean premixed burners. The plant now operates as four open cycle gas turbines (OCGT) with a combined output of 600MW.

The specification of the Siemens SGT5-2000E gas turbine is shown in Table 1. However, it must be noted that the Killingholme units have a different specification to that shown Table 1 due to them being a different variant.

TABLE 1: SIEMENS SGT5-2000E GAS TURBINE SPECIFICATION [3].

Simple cycle power output (MW)	198
Gross efficiency (%)	37.6
Heat rate (kJ/kWh)	9,582
Pressure ratio	12.8:1
Exhaust mass flow (kg/s)	558
Exhaust temperature (°C)	536

The previous study [2] concluded that it was likely that this gas turbine combustion system could be operated on both natural gas and evaporated ethanol in lean premix mode *without modification to the burner*. It was thought that NO_X emissions would remain approximately constant when firing at the same flame and turbine inlet temperatures with natural gas or evaporated ethanol.

It was recognized that flashback risk would be increased when operating on evaporated ethanol due to the increased flame speed. Comparison with a similar burner operating on natural gas/hydrogen blends suggested that it was likely that there would be sufficient flashback margin which, if the assessment should prove optimistic, a modest reduction in firing temperature would restore.

These preliminary findings were encouraging and justified further investigations. As the previous study only considered pure ethanol, more detailed studies were needed to:

1. Assess the impact of water content and denaturants added to avoid alcohol tax.
2. Confirm findings of the preliminary study.

The present study further investigates the impact of water content, analysing the predicted NO_X emissions and performing CFD mixing studies on a full premixed burner geometry.

The previous modelling study [2] concluded that whilst it would not be possible to burn evaporated methanol in an unmodified natural gas burner, it may be possible to modify the burner to accommodate the increased fuel flow required. Methanol as a potential "green" fuel has gained significant interest in recent years. According to estimates from the Methanol Institute [4], global green methanol production is expected to increase from approximately 0.8 million tons in 2023 to 40 million tons by 2030, with the majority being produced by power-to-fuel systems. Thus, significant quantities of low carbon methanol are likely to be available in the near future making it an attractive alternative fuel for power generation.

To burn evaporated methanol a source of heat is required to evaporate the liquid methanol and waste exhaust heat could be used, however this is only available after the gas turbine is in operation, thus an alternative starting fuel is required. It should also be noted that for safety reasons it may not be possible to start on evaporated alcohols.

This paper considers using a dual fuel burner with modified gas circuits and unmodified liquid fuel circuits to burn liquid methanol after starting and for short-term operation. Evaporated methanol would be burnt using the modified gas fuel circuits once exhaust heat is available as this significantly improves the fuel economy.

This work considered base load conditions for the Killingholme machines as shown in Table 2 to be representative of the required operating conditions.

TABLE 2: REPRESENTATIVE BURNER INLET CONDITIONS AND TOTAL GAS TURBINE MASS FLOWS AT BASE LOAD.

Compressor discharge pressure (bara)	11.2
Compressor discharge temperature (K)	608
Fuel (natural gas) temperature (K)	294
Fuel (natural gas) LHV (MJ/kg)	47.1
Fuel (natural gas) net mass flow (kg/s)	9.2
Compressor outlet (air) mass flow (kg/s)	513
Fuel Supply Pressure (bara)	18

Throughout this paper, pure methane is used a surrogate for natural gas. Pure ethanol is also considered with the effects of contaminants modelled by adding water and methanol as indicated in Figure 1. Pure methanol is also used as a base fuel with contaminants modelled by the addition of water and ethanol as indicated in Figures 11 and 12.

Where required, mass flows for all fuels were calculated to give the same fuel energy input on a Lower Heating Value (LHV) basis as the natural gas in Table 2.

2. FURTHER INVESTIGATIONS INTO EVAPORATED ETHANOL

Ethanol is subject to taxation by the governments due to its potential for human consumption. Avoiding an "alcohol tax" is of economic importance, so adding contaminants (denaturants) to render ethanol undrinkable becomes essential. European Union regulations [5] recommend denaturants such as methyl ethyl ketone, isopropyl alcohol, and denatonium benzoate, but based on the UK HM Revenue and Customs (HMRC) guidance [6], adding up to 5mass% methanol may be seen as an acceptable approach within the UK. However, confirmation of acceptability would be required by HMRC Commissioners. Because of the similar physical and chemical characteristics of ethanol and methanol, methanol is particularly attractive as a denaturant for fuel applications.

During bioethanol production, a significant quantity of water is produced as a side product, and some degree of extraction is necessary. The distillation process used is extremely energy-intensive and accounts for up to 37% of the energy cost associated with ethanol production [7]. As such, a trade-off must be made between fuel cost and LHV. Given ethanol's azeotropic nature, achieving a concentration of ethanol above 96.4vol% necessitates substantial additional investment in terms of energy and capital [8].

Higher water content reduces the LHV of the fuel supplied to the gas turbine. Beyond its impact on the thermodynamic cycle and fuel mass flow required, the presence of water also influences the flame properties.

This study extends the previous study [2] of the use of evaporated ethanol in the combustion system of the SGT5-2000E gas turbines. The analysis uses chemical kinetic modelling to evaluate fundamental combustion properties such as laminar flame speed, autoignition delay time (ADT), and theoretical minimum NO_X. A constant 5mass% methanol content is chosen to represent the effect of denaturants and the effect of 5 and 10mass% water content is evaluated. Results are compared with methane (as a substitute for natural gas) and pure ethanol.

In line with the previous study [2] the mechanisms developed by the CRECK group [9] were considered. Two mechanisms, CRECK_2003_TPRF_HT_ALC_NOX, and CRECK_2003_C1_C3_HT_NOX were evaluated over a wide range of conditions for ethanol and were found to produce similar results for the key properties, laminar flame speed and ADT. CRECK_2003_C1_C3_HT_NOX was chosen for the chemical kinetic parts of this work using the chemical kinetic code Ansys Chemkin.

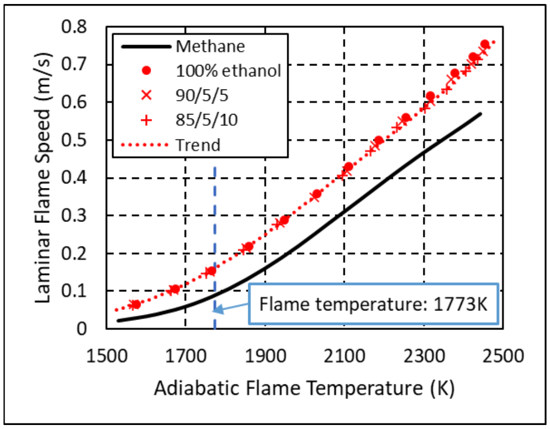

FIGURE 1: SIMULATION OF LAMINAR FLAME SPEED FOR METHANE, PURE ETHANOL AND MIXTURES CONTAINING 90% ETHANOL, 5% METHANOL, 5% WATER AND 85% ETHANOL, 5% METHANOL, 10% WATER.

At relevant gas turbine conditions, the flame speed of pure ethanol is approximately 80% higher than that of methane [2]. Kinetic simulations using the CRECK mechanism show that increase in water content tends to slightly reduce the flame speed when comparisons are made on a fixed equivalence ratio basis, but when comparing the laminar flame speed as a function of adiabatic flame temperature (Figure 1) the difference between different ethanol qualities is negligible. It is important to make comparisons on a flame temperature basis as in the gas turbine the same flame temperature will be targeted irrespective of the fuel used.

Water content was found to increase ADT at all temperatures reducing the risk of autoignition in recirculation zones that had been previously identified as a theoretical possibility [2].

NO_X emissions were modelled as a perfectly stirred reactor with a residence time of 15ms, a pressure of 11.2 bar, and a range of flame temperatures from 1700 to 1900K spanning the anticipated flame temperature (1773K) for this burner [2]. This represents the lowest NO_X that could be produced in a perfect lean premix burner with a given average flame temperature. It is recognised that this does not represent the situation in practical combustion systems, however comparison of NO_X produced by different fuels in this idealised situation gives a measure of contribution that chemical kinetic properties of the fuels make to the overall NO_X. In the practical burner NO_X will also be significantly impacted by mixing quality, heat losses and other factors affecting local flame temperature.

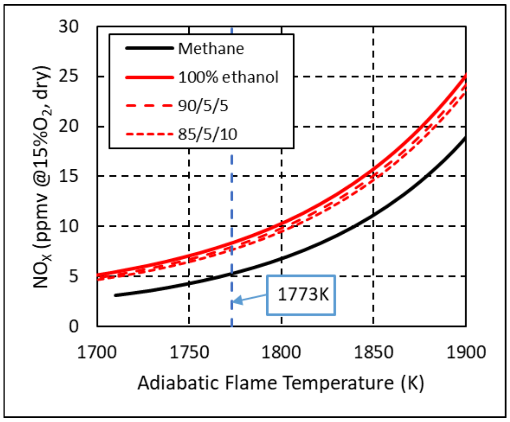

FIGURE 2: SIMULATED NO_X EMISSIONS FOR WELL MIXED COMBUSTION AS A FUNCTION OF FLAME TEMPERATURE FOR METHANE, ETHANOL AND ETHANOL/METHANOL/WATER MIXTURES.

Figure 2 shows that ethanol will produce significantly higher levels of NO_X than methane at the representative flame temperature. The addition of water and methanol has only a small effect on NO_X production, and it should be noted that adding 10% water produces slightly higher NO_X than 5% water. This is surprising as the NO_X formation in the presence of hydrocarbons at high pressure is expected to be similar for all fuels because thermal NO_X should dominate. Our previous study assumed [2] that this would be the case at a given flame temperature. However, this analysis suggests that chemical kinetic behaviour could have a significant impact on NO_X production. This result requires further investigation to determine whether it is a real effect or a kinetic mechanism specific artefact.

CFD studies on a realistic burner geometry showed that the mixing quality for ethanol would be worse than previously predicted using a simplified geometry [2] which overestimated the degree of air fuel mixing. Thus, even if the kinetic effect identified above is not real, NO_X emissions for this burner are likely to be significantly higher when firing evaporated ethanol than natural gas/methane.

It is a normal requirement that the fuel supply temperature should be at least 15K above the fuel dew point [10]. For a typical fuel supply system pressure of 18 bar (Table 2), the evaporation temperature of pure ethanol is 452K, thus a fuel temperature of 467K is required. However, if the water content exceeds that of the ethanol/water azeotrope, the fuel needs to be heated to the water evaporation temperature (480K) to ensure full evaporation and thus, to be 15K above the dew point, a fuel temperature of 495K is needed. This results in fuel temperatures significantly above 200°C which are unlikely to be acceptable in the existing fuel supply system.

The addition of water reduces the LHV of the fuel thereby increasing the fuel flow requirement. Additionally, the increased fuel supply temperature due to the higher dew point further increases the fuel volume flow, increasing the pressure drop in the burner. It is unlikely that the required flow could be achieved without either increasing the fuel supply pressure or modifying the burner. Increasing the supply pressure would further increase the dew point, exacerbating the temperature issue. Thus, it is likely that burner modifications would be required to burn ethanol with water content greater than that of the azeotrope.

Even though further research is needed regarding NO_X formation this analysis strongly suggests that burning evaporated ethanol in the unmodified lean premix natural gas burner is not as attractive as previously suggested [2]. However, the concept may be viable in some circumstances, particularly if low water content ethanol is economically available and some de-rating is considered acceptable to reduce system pressure drop, flashback risk and NO_X emissions.

3. METHANOL FIRING

3.1 Methanol Dual Phase Concept

The previous section shows evaporated ethanol to be less attractive than previously thought [2] and that viable operation is likely to require burner modification and replacement. Dual fuel burners are available for the Siemens SGT5-2000E, and it is suggested [10] that the liquid (distillate) pathways can be used without modification to burn liquid methanol by using both premix and diffusion nozzles simultaneously. However, modifications to the liquid fuel nozzles can optimise operation and modifications to the natural gas fuel pathways should allow operation on evaporated methanol. Thus, in principle this system could be used as a "dual phase" liquid methanol and evaporated methanol burner. This would allow operation on liquid methanol from start-up when insufficient exhaust waste heat is available for evaporation of the methanol and as waste heat is generated, the system could switch to evaporated methanol and gain a significant efficiency benefit.

Kliemke and Johnke [10] state that the dual fuel version of this burner can burn liquid methanol unmodified. Also, liquid methanol firing tests on other burners are very encouraging. For example, tests conducted by Siemens Energy on the diffusion burner of the SGT-A20, [11, 12], demonstrated the potential to reduce NO_X and CO emissions by up to 80% and 15% respectively compared to kerosene firing, and suggested that there was the potential to increase the gas turbine's power output by up to 10%. However, in this case the flow capacity of the injectors has been increased by a factor of 1.95 to reduce the required fuel pressure. Also, a detailed study of Siemens Energy industrial atomisers [13] shows that the Weber number, a key dimensionless group relating to spray behaviour, is similar for methanol and Viscor (a diesel fuel test substitute) suggesting similar spray behaviour. In tests, they found that methanol and Viscor are subject to similar wave dynamics at analogous operating conditions giving similar droplet formation characteristics. This supports the assertion [10] that the dual fuel burner under consideration will be able to fire liquid methanol. However, methanol produced a wider spray cone angle than Viscor. This would increase the risk of impingement of the liquid on the outer wall of the premix section in the burner under consideration, which. needs to be avoided [14].

Evaporated methanol has not been investigated previously and has the potential to reduce NO_X emissions operating in a controlled lean premix mode and to improve overall efficiency through waste heat recovery. Table 3 shows the heat required for evaporation and thus the potential heat that could be recovered. Temperatures were based on the requirement [10] that the fuel must be 15K above its evaporation temperature. The analyses were performed with pure methane as the baseline, adjusting the fuel mass flow of ethanol and methanol to provide the same energy input as natural gas on an LHV basis. This shows that the utilisation of waste heat recovery could reduce methanol consumption by 5 to 6%.

TABLE 3: HEAT REQUIRED FOR EVAPORATION OF ETHANOL AND METHANOL.

Fuel	Heat required for evaporation [MW]	Heat required for superheating [MW]	Total heat required [MW]
Ethanol (467K)	18.5	0.7	19.2
Methanol (452K)	23.7	1.4	25.1

A range of methanol qualities are available with a range of specifications [15, 16] including: Man B&W Engines fuel class (>95% by weight of Methanol, <5% of Water by weight, <5% by weight Ethanol), GRADE A, GRADE AA and IMPCA (>99.85% Methanol), automotive American M100 (min. 96% by volume methanol, <2% by weight ethanol and <2% water by weight).

However lower quality (thus lower cost) methanol may be available and Siemens Energy recommendation [10] is at least

88% by volume methanol, and <12%vol water for OCGT operation.

It may also be possible to obtain semi-processed methanol which has approximately 80-85% by volume methanol, 10% by volume water and 5-10% by volume ethanol.

However, water contamination in methanol raises concerns related to stress corrosion cracking (SCC), as studied by Farina et al. [17], Kane et al. [18]. Small quantities of water between 0.01% to 0.5% can significantly increase SCC susceptibility, especially for carbon steel which is commonly used for fuel piping systems and tanks. Higher water concentrations may reduce SCC, but in an investigation conducted by Pedraza-Busulto et al. [19], it was observed that when ethanol's water content exceeds 5%, corrosion rates increase significantly. It is suggested that similar issues may occur with methanol, highlighting the challenges posed by water contamination in alcohols.

Note that unless it is stated otherwise, all fuels are assumed to be in their pure form with no contaminants.

3.2 Chemical Kinetics

The adiabatic flame temperature, laminar flame speed and ADT are assessed for relevant conditions using the chemical kinetic code Ansys Chemkin.

3.2.1 Mechanism Validation

For continuity, the same chemical kinetic mechanism for methanol was considered as for ethanol and the CRECK_2003_C1_C3_HT_NOX mechanism [9] was selected for further assessment.

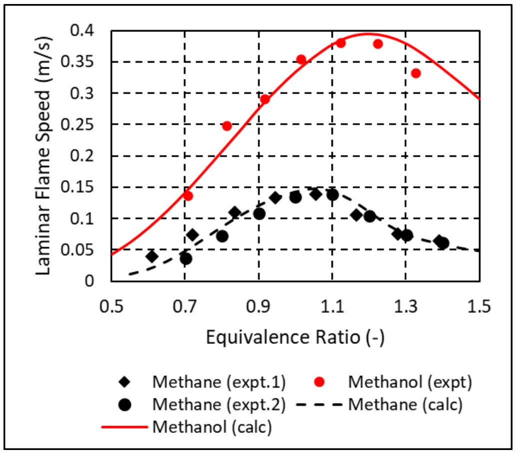

FIGURE 3: COMPARISON OF CALCULATED LAMINAR FLAME SPEEDS AND EXPERIMENTAL RESULTS AT 10 ATM. MIXTURE TEMPERATURE ~373K (METHANOL), OR ~298K (METHANE). EXPERIMENTAL DATA FOR METHANOL FROM [20] AND FOR METHANE FROM [21] AND [22].

The laminar flame speed showed good agreement across a wide range of conditions; however, only conditions close to those in the engine (References: [20-22]) are presented in Figure 3. Good agreement can be seen between the chemical mechanism and experimental data, with trends based on the equivalence ratio effectively capturing the differences between methanol and methane.

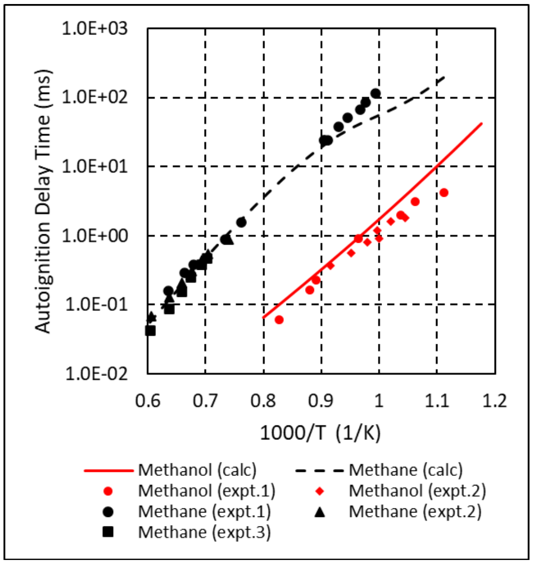

FIGURE 4: COMPARISON OF CALCULATED ADT WITH EXPERIMENTAL RESULTS AT EQUIVALENCE RATIO 1 FOR METHANOL AT 13.1 ATM WITH OXIDIZER (0.21 O_2 AND 0.79 AR) AND METHANE AT 10ATM WITH AIR AS OXIDIZER. DATA FOR METHANOL FROM [24] AND [25]. DATA FOR METHANE FROM [23], [26] AND [27].

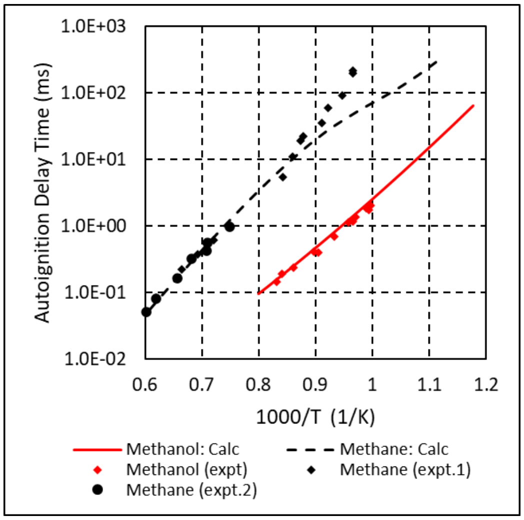

FIGURE 5: COMPARISON OF CALCULATED ADT WITH EXPERIMENTAL RESULTS AT EQUIVALENCE RATIO 0.5 FOR METHANOL AT 13.4 ATM WITH OXIDIZER (0.21 O_2 AND 0.79 AR) AND METHANE AT PRESSURE 10ATM WITH AIR AS OXIDIZER. DATA FOR METHANOL FROM [25]. DATA FOR METHANE FROM [23], [26].

The ADT has also been compared for both fuels across a wide range of conditions; however, only conditions close to the gas turbine's operating parameters are presented here. Experimental results from Burke et al. [23], Fieweger et al. [24], Pinzón et al. [25], Zeng et al. [26], and Hu et al. [27] were used for this validation. The results show good agreement, as illustrated in Figure 4 and Figure 5.

Although good agreement in trends is observed for both methanol and methane when compared to the experimental data, at higher temperatures, the calculated values for methane display an offset, though they remain within a similar magnitude. For methanol, under the given conditions, the experimental and calculated values are closely aligned. As the simulated ADT is shorter than the experimental value, calculated values from the CRECK mechanism will be conservative.

3.2.2 Turbine Conditions

The same methodology has been used to calculate laminar flame speed, adiabatic flame temperature and ADT at operating conditions representative of the gas turbine (Table 2). Values for ethanol have been taken from the previous study [2].

As seen in Figure 6, both methanol and ethanol, under the given conditions, exhibit a higher laminar flame speed than methane. However, at lower temperatures, the laminar flame speed of methanol is slightly higher than that of ethanol, which indicates a potentially higher risk of flashback, and a lower risk of lean blowout compared to ethanol. This also suggests that methanol is more reactive than ethanol at lower temperatures. At the specified flame temperature of 1773K, the laminar flame speeds of methanol and ethanol are nearly identical.

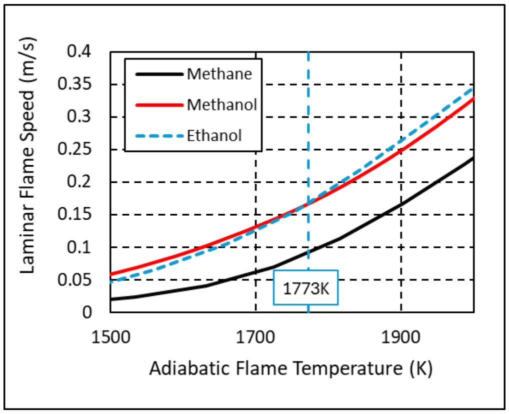

FIGURE 6: LAMINAR FLAME SPEED AS A FUNCTION OF ADIABATIC FLAME TEMPERATURE FOR METHANE, METHANOL, AND ETHANOL (P=11.2 BAR, T=608K).

The adiabatic flame temperatures are presented in Figure 7. Methanol and ethanol exhibit higher flame temperatures than methane for lean mixtures. Whilst methanol shows slightly higher flame temperatures for lean mixtures with an equivalence ratio between 0.3 and 0.6, this trend reverses for equivalence ratios between 0.6 and 1.1, where ethanol displays higher flame temperatures. Under stoichiometric conditions, methanol has the lowest adiabatic flame temperature compared to both methane and ethanol.

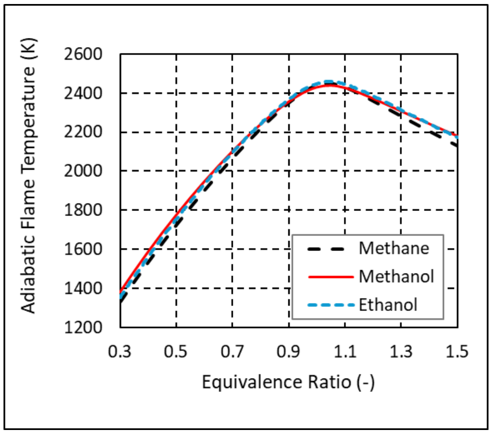

FIGURE 7: ADIABATIC FLAME TEMPERATURE OF METHANE, METHANOL AND ETHANOL AS A FUNCTION OF EQUIVALENCE RATIO (P=11.2 BAR, T=608K).

A reactor model has been developed to investigate ADT for stoichiometric mixtures and mixtures with an equivalence ratio of 0.5. The results presented in Figure 8 show that methanol exhibits an ADT approximately 10 times shorter than that of methane, increasing the likelihood of autoignition in recirculation zones near the flame which have been estimated to have a typical temperature of 1023K [28], [2]. At higher temperatures, between 800K and 1773K, the ADTs of methanol and ethanol are similar. However, at lower temperatures, methanol's ADT is longer, reducing the likelihood of autoignition in colder regions compared to ethanol.

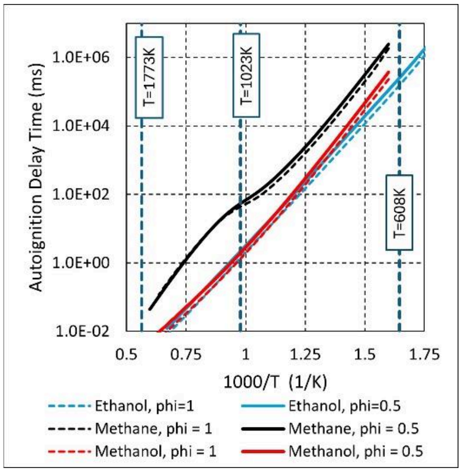

FIGURE 8: ADT FOR METHANOL, ETHANOL AND METHANE FOR EQUIVALENCE RATIOS OF 1 AND 0.5 (P=11.2 BAR).

To estimate the potential impact on emissions when switching fuels, a simplified model was created in Chemkin, based on a perfectly stirred reactor. Correa et al. [29] identified that typical residence times for industrial gas turbines range between 10 and 20 ms. Figure 9 presents model results for different fuels, assuming a residence time of 15 ms. As shown in Figure 9, methanol results in approximately 80% lower NO_X emissions compared to ethanol and 10% lower emissions than methane at a flame temperature of 1773K. These results suggest that using pure methanol as a fuel for gas turbines will slightly reduce NO_X emissions at the specified flame temperature. As discussed in Section 2 it is recognised that the perfectly stirred reactor does not represent the real combustor but gives a measure of the impact of the different fuel chemical kinetics of NO_X production. Thus, for a given mean flame temperature, achieving low NO_X when firing ethanol will be a significantly greater combustion challenge than when firing methane. Firing methanol will be a slightly easier combustion challenge than firing methane from a NO_X perspective.

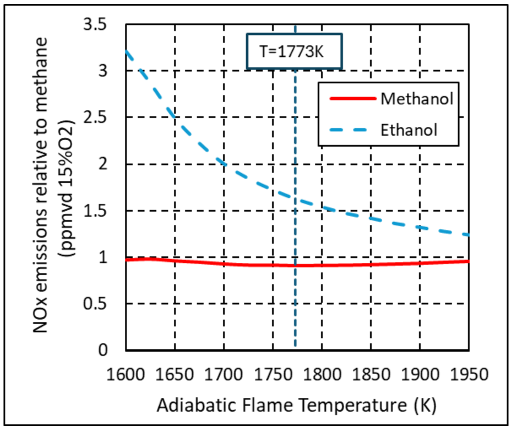

FIGURE 9: NO_X EMISSIONS FOR A PERFECTLY STIRRED REACTOR FOR METHANOL AND ETHANOL FOR 15ms RESIDENCE TIME NORMALISED BY THE VALUE FOR METHANE.

In real "premixed burners" mixing is not perfect and because NO_X emissions are highly dependent on mixing quality [30] on engine emissions will be significantly higher.

3.2.3 Water contamination

Similar to ethanol, being able to tolerate higher water contamination in the fuel may provide economic benefit. A similar approach to modelling impurities as discussed in Section 2 for ethanol was taken, noting that only limited data was available to validate chemical kinetic mechanisms.

A study conducted by Liang and Stone et al. [31] indicated that water contamination significantly reduces laminar flame speed. At 20%vol water content, there is a predicted 40% reduction in laminar flame speed under stoichiometric conditions. Additionally, experimental chemical kinetic studies based on the same conditions, using the San Diego mechanism, demonstrate results that align with modelling in terms of general magnitude, although they differ slightly in trend. A similar pattern has been observed using the CRECK mechanism, as shown in Figure 10.

However, a study conducted by Li et al. [32] demonstrated that by modifying the NT-M Mechanism, it is possible to more accurately capture the underlying physics of water contamination, based on experimental results from Liang's research. Li identified two main factors that influence the magnitude of the laminar flame speed: physical and chemical effects. The physical effect of water was found to have a more significant impact, reducing the laminar flame speed, while the chemical effect led to a slight increase in laminar flame speed.

Li et al. [32] also highlighted the limitations due to the lack of experimental studies examining the IDT of methanol-water mixtures.

Chemical kinetic studies were undertaken on the impact of water/ethanol contamination on methanol on laminar flame speed and ideal NO_X emissions at gas turbine conditions. However, the results should be treated with caution due to the inability of the kinetic mechanism to adequately capture the magnitude of the impact of water content on laminar flame speed.

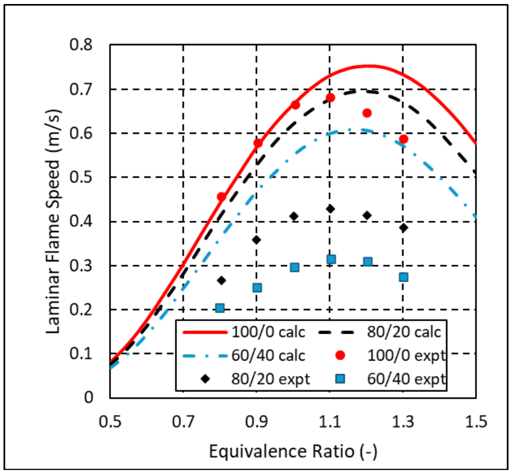

FIGURE 10: LAMINAR FLAME SPEED VALIDATION FOR WATER CONTAMINATION (METHANOL/WATER) BASED ON RESULTS PRESENTED IN EXPERIMENT IN [32] AT 1 BAR AND 400K.

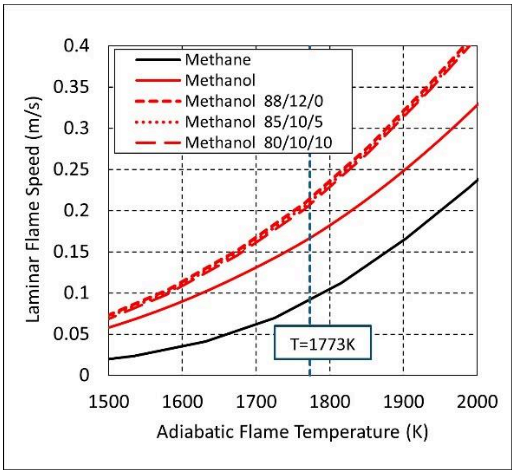

FIGURE 11: EFFECT OF METHANOL COMPOSITION ON ADIABATIC FLAME TEMPERATURE (METHANOL COMPOSITION: METHANOL/WATER/ETHANOL IN VOL%).

It can be seen (Figure 11) that for a given flame temperature, increased water content (12vol%) is predicted to increase the laminar flame speed, increasing the risk of flashback. Very similar results are seen for mixtures containing water and ethanol. It should be noted that for the same equivalence ratio, the flame speeds reduce, but because of the relationship between equivalence ratio and adiabatic flame temperature, for the same temperature the flame speed increases.

Figure 12 shows the impact of methanol composition on idealised NO$_X$ emissions. At the nominal flame temperature, water addition increases NO$_X$ emissions from a perfectly stirred reactor. This may, at first sight, be surprising as water addition is often used to reduce NO$_X$. However, when used for NO$_X$ reduction the local flame temperatures are reduced. In this case the flame temperature is maintained which means that there will be higher fuel input and greater gas turbine power output.

These results suggest that the impact of water contamination or the presence of residual ethanol in the fuel will have only a small impact on emissions but could have an adverse effect on flashback risk. However, as previously stated, this should be treated with caution and these findings further emphasise the need for high quality experimental data on the impact of water and other contaminants on the combustion properties of methanol and ethanol and improved kinetic mechanisms to capture the effects of contaminants.

The CFD studies in Section 3.3 will only directly consider pure methanol.

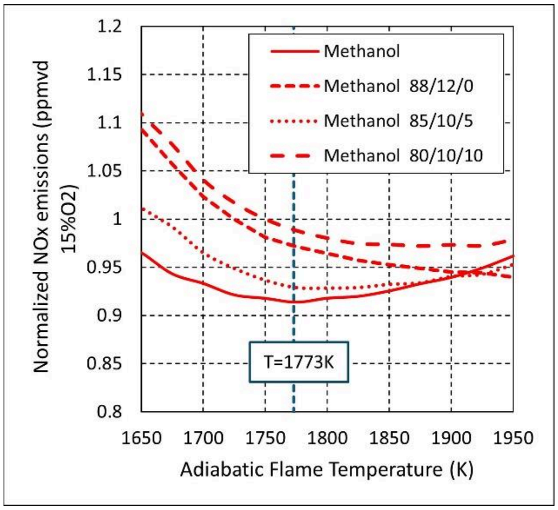

FIGURE 12: IMPACT OF METHANOL COMPOSITION ON NO$_X$ EMISSIONS FOR A PERFECTLY STIRRED REACTOR FOR 15ms RESIDENCE TIME NORMALISED BY THE VALUE FOR METHANE. (METHANOL COMPOSITION: METHANOL/WATER/ETHANOL IN VOL%).

3.3 CFD

The assembly and geometry of the main and pilot burners considered in this study are shown in Figure 13 and the simulation domain used in the main study is shown in Figure 14 which represents an idealised single burner can combustor.

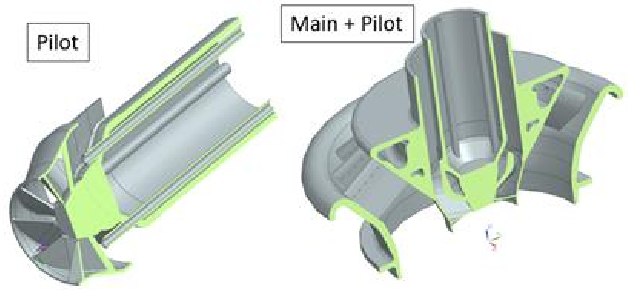

FIGURE 13: CROSS SECTION OF A REPRESENTATIVE BURNER MODEL.

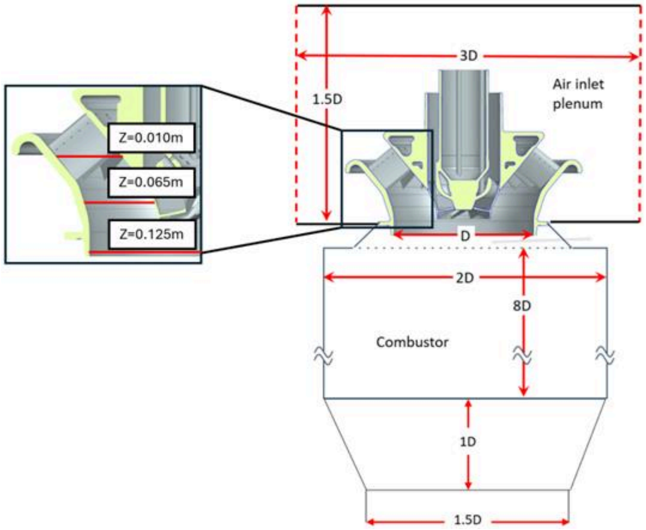

FIGURE 14: SKETCH OF COMPUTATION DOMAIN USED FOR BURNER ANALYSIS SHOWING PLANES AT WHICH MIXING RESULTS ARE PRESENTED.

3.3.1 Turbulence Model Validation

This burner generates good air fuel mixing by using a series of fuel jets in a cross flow of air. Thus, the CFD model needs to capture the mixing behaviour of jets in cross flow.

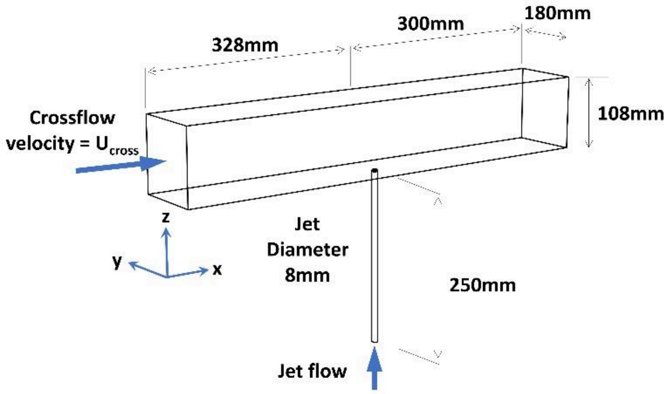

FIGURE 15: NUMERICAL DOMAIN USED FOR TURBULENCE MODEL VALIDATION BASED ON [33].

For turbulence model evaluation, experimental data for a simple jet in cross flow obtained by Galeazzo et al. [33] were used. This investigation considered a single jet in cross flow with a velocity ratio R of 4.15. The numerical and experimental domains are shown in Figure 15, with boundary conditions detailed in Table 4. Based on these conditions, CFD simulations were conducted in Ansys Fluent using both Realizable k-epsilon and k-omega Shear Stress Transport (SST) turbulence models. Velocity profiles at reference planes similar to those in the experimental data were generated (Figure 16). However, the primary focus for our case is the mixing characteristics (Figure 17).

TABLE 4: BOUNDARY CONDITIONS FOR CFD VALIDATION CASE BASED ON [33].

	Inlet Bulk Velocity [m/s]	Turbulence Intensity [%]	Reynolds Number [-]
Cross flow	9.08	1.5	62 400
Jet	37.72	7	19 200

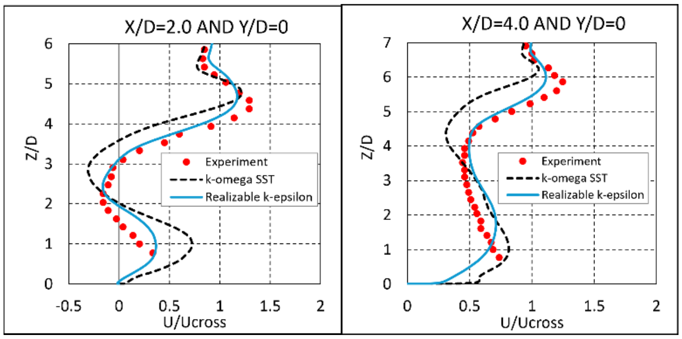

FIGURE 16: COMPARISON OF VELOCITY PROFILES FOR REFERENCE LINE FOR TURBULENCE MODELS TO EXPERIMENTAL DATA FROM [33].

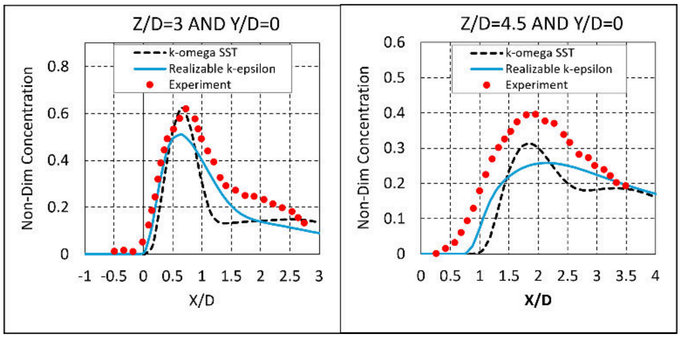

FIGURE 17: COMPARISON OF CONCENTRATION PROFILES FOR REFERENCE LINE TO EXPERIMENTAL DATA FROM [33].

Figure 16 and Figure 17 show that the Realizable k-epsilon model more closely follows the experimental trends for velocity profiles. However, the concentration profiles are less conclusive. To address this, the area under the concentration curve was calculated using the trapezoidal method to provide a quantitative assessment. These calculations indicated that the Realizable k-epsilon model more accurately captures the concentration distribution at the reference location, making this turbulence model more suitable for our case.

3.3.2 Burner Model

The burner model geometry is as shown in Figures 13 and 14. The boundary conditions for this model were established based on baseload conditions (Table 2). Air flow was selected to give a target flame temperature of 1773K when firing natural gas and kept constant for all cases. Fuel flow was selected to give the same fuel energy input as the natural gas case.

Spatial discretization was performed using polyhedral elements. These elements offer the accuracy of hexahedrons while allowing the easy generation of tetrahedrons, enhancing both mesh quality and calculation stability. Additionally, polyhedral elements reduce numerical diffusion, thereby improving solution accuracy with fewer cells due to superior gradient approximation and reduced sensitivity to mesh stretching. The mesh parameters and model setup are summarized in Table 5.

TABLE 5: BURNER CFD SPATIAL DISCRETIZATION PARAMETERS AND MODEL DETAILS.

Number of elements	22.5 million
Minimum Orthogonal Quality	0.12
Maximum Squish Index	0.89
Air Inlet	Mass flow inlet
Main Fuel Inlet	Mass flow inlet
Pilot Fuel Inlet	Mass flow inlet
Combustor Outlet	Pressure outlet (Set to prevent reverse flow)
Turbulent Schmidt Number	0.7
Energy Prandtl Number	0.85
Turbulence Model	Realizable k-epsilon
Wall Approach	Scalable Wall Function
Species Transport	Standard Species Transport equation for mixing

For this analysis, three cases were considered, each with the same airflow and air inlet conditions but with different fuel conditions as follows: Case 1: Methane at 293K, Case 2: Methanol at 452K and Case 3: Methane at 452K.

Case 1 represents the current operating conditions for the Killingholme machines. Case 2 represents operation on evaporated methanol. Case 3 represents operation on natural gas preheated to the evaporated methanol temperature.

To identify potential rich and lean regions in the mixing study, contours of the non-dimensional air-fuel ratio were used. This ratio is defined as the local equivalence ratio divided by the global equivalence ratio of the combustor.

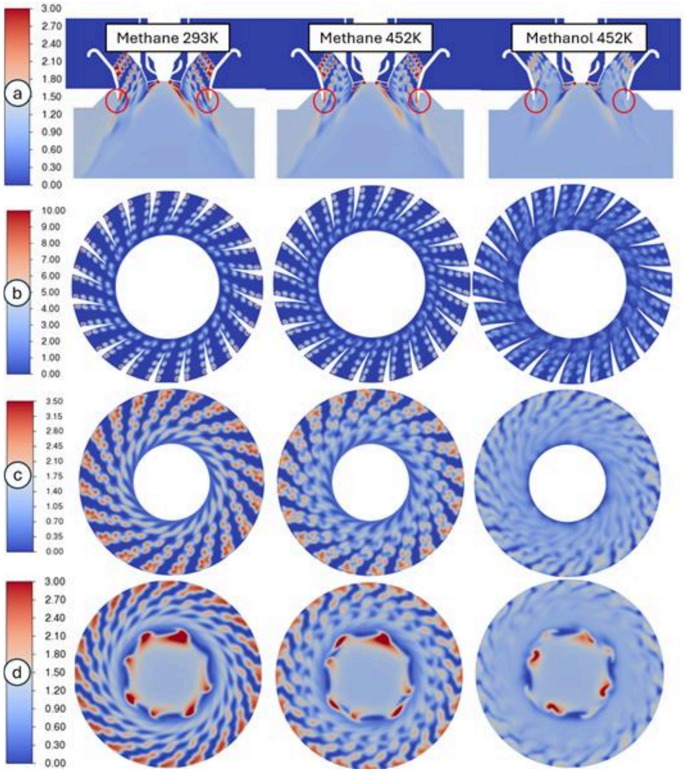

FIGURE 18: NORMALIZED EQUIVALENCE RATIO FOR METHANE AT 293K, 452K AND METHANOL AT 452K. a) VERTICAL CROSS SECTION, b) HORIZONTAL CROSS SECTION, Z=0.01m, c) Z=0.065m, d) Z=0.125m. (SEE FIG. 12).

Figure 18 presents cross sections of the three cases, showing the non-dimensional equivalence ratio without any modifications to geometry and across different planes within the main burner. The bottom section (Figure 18 (d)) shows the plane where the main mixture interacts with the pilot mixture. As observed, in the unmodified geometry, methanol achieves near-perfect mixing in the main burner, with an almost ideal equivalence ratio. This improved mixing for methanol whist reducing NO_X emissions associated with incomplete mixing. Additionally, the rich region near the burner exit seen in the methane cases is eliminated in the methanol case. This would reduce the risk of flashback relative to the methane case (circled in Figure 18(a)).

However, for the methanol case there is a significant increase in pressure drop across the fuel injection nozzles, which is 4.8 times greater than in the standard methane case at 293K. To address this, modifications such as increasing the diameter of the injection holes, or the number of holes were considered. Based on manual calculations, the optimal diameter of the injector holes should be approximately 1.44 times larger than in the standard case. Contours comparing the normalized equivalence ratio for the modified geometry are presented in Figure 19.

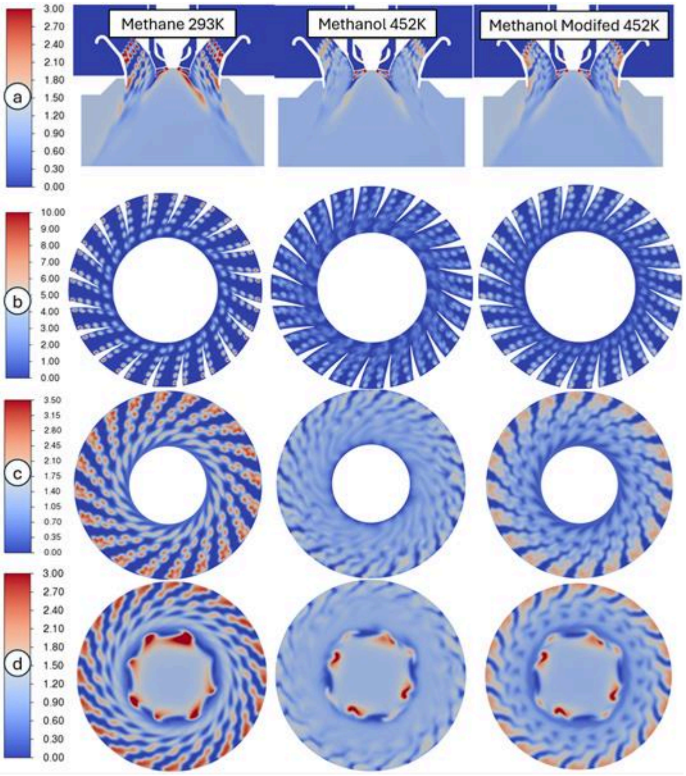

FIGURE 19: NORMALIZED EQUIVALENCE RATIO FOR MODIFED AND UNCHANGED GEOMETRY FOR METHANOL AT 452K FROM UP TO DOWN FOR CROSS SECTION PLANE, Z=0.01m, Z=0.065m, Z=0.125m RESPECTIVELY.

As observed, these modifications simultaneously increase the ratio of rich mixtures in the burner and raise the risk of flashback near the wall relative to the unmodified burner, where the velocity magnitude is lower. However, based on the previously presented contours, the equivalence ratio in the flame region, even after modifications, remains more uniform compared to methane at any temperature. This uniformity will reduce hot spots and lower NO_X emissions.

It is important to note that these contours only give a subjective impression of mixing quality. To quantify mixing objectively, the "unmixedness" parameter, as defined by Hornsby and Norster. [34], has been applied. This parameter, which is calculated using the equation below, provides a more direct assessment of mixing quality.

$$\boldsymbol{S} = \sqrt{\frac{\sum(\boldsymbol{C}_{\boldsymbol{i}}^{2}\boldsymbol{M}_{\boldsymbol{i}})}{\sum \boldsymbol{M}_{\boldsymbol{i}}} - \left(\frac{\sum \boldsymbol{C}_{\boldsymbol{i}}\boldsymbol{M}_{\boldsymbol{i}}}{\sum \boldsymbol{M}_{\boldsymbol{i}}}\right)^{2}} \qquad \textbf{(1)}$$

Where: C_i is the mass fraction of fuel at cell i, and M_i is the mass flow through cell i.

When S=0, air and fuel are perfectly mixed. However, since S is not a normalized function, its value for fully un-mixed air and fuel depends on the overall mass-based air-fuel ratio. This dependency makes it challenging to compare the mixing quality across different fuels or equivalence ratios. Sun et al. [35]

identified that a normalized unmixedness function can be defined as follows:

$$S_N = \frac{S}{S_0} \qquad (2)$$

Where S_0 is the value of S for un-mixed air and fuel and is given by:

$$S_0 = \sqrt{\frac{1}{\left(\frac{A}{F}+1\right)} - \left(\frac{1}{\frac{A}{F}+1}\right)^2} \qquad (3)$$

Where *A/F* represents the mass-based air-fuel ratio. Using this normalization, S_N=1 for fully un-mixed conditions and S_N=0 for fully mixed conditions, regardless of fuel mass flow or composition. This approach allows for a direct comparison of mixing quality between methane and methanol.

The impact of hole size on mixing was assessed by considering three fuel hole sizes, 1.33, 1.44 and 1.56 times the original hole diameter (Figure 20). Different hole sizes yield distinct mixing characteristics. For methanol, increasing the diameter by a factor of 1.44 achieves nearly the same mixing quality as methane at 293K. However, further increasing the diameter reduces mixing quality, which could potentially impact NO_X emissions, though it would further reduce pressure losses across the nozzles.

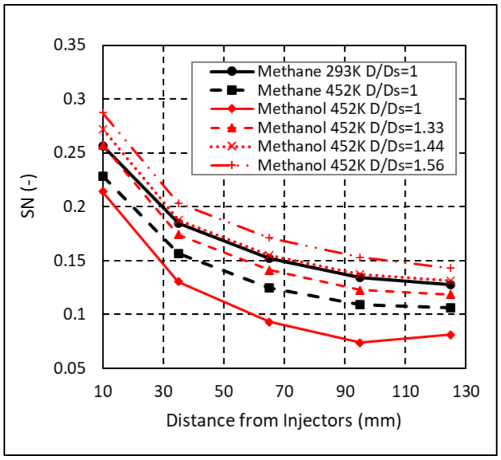

FIGURE 20: UNMIXEDNESS ACHIEVED FOR DIFFERENT FUELS FOR DIFFERENT FUEL NOZZLE DIAMETERS.

The initial manual calculation only considered the pressure drop across the fuel nozzle and did not include flow entry losses into each swirler vane. To evaluate the effects of hole size on the required total pressure at the vane inlet, the pressure drop between the vane inlet and nozzle outlet was evaluated for each case (Figure 21). A 1.44 increase in injector diameter can roughly compensate for pressure drops when compared to methane at 452K. However, to match the pressure drops across the vanes exactly for the current configuration (methane at 293K), the diameter would need to be increased by a factor of 1.67.

This further increase could negatively impact mixing characteristics, potentially leading to higher NO_X emissions. Another critical aspect is the formation of rich regions near the wall, which may result in issues such as flame instabilities, flashback, and other phenomena associated with incomplete fuel-air mixing.

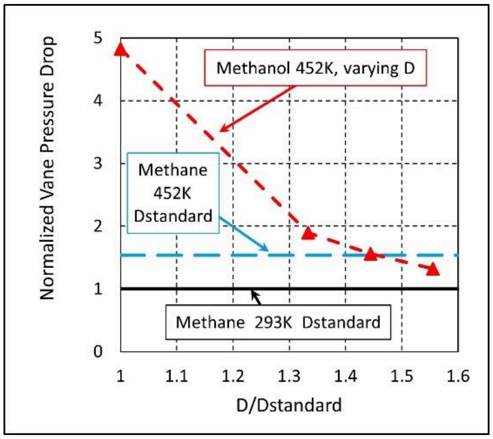

FIGURE 21: PRESSURE DROP ACROSS INLET FUEL VANE FOR STANDARD GEOMETRY (METHANE AND METHANOL) AND MODIFED GEOMETRY (METHANOL).

4. DISCUSSION

Although the previous study [2] suggested that evaporated ethanol may be suitable for use in unmodified lean premix burner as used at Killingholme, the present work suggests that while it may be viable for high quality ethanol (water content less than the azeotrope) it was likely that NO_X emissions would be significantly higher than when firing methane. A significant reduction in firing temperature would be required to reduce NO_X emissions to those achieved with methane.

Firing ethanol with higher water content would require higher evaporation temperatures than is acceptable with current fuel supplies. Furthermore, higher supply pressures would be required due to the increased fuel flow requirement, unless the fuel injection nozzle size was increased, thus necessitating burner modification.

If burner modifications are considered, then methanol may become an attractive alternative and the use of a “dual phase” liquid methanol and evaporated methanol burner has been considered. Liquid methanol has only been given brief consideration because Kliemke and Johnke [10] state that the dual fuel version of the type of burner used at Killingholme can burn liquid methanol unmodified, and liquid methanol firing tests on other burners and experimental studies undertaken by Siemens Energy [11-13] suggest there should be no major challenges. However, if the concept were to be taken forward, the optimum liquid fuel nozzle configuration would need to be investigated.

Burning evaporated methanol has not been considered previously and this study shows that ideal NO_X emissions for evaporated methanol are slightly lower than for methane (Figure 9) and thus the impact of methanol firing on NO_X will be primarily driven by air fuel mixing. Similar mixing quality to unheated methane could be achieved by increasing fuel nozzle diameter by a factor of 1.44 (Figure 20). The kinetic studies suggest lower NO_X may be achieved with evaporated methanol than with methane for the same degree of mixing. Thus, comparable NO_X to methane may be achieved with poorer mixing, allowing a further increase in nozzle size and consequent reduction in burner pressure drop.

The kinetic study showed that at flame conditions the laminar flame speed for methanol and ethanol were similar (Figure 6), but methanol has a slightly higher flame speed at lower flame temperatures. Both ethanol and methanol have significantly higher flame speeds than methane increasing flashback risk. However, the flashback margin for this burner is not known.

The previous study [2] identified that based on hydrogen blending studies for a similar Siemens burner [36] there may be sufficient flashback margin to accommodate the increased flame speed for ethanol. However, a reduction in firing temperature from 1773K to 1726K may be needed to mitigate all remaining risk. This would result in some de-rating of the machine but may be an acceptable mitigation measure. Alternatively experimental results (Figure, 10 [32]) show that water addition significantly reduces the flame speed for methanol, but the kinetic models used do not adequately capture this. Thus, some degree of water addition may be an appropriate mitigation measure, but there is currently insufficient evidence to fully evaluate this.

Fuel placement is also important. If flammable fuel mixtures form in low velocity zones, such as close to solid walls, the flame can propagate into these regions and cause flashback. Examination of Figures 18 and 19 shows that for the methane cases there is a rich zone close to the downstream end of the outer wall of the mixing tube. This would suggest potential flashback issues, but these are not experienced in practice. However, removing these zones would be expected to reduce flashback risk. The unmodified burner does not display this rich region (Figure 18) suggesting that nozzle size optimisation could be used to further reduce the risk of flashback due to the increased flame speed of methanol. This would also reduce NO_X emissions as the reduction in the rich zone occurs at the same time as improvement in mixing quality at the burner exit (Figures 19 and 18). This would however be a trade-off with increased burner pressure drop unless other more significant burner modifications were undertaken.

Lean premix burner performance is strongly dependent on fuel placement and mixing. The significant impact of changing from methane to evaporated methanol on fuel placement and mixing quality (Figure 18) means that modifying the burner for optimum operation on methanol is likely to result in poorer emissions performance compared to operation on natural gas. It may be operationally desirable to be capable of operating on both methanol and natural gas. If this is required, careful evaluation of the modifications would be needed to achieve acceptable operation on both fuels.

It is important to consider thermoacoustics whenever considering combustion changes. Thermoacoustics is a complex issue and without detailed information about flame acoustic properties (Flame Transfer Function (FTF)) it is not possible to make any definitive statements about thermoacoustics, however some general comments can be made.

The previous study [2] indicated that, in simple terms, the phase of the FTF is related to the convection time from fuel injection to the flame front and/or a residence time within the flame depending on whether the driving mechanism is air/fuel ratio fluctuations generated as the air and fuel mix, or bulk flow fluctuations into the flame. The increased flame speed relative to methane will tend to move the flame closer to the burner reducing the convection time. It will also reduce the flame length, decreasing flame residence time. Thus, whichever mechanism is relevant there will be a reduction in the characteristic time that determined the phase of the FTF.

Beita et al. [37] review the impact of hydrogen addition to natural gas on thermoacoustic stability and conclude that hydrogen enrichment is likely to favour higher frequency instabilities, due principally to the reduction in flame length. The reduction in flame length due to the use of evaporated methanol would result in a similar effect. The Killingholme gas turbines have large silo combustors with relatively low-frequency characteristic modes and therefore the tendency for shorter flames to favour higher frequency modes is likely to be of benefit, but combustion tuning is likely to be required on switching from natural gas to evaporated methanol.

Ideally the energy for the evaporation of the methanol should be sourced from waste heat from the gas turbine exhaust, but this will not be available during start-up and thus the gas turbine would have to be started on an alternative fuel, or an alternative source of evaporation energy would be required.

It is unlikely that it will be possible to start the gas turbine on evaporated methanol because of the higher reactivity than natural gas and for practical reasons an alternative starting fuel would be desirable for operation until sufficient waste heat was available for methanol evaporation. For operation on liquid methanol, GE recommend that, because of the potential for liquid accumulation after a failed start together with the low flash point, an alternative starting fuel (natural gas or distillate) should be used [38]. The low flashpoint (12°C) and wide explosive limits (6 to 36vol%) make starting on methanol challenging, but the development of a safe starting protocol for liquid methanol would greatly benefit the concept of a "dual phase" liquid and gaseous methanol burner.

Firing methanol in the SGT5-2000E has the potential to give performance benefits and carbon reductions relative to alternatives for the gas turbines which could continue to fire natural gas or change to another low carbon fuel such as HVO. The relative benefits in performance, carbon output and costs of the potential options have yet to be evaluated. However, Clifford et al [11] predicted a significant increase in output power (10.8%) and thermal efficiency (4.2%) when switching from diesel to liquid methanol firing in a Siemens Energy SGT-A20 gas turbine. Because of the similarities between diesel and HVO similar benefits may be expected for methanol relative to HVO. While these benefits were seen in a different gas turbine to the one under consideration it shows that methanol can give significant advantages.

The use of waste heat to evaporate the methanol has the potential to reduce the base load fuel consumption by about 6% (see Table 3) relative to firing liquid methanol at the same firing temperature. This is in addition to benefits that may be obtained from firing methanol as opposed to natural gas or HVO.

Carbon benefits depend on the carbon intensity of the methanol used. Clifford et al [11] point out that methanol produced conventionally from fossil fuel (grey methanol) has a CO_2 footprint of about 80-90gCO_{2eq}/MJ_{th}. "Green" methanol produced as e-methanol or bio-methanol can have significantly reduced CO_2 footprint depending on production pathways. In principle e-methanol could be "carbon neutral" as during combustion it releases the same amount of carbon as has been captured in its production. However, in reality there will be some residual CO_2 footprint. Depending on the details of manufacture and transport, e-methanol could have a carbon footprint of about 10gCO_{2eq}/MJ_{th} [11]. Thus, the manufacturing methods and carbon intensity of the methanol is an important consideration when purchasing the fuel. A comprehensive study of the potential performance and carbon benefits of possible options is underway.

This study has considered the SGT5-2000E gas turbine with lean premix, dual fuel (natural gas/distillate) burners and the conclusions are based on a combination of the results of the chemical kinetic analysis and CFD mixing studies. These results would only relate directly to these burners. However, similar conclusions are likely for combustors with similar burners such as the SGT5-4000F. The chemical kinetic analyses alone are more generally applicable to lean premix burners. For example, the increased flame speeds relative to natural gas, will result in an increased flashback risk. However other lean premix designs will have different flashback margins. Thus, the chemical kinetic analyses will have wider application, but appropriate consideration is needed for each burner type.

For the chemical kinetic analysis this study has compared results for the chosen mechanism with a wide range of experimental data from the literature, however, we have identified unexpected results for NO_X production for ethanol and issues with the prediction of the impact of water contamination on the laminar flame speed of methanol.

The CFD study primarily considered the impact of fuel change on fuel placement and mixing. Comparison of the methodology with published data for a simple jet in cross flow showed the key features of the velocity and concentration profiles were generally captured, but with varying fidelity depending on the turbulence model chosen. The mixing study gives a strong indication of the likely trends in mixing and placement when changing fuel.

5. CONCLUSIONS

In principle both methanol and ethanol in both liquid and gaseous states could be used as low carbon fuels for power generation.

Considering the Siemens SGT5-2000E gas turbines at Uniper's Killingholme power plant, it is concluded that the unmodified burners could fire evaporated ethanol. However, NO_X emissions are likely to be higher than on methane/natural gas, requiring de-rating to maintain current emissions levels.

If the water content exceeded that of the azeotrope, the required fuel supply temperature and burner pressure drop are likely to be too high and would require burner modifications.

If burner change and modification is required, then methanol becomes an attractive alternative.

In principle a standard dual fuel burner suitable for the Killingholme gas turbines could fire liquid methanol, but modifications to the fuel gas path would be needed to burn evaporated methanol. If modifications to burner are being considered, then both liquid and gas fuel paths could be optimised. Utilising waste heat from the gas turbine exhaust would increase the efficiency when operating on evaporated methanol.

For evaporated methanol operation, ideal NO_X emissions are predicted to be slightly lower than for methane and without burner modification, mixing quality is significantly better. Whilst this would result in significantly reduced NO_X the pressure drop would be excessive.

A simple increase in gas fuel hole sizes would be sufficient to reduce pressure drop and enable operation on evaporated methanol with acceptable emissions performance.

There is a greater risk of flashback due to increased flame speed when firing evaporated ethanol or methanol. Comparison with similar burners firing natural gas/hydrogen blends suggests that there may be sufficient flashback margin, although some de-rating may be necessary. When firing methanol, water content is seen to significantly reduce flame speed which may mitigate the risk of flashback. However, available kinetic mechanisms do not adequately capture the influence of water on flame speed.

It would be highly beneficial if the gas turbine could be started on liquid methanol precluding the need for an additional starting fuel. Further work to develop safe starting schemes for liquid methanol would give significant benefits to methanol gas turbines, both for normal liquid fuel operation and for the "dual phase" liquid/evaporated methanol concept suggested here.

It is possible that evaporated alcohols could be used in lean premix mode in a power generation gas turbine, but in many cases burner modifications would be required. However, each combustion system would have to be individually evaluated to determine its potential for alcohol firing.

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Decarbonisation of industrial power generation gas turbines with bio-alcohols

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