

The combustion mitigation of methane as a non-CO₂ greenhouse gas

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ABSTRACT:

Anthropogenic emissions of non-CO₂ greenhouse gases such as fugitive methane contribute significantly to global warming. A review of fugitive methane combustion mitigation and utilisation technologies, which are primarily aimed at methane emissions from coal mining activities, with a focus on modelling and simulation of ultra-lean methane oxidation/combustion is presented. The challenges associated with ultra-lean methane oxidation are on the ignition of the ultra-lean mixture and sustainability of the combustion process. There is a lack of fundamental studies on chemical kinetics of ultra-lean methane combustion and reliable kinetic schemes that can be used together with computational fluid dynamics studies to design and develop advanced mitigation systems. Mitigation of methane as a greenhouse gas calls for more efforts on understanding ultra-lean combustion. Recuperative combustion provides a promising means for mitigating ultra-lean methane emissions. Progress is needed on effective methods to ignite and to recuperate and retain heat for oxidation/combustion of the ultra-lean mixtures. Catalysts can be very effective in reducing the temperatures required for oxidation while plasmas may be utilised to assist the ignition, but thermodynamic/aerodynamic limits of burning ultra-lean methane remain unexplored. Further technological developments may be focussed on developing innovative capturing technology as well as technological innovations to achieve effective ignition and sustainable oxidation/combustion.

Keywords: ventilation air methane, ultra-lean, recuperative combustion, MILD combustion, ignition, combustion stability

Abbreviations

CFC	chlorofluorocarbon
CFD	computational fluid dynamics
CFRR	catalytic flow reversal reactor
CMM	coal mine methane
CMR	catalytic monolith reactor
CO ₂ -eq	CO ₂ -equivalent
CSIRO	Commonwealth Scientific and Industrial Research Organization
DNS	direct numerical simulation
EDC	eddy dissipation concept
EEC	excess enthalpy combustion
EGR	exhaust gas recirculation
GHG	greenhouse gas
GT	gas turbine
GWP	global warming potential
HFC	hydrofluorocarbon
LEM	linear-eddy model
LES	large eddy simulation
LLGHG	long-lived greenhouse gas
MD	molecular dynamics
MILD	moderate or intense low-oxygen dilution
ODS	ozone-depleting substance
ODT	one-dimensional turbulence
PDF	probability density function
PFC	perfluorocarbon
PSA	pressure swing adsorption
RANS	Reynolds-averaged Navier-Stokes
SGS	sub-grid scale
TFRR	thermal flow reversal reactor
TST	transition state theory
UQ	uncertainty quantification
VAM	ventilation air methane

1. Background

Addressing climate change associated with anthropogenic emissions, either from human activities or from processes that have been affected by human activities, of greenhouse gases (GHGs) is a global challenge. Earth's climate is adversely affected as a result of the emissions of GHGs with carbon dioxide (CO₂) being the largest contributor, mainly from the utilisation of fossil fuels in combustion applications for energy conversion. Anthropogenic emissions of non-CO₂ greenhouse gases [1], such as methane (CH₄), nitrous oxide (N₂O), ozone-depleting substances (ODSs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), sulphur hexafluoride (SF₆) and nitrogen trifluoride (NF₃) also contribute significantly to warming. In terms of the abilities to absorb available infrared radiation and their persistence in the atmosphere, these non-CO₂ GHGs are very different from CO₂. The global warming potential (GWP), defined as the climate influence integrated over time and expressed relative to that of an equivalent mass of CO₂ emission, can be used to indicate the effectiveness of these non-CO₂ GHGs on global warming. All the major non-CO₂ GHGs have very large GWPs, e.g. CH₄ has a value of 25, N₂O has a value of 298, SF₆ has a value of 22,800 and NF₃ has a value of 17,200 over a 100-year time horizon [2].

In the global combat against the adverse effects of GHG emissions, non-CO₂ GHGs must be taken into account, as non-CO₂ GHGs currently account for about one-third of total CO₂-equivalent (CO₂-eq) emissions and 35–45% of total climate forcing from all long-lived GHGs (LLGHGs) [1]. Since most anthropogenic emissions of the non-CO₂ GHGs are linked to society's fundamental needs for food, energy and industrial products, their emissions will continue to increase and further warm the earth unless substantial efforts are undertaken to reduce them worldwide. Although the major GHGs CO₂, CH₄, and N₂O occur naturally in the atmosphere, human activities have greatly changed their atmospheric concentrations. From the pre-industrial era ending at about 1750 to the present, concentrations of these three greenhouse gases have increased globally by 43, 152, and 20 percent, respectively [2]. This can cause a huge problem for the climate as the natural balance in our environment can be broken. For example, the global carbon cycle is made up of large carbon flows and reservoirs. Billions of tons of CO₂ are absorbed by carbon "sinks" such as oceans and living biomass, meanwhile they are emitted to the atmosphere through various "sources". When in equilibrium, the emissions of CO₂ to and the removals of CO₂ from the atmosphere are roughly balanced. Once the balance is broken, adverse or even catastrophic consequences might happen. The climate can also be adversely affected if the balances of non-CO₂ GHGs are broken.

Among the various non-CO₂ GHGs, N₂O is mainly produced by biological processes that occur in soil and water and by a variety of anthropogenic activities in the agricultural, energy-related, industrial and waste management fields. Agricultural soil management, manure management, mobile source fuel combustion and stationary fuel combustion have been the major common sources of N₂O emissions. Presently anthropogenic N₂O emissions account for 3.1±0.8 GtCO₂-eq per year [1], which is about 9% of the total radiative forcing (the difference of solar irradiance absorbed by the Earth and energy radiated back to space). The

enhanced use of fertilizer could increase N₂O emissions, and most emissions of N₂O are associated with feeding the world's growing population. Because of the relevance to food production, careful measures need to be taken when reducing the N₂O emissions. The N₂O mitigation strategies [1] could include more judicious application of fertilizer, increasing nitrogen uptake efficiency by crops, expanding the use of nitrification inhibitors, improving manure management strategies and expanding access to sewage treatment [3-5].

In the global effort to control non-CO₂ GHG emissions, there was a success associated with the significant reduction in ODSs of about 5 GtCO₂-eq per year since 1990 [1], primarily because of the effectiveness of the Montreal Protocol on Substances that Deplete the Ozone Layer [6]. ODSs are man-made chemicals that damage the ozone layer in the upper atmosphere (the stratosphere), including chlorofluorocarbons (CFCs) and halons etc. Measures following the Montreal Protocol such as banning the use of CFCs and limiting the critical use of halons had certainly helped. HFCs and PFCs are families of synthetic chemicals that do not deplete the stratospheric ozone layer; thus, have been used as acceptable alternatives for ODSs under the Montreal Protocol. These compounds, however, along with SF₆ and NF₃, which are used in industrial sectors such as electrical transmission and distribution, semiconductor manufacturing, aluminium production, magnesium production and processing, are potent greenhouse gases. In addition to having high GWPs, SF₆ and PFCs have extremely long atmospheric lifetimes, resulting in essentially irreversible accumulation in the atmosphere once emitted. Although HFCs, PFCs, SF₆ and NF₃ are generally of small amounts [1], their controlled use is certainly important in the combat against global warming.

In the context of energy utilisation and GHG emissions, CH₄ and CO₂ are of paramount importance. Due to the vast amounts of literature available on CO₂ as a GHG, this review will not be focussed on CO₂ but on CH₄, which is not only the predominant constituent of natural gas as one of the major fossil fuel sources but also the second largest GHG next to CO₂. Presently CH₄ is the most abundant non-CO₂ GHG in the atmosphere. Methane's atmospheric increase since 1750 implies anthropogenic emissions of 340±50 TgCH₄ per year or 8.5±1.3 GtCO₂-eq per year [1], which accounts for about 20% of the total radiative forcing from all of the long-lived and globally mixed GHGs, estimated at around 40-50 GtCO₂-eq per year. Agriculture and fossil fuel exploitation together account for about 230 TgCH₄ per year or 5.8 GtCO₂-eq per year, or two-thirds of all human-derived CH₄ emissions. The energy sector is a significant contributor to anthropogenic methane emissions, at around 30% [7]. The main activities causing methane emissions in the energy sector include oil and natural gas systems, coal mining and biomass combustion. Meanwhile, waste treatment and other industrial processes lead to smaller amount of CH₄ emissions.

Greenhouse gas emissions including those from non-CO₂ sources are not entirely understood. Although the GHG emission inventory (the percentage contributions of gases to anthropogenic GHG emissions) provides a solid foundation for the development of a more detailed and comprehensive strategy for the global action against climate change, there are uncertainties associated with the emission estimates. Acquiring a better understanding of the uncertainties associated with inventory estimates will help to improve the overall quality of

the inventory and prioritise future efforts. Some of the current estimates, such as those for CO₂ emissions from energy-related activities and other industrial processes, are considered to have low uncertainties. For some other categories of emissions such as non-CO₂ GHG emissions, a lack of data or an incomplete understanding of how emissions are generated increases the uncertainties associated with the estimates presented. Considering the inaccuracy in obtaining the historic data over a global scale and uncertainties of the inverse modelling, it is not unexpected that the inventory varies in the literature especially their exact percentages [1, 7]. The following percentage data [7] can therefore only be taken as a rough guideline: CO₂ 74%, CH₄ 16%, N₂O 9% and consumptions of CFCs, HFCs, PFCs, SF₆ 1%. Nevertheless, the general trends are consistent: (1) anthropogenic emissions of CO₂ are the largest contributor to warming with CH₄ the second, followed by N₂O as the third; (2) among the three main GHGs, large-scale industrial activities since 1750 have led to the highest percentage increase in CH₄ concentrations in the atmosphere followed by CO₂, with N₂O having the least amount of percentage increase.

The GHG emissions of CH₄ can evolve into a positive feedback due to the interactions between human activities and natural processes. The contribution of wetlands dominates natural CH₄ emissions at 150–180 TgCH₄ per year [8, 9]. The sensitivity of natural CH₄ emissions from wetlands to warmer, wetter climates suggests a positive feedback between emissions and climate change [1]. A doubling of CO₂ (corresponding to a global temperature change of 3.4 °C) would result in an increase in wetland emissions of CH₄ equal to about one-third of present anthropogenic emissions of CH₄ [10]. There is no doubt that CH₄ is a significant driver of global climate change, and more worryingly, it may be a key to positive feedback loops involving Arctic permafrost and methane hydrates stored in the oceans. The methane stored in the permafrost and clathrates may be more than all other fossil fuels combined and is poised to be atmospherically released as the Arctic temperature rises. As reported in Nature [11], the cost of this methane release could be \$60 trillion and the outcome could be disastrous for the climate and world economy.

The atmospheric concentration of CH₄ depends on its generation and loss mechanisms [1, 12, 13]. The loss of atmospheric CH₄ is primarily the result of methane oxidation by the hydroxyl radical (OH^{*}). This sink links the abundance of CH₄ to the complex atmospheric chemistry that influences OH^{*} concentrations on a global scale and creates a positive feedback between CH₄ and its own abundance [1]. In addition, the decreased OH^{*} concentrations in the atmosphere associated with increased CH₄ concentrations can also enhance climate influences of other GHGs such as HFCs. Furthermore, the atmospheric concentrations of CH₄ interact with other atmospheric species or pollutants. Short-lived substances such as the combustion pollutant NO_x (generic term to refer both NO and NO₂ compounds) and tropospheric ozone (which have lifetimes of days to months) can affect climate forcing on longer timescales through their influence on the concentrations of OH^{*}, which in turn affects the atmospheric concentrations of CH₄. Methane as a GHG has a much larger GWP and a much shorter lifetime than CO₂, so reducing CH₄ emissions offers an important opportunity to have a larger impact on GHG reduction and lessen future climate change. The global warming potential can

be massively reduced by oxidising CH₄ emissions into CO₂. In addition, this process offers some potential to utilise the thermal energy from methane oxidation. In recent years, methane emitted from coal mines has been successfully utilised to generate electricity or to provide other forms of energy supply. The opportunities are particularly important for the energy sector, where CH₄ emissions from the extractive activities in the oil and gas industry and coal mines are significant and relatively concentrated point source emissions.

In the energy sector, CH₄ emissions are commonly encountered. In coal mines, CH₄ is formed during the coalification process and is often contained in coal seams and adjacent rock strata. Unless it is intentionally drained from the coal and rock, the process of coal extraction liberates the coal mine methane (coalbed CH₄) into the mine workings, which poses a serious hazard to mine workers. To ensure mine safety, fresh air is circulated through underground coal mines using large ventilation systems to dilute in-mine concentrations of methane to levels well below explosive limits. Mine safety authorities in each country regulate these concentrations. Typically, methane concentrations in ventilation air range from 0.1% to 1.0%. Mine operators employ large-scale ventilation systems to remove coalbed methane from mine working areas. Although the concentration of ventilation air methane (VAM) in the exhaust is quite low, the volume of mine air that ventilation systems move is very large. In oil and gas extractive activities, methane emissions are also very significant. Natural gas is mainly methane, some of which escapes during the drilling, extraction, and transportation process. Such outbreaks are also known as fugitive emissions.

Underground coal mines emitting large quantities of methane to atmosphere is one of the major sources of CH₄ in the atmosphere. Approximately 70% of the methane emitted from coal mines is released as VAM [7], accounting for about 6% of the total anthropogenic CH₄ emissions. Unfortunately, due to the low methane concentration (practically 0.1–1.5%) in ventilation air, its effective utilisation is considerably low. VAM has been investigated extensively in recent years, e.g. [7, 14-19]. Energy recovery may be possible as the products of oxidation are emitted above the ambient temperature. Commercially available technologies such as thermal flow reversal reactors (TFRRs), catalytic flow reversal reactors (CFRRs), catalytic monolith reactors (CMRs), catalytic lean-burn gas turbines (GTs), recuperative gas turbines or regenerative thermal oxidisers have been developed and proven to be useful in cutting the VAM emissions. However, they are not very effective in dealing with diluted methane/air mixtures with less than 0.5% fuel. There are significant challenges in developing effective technologies because most methane releases occur at extremely low concentration levels that current technologies cannot effectively mitigate.

The extractive activities in the oil and gas industry including shale gas generate about three times CH₄ emissions of that from coal mines [7] (more than 20% of the total anthropogenic CH₄ emissions), although the question of how much methane escapes from natural gas and oil wells into the atmosphere remains unknown and challengeable. As with coal, the geological formation of oil can result in large methane deposits that are sometimes released untreated, as the oil is more economically valuable. During oil drilling and extraction, the trapped methane is released to the atmosphere. Targeted collection of the

methane related to oil extraction can vastly reduce emissions from this source, with the collected methane being flared off as carbon dioxide or even providing an additional fuel source [20]. The loss of methane during natural gas extraction obviously has both a direct greenhouse gas impact and an economic cost. The recent emergence of fracking and shale gas has drawn increased attention to this issue. It was reported [21] that 3.6% to 7.9% of the methane from shale-gas production escapes to the atmosphere in venting and leaks over the lifetime of a well, which is at least 30% more than and perhaps more than twice as great as those from conventional gas. Table 1 summarises the estimated contributions to total radiative forcing of the non-CO₂ GHGs, their major sources and mitigation challenges. Apparently methane is the most important non-CO₂ GHG and its emissions include both point and non-point sources, leading to difficulties for mitigation.

Methane capture and utilisation in the energy sector can be a very demanding task, involving technological and economical challenges. Options to reduce methane emissions from the oil sector include flaring (burning off the CH₄-containing flammable gas without commercial purposes), direct use, and reinjection of methane into oil fields [22]. Onshore oil operations usually inject the captured methane into a pipeline. Offshore oil operations (oil platforms) tend to use captured methane directly because flaring is economically unattractive. Captured methane can also be injected into an oil production field to enhance future oil recovery. Although the estimates varied widely [23], CH₄ emissions from the gas industry are much larger than those from the oil industry. Emissions from the natural gas supply chain are a key factor in determining the GHG footprint of natural gas production and use. Current barriers to methane capture from oil and natural gas systems include environmental and economic regulations, financial constraints, as well as the availability and the cost of the technology. For methane emissions from coal mines, depending upon the gas quality and volumes, the coal mine methane could be used in a variety of ways [24], including natural gas pipeline injection, power generation, VAM oxidation, power electricity generators for the mine or local region, use as an energy source such as co-firing in boilers, district heating, coal drying and flaring etc.

Although the fugitive emissions from the oil and gas industry and those from coal mines have differences in their origins and possible capturing technologies, they bear some similarities in their utilisation. For CH₄ emissions at relatively high concentrations, e.g. gas drained from the coal seam before mining with 60–95% CH₄ and gas drained from worked areas of the mine with 30–95% CH₄, utilisation technologies are readily available [15], including purification for utility gas supply, power generation and production of chemical feedstocks. For utility supply, the captured gas needs to be purified to a high level since a minimum of 95% methane is often required to meet the quality specifications for natural gas pipeline sales [15]. However, there is a significant challenge when the CH₄ concentration is very low so that a purification technology becomes economically impractical. Under these circumstances, oxidation/combustion at low concentrations will need to be employed to firstly convert CH₄ to CO₂ for a much lower negative climate impact, and secondly provide a possibility to utilise the thermal energy from the oxidation/combustion. Currently there is a

lack of available technology for methane capture and utilisation for low concentration conditions. The mitigation of these mixtures becomes important for large volumetric flows. For instance, applications such as coalmining, low concentration CH₄ emissions have to be dealt with as VAM contributes to most of the coalmine methane emissions from typical gassy coal mines [15].

Table 1

Estimated contributions to total radiative forcing of the non-CO₂ GHGs, their major sources and mitigation challenges.

Non-CO ₂ GHGs	CH ₄	N ₂ O	ODSs	HFCs, PFCs, SF ₆ , NF ₃
Estimated contribution to total radiative forcing	20%	9%	Presently negligible <1% (accumulative effects of the Montreal Protocol)	1%
Major sources	Agriculture source at slightly more than 1/3, the energy sector at slightly less than 1/3, while other industry and waste processing at around 1/3 of all human-derived sources	Agricultural soil management, manure management, mobile source fuel combustion and stationary fuel combustion	Man-made chemicals such as CFCs and halons etc.	Electrical transmission and distribution, semiconductor manufacturing, aluminium production, magnesium production and processing etc.
Mitigation challenges	The positive feedback mechanism (including that between the anthropogenic and natural emissions), low concentration emissions, and emissions from both point and non-point sources	Enhanced use of fertilizer in agriculture (related to most of the increased N ₂ O emissions)	N/A	Coordinated efforts from the relevant manufacturing sectors

The greenhouse gas mitigation and utilisation of methane emissions from the energy sector call for effective technologies. The main aspects of the technical solutions such as

oxidation/combustion method, operational conditions, technical feasibility and engineering applicability are all important, where advanced knowledge on low concentration combustion is called for. This review deals with the combustion mitigation of methane emissions under lean mixture conditions outside the operational range of conventional combustion systems. It is not focussed on experimental methods and combustion diagnostics. Instead, it is intended to provide an overview of the progress on the topic mainly from the perspectives of modelling/simulation, where some basic information on the methodological approaches is presented. The review addresses the scientific challenges of ultra-lean oxidation/combustion in Section 2, including an overview of the ultra-lean methane combustion, chemical kinetics, as well as the challenges of combustion modelling in applications of computational fluid dynamics (CFD) for reacting flows. Section 3 highlights the technological challenges of ultra-lean methane oxidation/combustion, where the focus is on the VAM mitigation technologies. Finally, Section 4 summarises the subject with additional information, with concluding remarks on combustion chemistry of ultra-lean methane mixtures and some promising research directions.

2. Combustion mitigation and the scientific challenges

The combustion mitigation of fugitive methane not only reduces the greenhouse gas effects by oxidising CH_4 to CO_2 , but also provides an opportunity to utilise the thermal energy from the methane oxidation/combustion process. The scientific challenge of combustion mitigation of ultra-lean methane is mainly associated with the fundamental understanding on the underlying physicochemical factors affecting the flammability limits of methane/air mixture. Such mixture will burn only if the fuel concentration lies within well-defined lower and upper bounds determined experimentally, referred to as flammability limits or explosive limits. These limits vary with temperature and pressure, which are normally expressed in terms of volume percentage at 25°C and atmospheric pressure. The limits are relevant to initiating combustion or explosion, as in an engine, or to preventing it, as in uncontrolled explosions. Physicochemical factors such as initial temperature and pressure have a major impact on the methane/air mixture ignition and combustion, which can be affected by external factors such as the presence of an external energy source, e.g. a plasma source [25, 26]. Chemical reactions are usually characterised by the local temperature and pressure of the mixture. However, when the mixtures ignite near the burn-off limits, the effects of heat and mass transfer also play an important role and must be taken into account. In particular, the presence of catalysts can significantly alter the chemical pathways. These external factors influence the chemical reactions for ignition and oxidation/combustion, which in turn affect the flammability limits.

As the main challenge of CH_4 mitigation and utilisation technology is associated with low concentrations at large volumetric rates, ultra-lean methane combustion is reviewed with focus on the chemical kinetics, which is perhaps the least understood subject for this topic. Because coal mining is one of the most significant sources of fugitive CH_4 emissions and the methane is conveniently contained in a controlled airflow from the ventilation system, the

development of technology for mitigating VAM has been more straight forward to implement than the complex systems encountered in other industries such as gas and oil; thus, the following discussion is focussed on VAM mitigation technologies. While the content deals with a specific application, it is also relevant to a wide range of other potential applications of low concentration CH₄ emissions including those from the oil and gas industries and the agriculture sector as the fundamental science of ultra-lean methane oxidation/combustion remains the same. In the context of VAM, since the existing literature is primarily on the design of the systems and experimental studies, e.g. [7, 14-19], the following sub-sections will focus on the physicochemical modelling and numerical simulations of the processes with a theoretical flavour, while Section 3 will discuss the technological aspects. The oxidation/combustion of such mixtures is assumed to occur in the lean premixed regime as the methane/air flow can be considered to be well mixed and highly diluted with air. Therefore, the study will be focussed on the modelling issues of lean premixed combustion instead of combustion in diffusion or nonpremixed flame as the premixed regime is a more relevant representation of the fugitive methane emissions targeted for reduction.

2.1 Ultra-lean methane combustion and the modelling approach

Ultra-lean methane combustion cannot be achieved using traditional combustion technologies because the thermal energy available in the system may not be sufficient to ignite the fuel and sustain the chemical reactions. Special technologies such as porous burners [27] may be considered to burn “ultra-lean” premixed fuel/air mixtures, where the methane concentration is actually below the lean flammability limit (5% methane by volume in air). By altering the physicochemical factors such as increasing the initial temperature of the methane/air mixture, ignition and combustion may take place at lower concentrations. The initial temperature for the oxidation/combustion can be increased by purposely designed system to retain heat such as recuperative combustion, by external factors such as the presence of an external plasma energy source or the presence of a catalyst, or a combination of these methods. Table 2 summarises the main technologies available for the mitigation/utilisation of ultra-lean methane/air mixtures, together with the principles of these technical measures and the scientific challenges involved. It is worth noting that many of these technologies require further developments, which are dependent on the scientific understandings underlying the methods.

2.1.1 Overview of ultra-lean methane combustion

For oxidation/combustion of ultra-lean methane/air mixtures, technologies are available for mitigation only or for combined mitigation and utilisation. In Table 2, porous burners, TFRRs, CFRRs and CMRs are primarily for mitigation only where it is difficult to extract useful energy from the system. On the other hand, gas turbine technologies can be used to extract energy for power generation in addition to the GHG mitigation effects. Porous burners operate on the principle that the solid porous matrix serves as a means of recirculating heat from the hot combustion products to the incoming reactants, resulting in high burning

velocities and extended lean flammability limits. Exhaust gas recirculation (EGR) can also be incorporated into porous burners with EGR as the heat recuperation mechanism. Although porous burners were shown to be able to burn mixtures with a fuel concentration of only 1% [27], the practical aspects of burner design and operation need careful attention in order to achieve optimised burner performances for lean-burn applications. The important technical aspects include suitable materials for the porous matrix, the length of the porous bed and the use of “multi-section” designs where different porous materials are used in each section. The incorporation of external heat exchangers to supplement the heat recirculation provided by the porous matrix also needs to be considered. There has been an extensive body of theoretical and experimental research on combustion using porous burners including the usage of catalysts, e.g. [28-32]. However, the controlling mechanisms still need to be better understood and the development of reliable models specifically for ultra-lean combustion in practical burners remains challenging.

Porous burners are potentially an effective technology for ultra-lean methane combustion. For the design of burners for practical applications, numerical methods can be particularly useful in understanding the controlling mechanisms and for optimising the design parameters. In industrial applications such as VAM oxidation, numerical simulations need to take into account the large gas volumes in the flow solver and the low CH₄ concentration combustion in the chemical solver. In such a numerical analysis, energy equations in both the gas phase and solid phase (porous structures) need to be solved with the radiative heat transfer taken into account. So far, numerical studies of porous combustion are scarce. In a simplified one-dimensional study using a commercial package [33], the chemistry and fluid flow were decoupled. A skeletal mechanism [34] developed from a full mechanism at 10 atm, 1000 K and 1-vol% CH₄ in moist air [35] was used. The need for an appropriate atmospheric pressure chemical mechanism for the combustion simulation was highlighted [33], because there was no suitable kinetics model available for ultra-lean atmospheric conditions.

Other technologies can also be used for lean CH₄ oxidation/combustion. In the case of VAM, ancillary uses include applications in pulverised coal-fired power stations, hybrid waste coal/tailings/methane combustion units, internal combustion engines and conventional gas turbines, while principal uses include TFRR, CFRR and CMR technologies, as well as lean-burn gas turbines [15]. Using a pilot flame, VAM oxidation was numerically simulated by the authors in a co-annular jet configuration using large eddy simulation (LES) [36]. Effects of preheating and methane concentration were examined in five computational cases. The results indicate that the oxidation of the VAM can take place provided that the preheating temperature is as high as 500 K for mixtures containing a low methane concentration of 0.5%. This encourages the continuation of research on oxidation of ultra-lean methane mixtures with the use of effective heat recovery systems that can deliver appropriate preheating conditions for the incoming mixture.

The current technologies available for ultra-lean methane oxidation/combustion are mainly based on increasing the temperature to initiate chemical reactions, along with increasing the initial pressure to extend the flammability limit. For applications where a high throughput is required such as gas turbines, operating the burner at elevated pressures might

be an option. Currently, studies on ultra-lean methane oxidation/combustion at elevated pressures are very scarce, and are an area that needs further investigation. Although the available technologies can deal with methane concentration lower than 1%, they are generally ineffective when the methane concentration is too low. In this regard, a concentrator could be used to enrich methane to levels that meet the requirements of lean-burn methane mitigation and utilisation technologies [15]. A concentrator may consist of an adsorber, a storage vessel for the adsorbent medium with the adsorbed methane, a desorber and a transporting/feeding system for the adsorbent medium. It can enrich 0.1-0.9% methane stream to a much higher concentration. In addition, the concentrator could act as a buffer to cope with variations in methane concentration and flow rate. However, the design and development of cost-effective concentrators remain technically difficult.

The central issue to ultra-lean methane oxidation/combustion is that ignition can take place at extremely low concentrations with stable flame propagation. Ignition primarily depends on the reaction pathways and transport properties, while stable flame propagation also depends on fluid dynamic and thermodynamic characteristics of the system. Apart from increasing the initial temperature of the system, ignition can also be enhanced by changing the reaction pathways where the energy required to initiate reactions is lowered. Catalytic combustion provides an effective means to enhance ignition and flame propagation. For instance, the minimum CH₄ concentration at which the reaction is sustainable or autothermic for the TFRR technology is around 0.2%, which reduces to 0.1% in a corresponding CFRR technology with the use of a catalyst [15]. Catalytic combustion is usually a multi-step process involving diffusion to the catalyst surface, adsorption onto the catalyst, reaction, and desorption of the product species from the catalyst surface and diffusion back into the bulk. Understanding of catalytic combustion depends primarily on kinetic studies, which become very complicated when considering heterogeneous reactions and remain an area requiring further investigations.

Plasma is also used as a new technology to increase the flame stability and achieve ultra-lean combustion [25]. It can produce active species and heat and modify transport processes. New reaction pathways can be introduced into combustion systems with the presence of plasma to modify the fuel oxidation pathways considerably; accordingly ignition may take place at much lower fuel concentrations. Over the last decade, significant progress has been made on the understanding of the fundamental chemistry and dynamic processes in plasma assisted combustion [25], while technological applications such as combustor dynamics control [26] are also drawing lots of attention. For the applications of plasma, new observations of plasma assisted ignition enhancement, ultra-lean combustion, cool flames, flameless combustion, and controllability of plasma discharge have been reported [25]. Plasma can electronically and vibrationally excite species and the presence of plasma can alter the kinetic pathways. Accordingly it can change the flammability limits so that ignition and combustion may take place at relatively low temperatures and low fuel concentrations. It has been found that plasma can assist low temperature combustion, and affect flame regime transition of the classical ignition S-curve and dynamics of the minimum ignition energy [25]. Non-equilibrium plasma discharge can also affect the fluid transport. However, it remains

unclear what kind of plasma is the best option for combustion enhancement in a given environment. Detailed plasma-combustion chemistry is still not well understood. For ultra-lean mixtures, whether a non-equilibrium plasma discharge can kinetically enhance flame speed and flammability limit or can only promote ignition is still debatable, among many unanswered fundamental questions behind plasma-assisted oxidation/combustion.

Table 2

The main technologies for the mitigation/utilisation of ultra-lean methane/air mixtures, their principles and the scientific/technological challenges.

Technology	Principles	Main Scientific/Technological Challenges
Porous burners	The premixed fuel/air mixture burns within the cavities of a solid porous matrix, which serves as a means of recirculating heat from the hot combustion products to the incoming reactants. Heat is recovered via the thermal energy of the exhaust gases or radiant heating from the porous solid [27-32]	The stability of the oxidation/combustion process to fluctuations in fuel concentration and flow rate, the development of reliable models for ultra-lean combustion, as well as optimising burner performance for lean-burn applications
TFRR	Recuperative combustion using flow reversal to transfer the heat of combustion to the incoming air via a solid heat storage medium [15]	Similar to those for porous burners, with design optimisation of the regenerative beds for heat recuperation
CFRR	The same as TFRR, but with the additional use of a catalyst	Similar to TFRR, with the complexities associated with the use of a catalyst
CMR	A honeycomb type monolithic reactor consisting of a structure of parallel channels with walls coated by a porous support containing catalytically active particles with very low pressure drop at high mass flows	A recuperator to pre-heat the mixture is needed and additional thermal storage in the recuperator may be required to allow for continuous operation
Catalytic & recuperative GTs	Lean-burn GT with a catalytic or a recuperative combustor and a heat recuperator	System stability and optimisation
Combustion air	Lean mixtures used as combustion air for power generation including GTs and internal combustion engines	Combustion stability and system optimisation

In the context of low concentration CH₄ oxidation/combustion, the concept of moderate or intense low-oxygen dilution (MILD) combustion [37] is relevant. The interest in MILD combustion has been mainly driven by the needs for low emission and high efficiency combustion. Despite that MILD combustion was originally developed to oxidize mixtures without the formation of large temperature gradients and localized heat sources, it has potential to oxidize low concentration fuel mixtures. As MILD combustion was not specifically developed for ultra-lean systems, there are important differences in the flow and combustion characteristics. The most significant difference is that the fuel concentration in MILD combustion is much higher (typically not ultra-lean) and therefore, the technologies to oxidize the fuel are also different. However, similar approaches can be used as the flow conditions after dilution of the fuel are representative of the oxidation process of ultra-lean mixtures under preheating conditions [38-40]. MILD combustion refers to conditions where temperature of the reactant mixture is higher than the autoignition temperature, while the temperature rise during combustion is relatively low [37, 38]. The concept of “autoignition temperature” helps to delineate the MILD regime boundary for operational purposes [38]. In a premixed combustion system, autoignition depends on complex chemical kinetics associated to particular operating conditions. Dilution influences the local composition and the thermodynamic state. It can lead to possible changes in chain branching reactions, and consequently it can affect the autoignition characteristics of the original mixture. MILD combustion involves low concentration reactant mixture and preheating of the mixture, which can be affected by physical aspects such as flow conditions (laminar or turbulent mixing), heat transfer characteristics, thermodynamic properties and chemical aspects. MILD combustion studies have been focussed on capturing and explaining the autoignition properties and parameters affecting the sustainability of the combustion process, where the flow and combustion characteristics are different from ultra-lean methane oxidation/combustion. Goh et al. [39, 40] recently investigated the physicochemical mechanisms of MILD (flameless) combustion under ultra-lean conditions. Although the underlying physicochemical mechanisms for MILD combustion remain to be fully investigated, a better understanding is starting to emerge, which will assist the understanding and technology developments of ultra-lean methane oxidation/combustion.

2.1.2 Numerical modelling approach for methane oxidation/combustion

For the mitigation and utilisation of ultra-lean methane mixtures, optimisation of practical systems for lean-burn applications is an essential step in the technological developments towards the reduction of greenhouse gases. In this context, CFD type of modelling and simulations can play a significant part in optimising system designs. Although experimental studies play a vital role in understanding the mechanisms of ultra-lean methane combustion as well as design of practical combustion systems, there are some difficulties when exploring the thermodynamic/aerodynamic limits of burning low concentration fuel mixtures in experiments. Some examples of technical limitations using experimental work are associated

to the minimization of heat losses from the system and maximization of fuel-air mixing for oxidation. In this regard, numerical simulations can be used to complement experimental studies by providing insight and identifying key physicochemical processes. Parametric numerical studies can also be used to optimise the practical design of the system such as optimising the initial energy level to initiate the oxidation or controlling the heat losses to the surroundings. In a numerical study considering constant-pressure autoignition and freely propagating premixed flames of cold methane/air mixtures mixed with equilibrium hot products [38], evidence of significant reactions involving intermediate species prior to the flame front was shown in premixed flame simulations at high dilutions. At the present time, the reacting flow of ultra-lean methane combustion has not been broadly studied using numerical simulations.

The governing equations describing the reacting flow field in a system are briefly given here to illustrate the modelling/simulation procedures. For commonly encountered turbulent reacting flows, the Favre-averaged equations for transient compressible flows can be solved. The overall mass conservation in tensor form is given as:

$$\frac{\partial \bar{\rho}}{\partial t} + \frac{\partial}{\partial x_j} (\bar{\rho} \tilde{u}_j) = 0 \quad (1)$$

where ρ is the density, t is time and u_j the Cartesian velocity in the x_j -direction, the overbar denotes either time (temporal), spatial or ensemble averaged quantities, while the tilde denotes mass-weighted or Favre averaged quantities. The Navier-Stokes momentum equations for the velocity components can be written as:

$$\frac{\partial}{\partial t} (\bar{\rho} \tilde{u}_i) + \frac{\partial}{\partial x_j} (\bar{\rho} \tilde{u}_i \tilde{u}_j) = - \frac{\partial \bar{p}}{\partial x_i} + \frac{\partial}{\partial x_j} (\bar{\tau}_{ij} - \bar{\rho} \widetilde{u_i'' u_j''}) + \bar{\rho} \tilde{f}_i \quad (2)$$

where p is pressure, τ_{ij} is the viscous stress tensor, u_i'' and the u_j'' are the fluctuating parts of the velocity components, and f_i is the body-force acceleration in the x_i -direction (e.g. the gravitational acceleration related to buoyancy force). For combustion applications, transport equations for the species also need to be solved. The transport equation for the mean mass fraction of an individual species Y_k in a mixture of N species can be written as:

$$\frac{\partial}{\partial t} (\bar{\rho} \tilde{Y}_k) + \frac{\partial}{\partial x_j} (\bar{\rho} \tilde{Y}_k \tilde{u}_j) = \frac{\partial}{\partial x_j} \left(\bar{\rho} D \frac{\partial \tilde{Y}_k}{\partial x_j} \right) - \frac{\partial}{\partial x_j} (\bar{\rho} \widetilde{u_j'' Y_k''}) + \bar{\omega}_k \quad (3)$$

where $k = 1, \dots, N_{species}$, $N_{species}$ is the number of species considered, D is the mass diffusion coefficient, and $\bar{\omega}_k$ is the averaged volumetric net rate of production of species k due to chemical reactions, i.e. the chemical species source/sink term. Neglecting the work done by body forces, the energy conservation equation formulated in terms of total enthalpy h can be given as

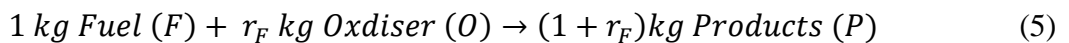
$$\frac{\partial}{\partial t} (\bar{\rho} \tilde{h}) + \frac{\partial}{\partial x_j} (\bar{\rho} \tilde{h} \tilde{u}_j) = \frac{\partial}{\partial x_j} \left(\bar{\rho} \alpha \frac{\partial \tilde{h}}{\partial x_j} \right) - \frac{\partial}{\partial x_j} (\bar{\rho} \widetilde{u_j'' h''}) + \bar{S}_h \quad (4)$$

where α is the thermal diffusivity and S_h is the internal production of thermal energy related to combustion heat release, i.e. the energy source term.

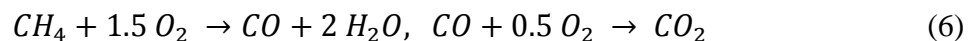
Equations (1)-(4) constitute the basic governing equations for turbulent reacting flows. However, they are not a closed set that cannot be solved without modelling closures for the Reynolds stress, turbulent fluxes and the chemical source terms $\overline{\omega_k}$ and $\overline{S_h}$. As there is a vast amount of literature available on turbulence modelling, e.g. [41], the modelling of the Reynolds stress and turbulent fluxes will not be discussed herein. In the traditional CFD approach based on Reynolds-averaged Navier-Stokes (RANS) modelling, turbulent combustion can be modelled using a variety of models, e.g. [42]. The most significant challenge in physicochemical modelling is related to the chemical kinetics, which needs to be coupled with modelling of turbulent flows. Extra difficulties are not expected for turbulence modelling of ultra-lean methane combustion, but attention is needed for modelling the chemical kinetics and turbulence-chemistry interaction under ultra-lean conditions. In practical CFD simulations, the calculations associated with the chemistry can be very time consuming, especially when one uses a detailed mechanism considering a large number of species. For instance, the conservation of chemical species presented in Eq. (3) will require individual equations with the number of $N_{species}$ and there will be a very large number of chemical source terms related to the reaction rates. Inevitably such a simulation will be very expensive in terms of computational costs. Furthermore, in finite-rate chemical kinetic schemes, Arrhenius formulas are usually employed for the reaction rates of individual reactions. Accounting for detailed chemistry requires having the temporal and spatial resolution to solve the fast and slow reactions as well as the formation of short-lived reactive species such as radicals that usually occur in thin zones. This contributes to stiff the governing equations and leads to numerical difficulties. This disparity of scales in turbulent combustion applications leads to the development of techniques to reduce the computational cost associated to the fluid mechanics and chemistry parts separately. From the fluid mechanics point of view, steady and unsteady flow approaches can be used to describe the fluid flow. Steady approaches as the ones used in RANS models are developed based on temporal- or ensemble-averaged equations to reduce the computational cost, while unsteady flow approaches such as LES or DNS are more accurate as most or all the scales are solved but they are more computationally intensive. From the chemical point of view, reduced schemes designed for particular operating conditions based on few steps can be used or one can apply chemical scale separation processes as the ones used in flamelet models. Flamelet models are based on chemistry tabulation, where the combustion chemistry information is stored in pre-calculated look-up tables so the source terms can be directly read or interpolated from the database while there is no need to solve $N_{species}$ equations for the species. Although the method is attractive computationally, one has to apply it with caution. The data tables are usually obtained based on many different parameters such as the original detailed mechanism, pressure, local temperature, heat loss, strain, pre-defined shape functions for turbulence-chemistry interactions, among others. Computational models based on chemistry tabulation must be used with caution because the thermochemical properties may not resemble the flow under consideration.

For modelling and simulation of combustion, the physicochemical modelling involves coupled chemical kinetics with turbulent effects when the flow is in the turbulent regime. Turbulence-chemistry interaction has to be addressed. Under ultra-lean conditions, the simple mixed-is-burnt model (assuming that the rate of combustion is determined solely by mixing processes, which was widely used in the simulations of industrial combustors and furnaces) is not valid. Because of the importance of extinction/re-ignition in ultra-lean CH₄ combustion, the reacting flow will be intrinsically unsteady. In this context, LES will be a more suitable tool than averaged RANS approaches. In LES, sub-grid scale (SGS) modelling for turbulence and turbulent combustion is essential, which is a continuously developing area. LES is a promising approach and may become a reliable modelling tool for numerical simulations of practical reacting flows with unsteadiness. In LES, the modelling uncertainty is inevitably associated with the inaccuracy of the SGS model. Nevertheless, ultra-lean conditions do not bring significant extra difficulties to SGS modelling for turbulence and turbulent combustion, apart from the requirements on predicting extinction/re-ignition with high fidelity.

One of the commonly used turbulent combustion modelling methods is the eddy dissipation concept (EDC) [43, 44] for turbulence-chemistry interaction. EDC gives an expression for the mean reaction rate, $\overline{\omega_k}$ in Eq. (3). The model assumes that chemical reactions occur where the dissipation of turbulence energy takes place, that is, in the fine structures, which have characteristic dimensions that are of the order of the Kolmogorov scales. These structures are not evenly distributed in time and space but are concentrated in certain regions (fine-structure regions) that occupy a fraction of the flow. Because of its simplicity, EDC has been used in engineering turbulent combustion modelling with a number of approaches for different scenarios such as the fast chemistry, detailed chemistry and local extinction approaches [42]. In turbulence modelling of the reacting flow field of ultra-lean methane combustion, the EDC model may prove not to be the most suitable one. It was chosen here to illustrate the turbulence-chemistry coupling in reacting flow simulations, which is a key issue in numerical simulations of ultra-lean combustion. The fast chemistry approach is the simplest in terms of formation, which is obtained by assuming that there is sufficient residence time in the fine structures. It is further assumed that combustion can be represented by a single irreversible one-step global reaction of the form



where r_F is the mass-based stoichiometric oxidiser-to-fuel ratio. Using the extended approach of EDC [42], it is also possible to use more than one global reaction, e.g. including the formation of carbon monoxide (CO) in CH₄ combustion, the reactions considered can be given as



In Eq. (6), stoichiometric coefficients are used to establish the mole ratio between reactants and products. The fast chemistry approach has the advantage of being easy to implement. However, the assumptions made are normally violated in ultra-lean conditions where local extinction might take place and the chemical mechanisms can be rather complex. For

oxidation/combustion of ultra-lean CH_4 mixtures, finite-rate chemical kinetics has to be considered. In the EDC detailed chemistry approach, finite-rate chemical kinetics are taken into account by treating the fine structures as constant-pressure and adiabatic homogeneous reactors. The EDC local extinction approach, assuming extinction takes place in the turbulent fine structures, applies a database of pre-calculated chemical time scales containing the influence of chemical kinetics. It showed significantly better results than the fast chemistry approach while having a comparably small computational cost [42]. An extension of the EDC model to account for local extinction seems to be a promising approach to model ultra-lean methane combustion, but further research needs to be conducted to assess its applicability and accuracy on practical cases.

For numerical simulations of ultra-lean combustion, finite-rate chemical kinetics need to be accounted for, in conjunction with turbulence and turbulent combustion modelling when the flow is in the turbulent regime. When oxidation/combustion takes place at highly diluted conditions, unsteadiness such as ignition, local extinction and re-ignition plays a major role in the combustion dynamics. In terms of capturing the flow unsteadiness, LES is significantly more advantageous than RANS approach based on time- or ensemble-averaging. LES of turbulent combustion has made significant progress in the last several decades, e.g. [45-48].

Turbulent combustion modelling is a vast area with a large number of approaches, e.g. the Bray-Moss-Libby theory is broadly used which is a second-order closure with special closure approximations appropriate to flame-sheet combustion [49]. Although turbulent combustion modelling still evolves with the advances on relevant branches of fluid flow and combustion sciences, it does not represent a specific challenge on the flow dynamics side for ultra-lean combustion. Chemical kinetics modelling represents the largest challenge for numerical simulations of ultra-lean combustion, since the numerical simulations need to accurately predict: (1) under which conditions the mixture ignites; and (2) under which conditions the oxidation/combustion will be sustainable. The chemical kinetics also affects the turbulence-chemistry interactions.

The progress in MILD combustion can help to better understand ultra-lean CH_4 oxidation/combustion. As a promising technology to reduce pollutant emissions and to improve combustion efficiency, a combination of air preheating and fuel dilution with combustion products of low oxygen concentration is the main feature of MILD combustion. It has been shown that the reaction mechanism used in CFD simulations affects the numerical results of natural gas combustion in the MILD combustion regime [50]. The study shows how several global reaction mechanisms obtained different nitrogen oxide and carbon monoxide levels during the combustion process. The turbulence-chemistry interaction was modelled using the EDC. The results showed that the temperature prediction was satisfactory using the global reaction mechanisms, but a severe over-prediction of the CO and H_2 concentration occurred due to the use of simplified reaction schemes. The study highlighted that the EDC turbulence-chemistry interaction model may be suitable for the calculation of MILD combustion processes, but the chemical kinetic mechanisms need careful attention. Modelling MILD combustion is very likely to require accurate descriptions of turbulence-chemistry

interactions. In this context, the transported probability density function (PDF) method for premixed turbulent flames [51] provides an advanced modelling approach.

In understanding the mechanisms of MILD combustion, direct numerical simulation (DNS) can be a useful tool. DNS resolves all the relevant time and length scales in the flow field using highly accurate numerical methods and significant amounts of computing resources. It can prove to be a powerful tool in gaining a deeper understanding of MILD combustion especially when one examines the thermodynamic/aerodynamic limits of burning a low concentration fuel mixture. In the study of MILD combustion, advanced CFD approaches such as LES and DNS are becoming increasingly important, e.g. [52, 53]. As LES and DNS are time-dependent three-dimensional (3D) simulations, the computational costs associated with these methods can be relatively high.

In general, the fluid flow and chemical kinetics are coupled together in combustion applications. For computer modelling and numerical simulation of ultra-lean CH_4 oxidation/combustion, the most significant challenge is associated with obtaining a high-fidelity representation of the combustion chemistry. The use of detailed chemistry may be necessary as the kinetics at ultra-lean conditions can be rather complex, while a reduced mechanism such as a skeletal mechanism may significantly reduce the computational costs without losing much of the accuracy. The skeletal mechanism for combustion within the porous burner described by Jazbec et al. [34] comprises 28 reactions and 12 species, which was developed specifically for use in CFD analysis and enabled the viability of the porous domain thermal transport model to be demonstrated for the high pressure level of 10 atm. Since the chemical mechanisms governing the oxidation process at such low concentrations have not been fully understood, reliable chemical kinetic models specifically developed for ultra-lean methane combustion are still in demand. In the following sub-section, the chemical kinetics for CH_4 oxidation/combustion especially for ultra-lean conditions is discussed.

2.2 Chemical kinetics for ultra-lean methane oxidation/combustion

In computational studies such as a CFD of ultra-lean methane oxidation/combustion, the chemical species source/sink terms as well as the energy source term have to be provided for the closure of the governing equations, such as those shown in Eqs. (3) and (4). These terms can be readily provided if the chemical kinetic schemes are known. In the following, some background on combustion chemistry for general methane oxidation, chemical description of ultra-lean methane oxidation, effects of catalysts, as well as reduced chemical kinetics for ultra-lean methane oxidation are briefly summarised.

2.2.1 General background on combustion chemistry for methane oxidation

This sub-section provides some basic background on methane oxidation kinetics, which serves as the basis for kinetic studies at ultra-lean conditions. The chemical kinetics for the oxidation of methane has been of primary interest in combustion science, since methane is one of the main hydrocarbon fuels and one of the most important energy sources. The

understanding of chemical kinetics governing the combustion of hydrocarbon fuels has been the subject of many studies since the late 1970s [54-56]. Studies were focussed on describing the chemical pathways leading to the formation of pollutants and radicals to improve efficiency and safety with reduced emission in combustion systems. The oxidation of hydrocarbon fuels can be systematically described using levels or hierarchies in reaction pathways of fragments of the initial fuel [56]. The kinetics can be split in individual chemical kinetics subsets, which in traditional hydrocarbons correspond to the chemistry of H₂-O₂, CO/CO₂, C₁-C_n hydrocarbon kinetics (where the subscript indicates the hydrocarbon order) and the chemistry of formaldehyde CH₂O, an intermediate species in most hydrocarbon oxidation processes [56]. In practice, most hydrocarbon fuels have considerable similarities in their combustion characteristics (major species, burning velocities and autoignition delay times) for practical fuels because the oxidation is dominated by common key elementary reactions [57-60]. Fundamental branching reactions at high temperatures are:



While at low-intermediate temperatures, the branching mechanism is different and is mainly related to the formation and decomposition of hydrogen peroxide [56]. The arrows indicate the direction of the chemical reaction considered, where “ \Rightarrow ” stands for irreversible reactions and “ \Leftrightarrow ” for reversible reactions.

Methane is the main compound in natural gas (above 90%), which is also an important by-product in many industrial processes and an intermediate product in the oxidation of more complex fuels. As it is the most commonly used gaseous fuel, methane combustion chemistry has been extensively investigated. The reaction mechanism of methane follows a complex scheme and usually can be decomposed into two main pathways depending on whether the fuel burns in lean or rich conditions [56, 57, 59]. For very rich fuel conditions, the oxidation pathways require full description of C₁ to C₄ paths, while for lean or stoichiometric conditions C₁ to C₂ subsets are sufficient to describe the chemical structure of the oxidation process. The main chemical pathways in most methane deflagrations at conditions of practical interest in combustion systems (near stoichiometric conditions) are shown in Fig. 1. Although the pathways shown in Fig. 1 are not expected to be fully applicable for ultra-lean methane oxidation/combustion, they can be taken as the reference point for the study of chemical kinetics under this extreme condition.

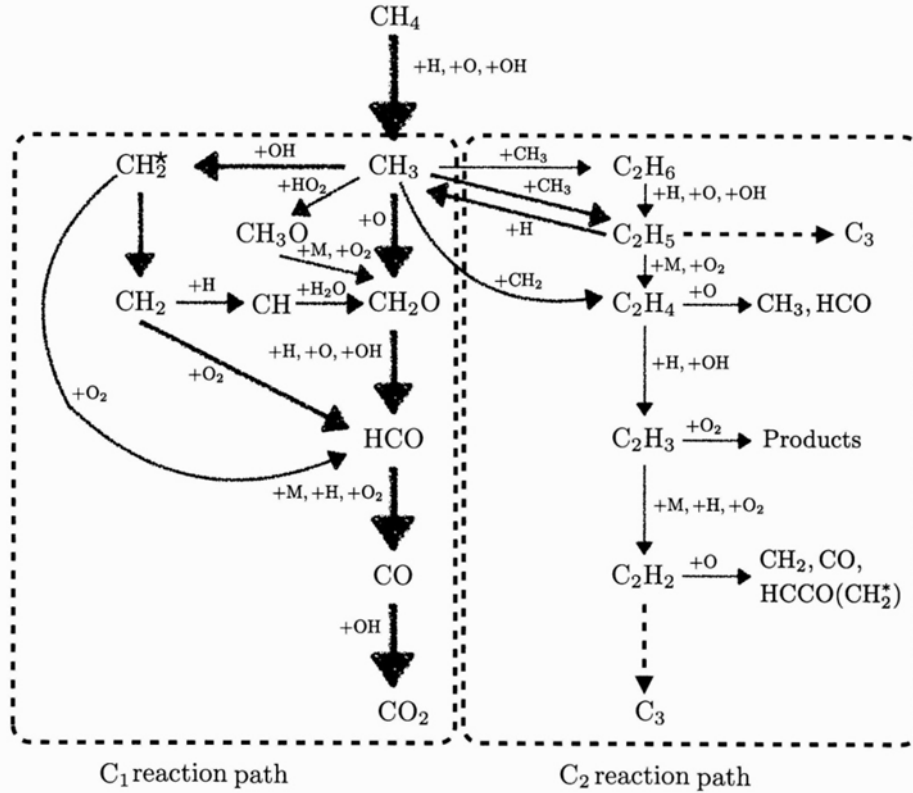
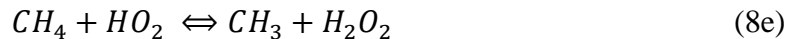
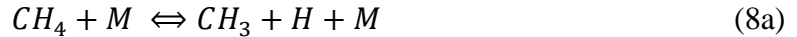


Fig.1. Main chemical pathways for methane oxidation involving C₁ to C₂ hydrocarbon orders valid under lean and stoichiometric conditions. Adaptation from Warnatz et al. [61, 62]

The thermal decomposition of methane to form the methyl radical occurs through hydrogen abstraction by means of the following reactions:

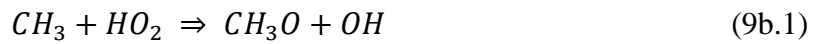


where M represents an energetic third body, from which energy is transferred during a molecular collision. In the above, reaction (8a) is dominant and the most important initiation reaction [63], and reactions (8b-e) exhibit substantial non-Arrhenius behaviour for the range of temperatures of interest in most combustion applications [56]. These reactions are critical to predict autoignition and become less important for steady flames. Therefore, these reactions should be taken into account when burning highly diluted mixtures as they influence the autoignition delay time of the fuel and indicate the operability of the fuel for certain operating conditions.

The consumption of the methyl radical CH₃ occurs via the global oxidation step given by reaction:



or more precisely by the OH or HO₂ radicals to form CH₂O and CH₃O. For moderate temperatures and high pressure, the formation of hydroperoxyl radicals governs the stabilization of the H₂ – O₂ sub-mechanism and CH₃ and HO₂ are dominant species in the radical pool influencing phenomena such as autoignition. The reaction paths include the thermal decomposition of the methylhydroperoxide CH₃OOH to form CH₂O and CH₃O and are given by the following reactions, although hydrogen abstraction forming CH₄ and O₂ can also occur.

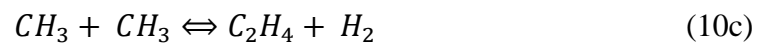


Reaction (9b.1) is most likely to occur for temperatures in the range of most combustion systems and pressures up to 100 bar. The reaction of the methyl radical with hydroxyl radicals is also a main chemical pathway for the oxidation of CH₃, and several kinetic paths are possible depending on temperature and pressure. The principal reaction paths are:

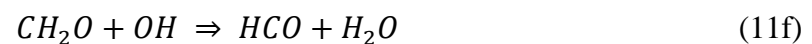
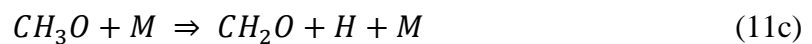


where reaction (9c.1) competes with reactions (9c.2) – (9c.5).

Recombination reactions can also take place in the case of rich conditions:



The additional reaction pathways of chain reaction leading to the formyl radical and eventually the carbon monoxide by dehydrogenation are:



Reactions (11a-h) are fast reactions and most intermediate radicals are consumed very rapidly.

The final oxidation of carbon monoxide to carbon dioxide is a slow process and coupled to the H₂-O₂ mechanism. The main reactions are:



The oxidation of methane and any hydrocarbon require the presence of a radical pool of H, OH, O and HO₂ that allow the aforementioned elementary reactions to take place. This is given by the chain-branching, chain-propagating and chain-breaking reactions of the H₂-O₂ mechanism [56]. Under ultra-lean conditions, the HO₂ chemistry is of particular importance, since it reduces the system reactivity. The principal HO₂ formation reaction at low temperature is



In this reaction, *M* represents a third body of any species. This reaction becomes an inhibiting reaction when it takes place at high temperatures because it competes with the reaction (7a) $H + O_2 \Rightarrow O + OH$.

The elementary steps are gathered together forming detailed chemical kinetics mechanisms that represent the combustion chemistry of any hydrocarbon fuel. These reaction mechanisms are designed to provide detailed information on the transformation of reactants into products at the molecular level and predict heat release, products and radicals at varied conditions of temperature, pressure and fuel dilution.

There are a number of well-established detailed chemical kinetics mechanisms for methane oxidation. This section introduces several detailed reaction mechanisms that represent the state-of-the-art in chemical kinetics for methane oxidation. The selection is not exhaustive, but includes some important reaction mechanisms used in the combustion community. These schemes can be used for general use under a wide range of operating conditions, but users should carefully check the actual conditions for which they are designed before applying them for particular applications.

The largest contribution to provide reliable data for methane oxidation (and also for natural gas) has been the Gas Research Institute initiative developed at The University of California at Berkeley, Stanford University, The University of Texas at Austin, and SRI International developing the GRI-Mech [64]. The GRI-Mech 3.0 (the last update) is a chemical scheme comprising 325 chemical reactions and 53 reactive species that provide rate reactions and thermochemical data for temperature in the range of 1000 to 2500 K, and pressure from 1.0 to 1000 kPa, with equivalence ratios from 0.1 to 5 in premixed systems for methane and natural gas. The GRI-Mech includes a comprehensive set of experiments such as shock-tube ignition delay, flow and stirred reactor data providing species profile measurements and laminar flame speed for all conditions. A small subset with 38 species and 190 reactions so-called RAMEC based on the early development of GRI-Mech (GRI-Mech 1.2) [65] was developed using additional reactions that are important in methane oxidation at lower temperatures [59].

A well-established reaction mechanism widely used in the combustion community for hydrogen and also for hydrocarbon flames is the San Diego mechanism [66]. It comprises 357

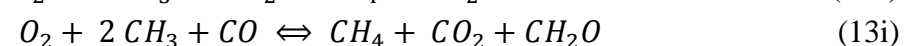
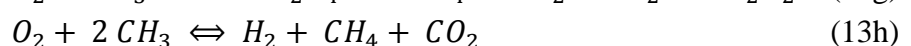
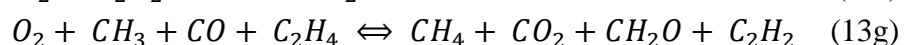
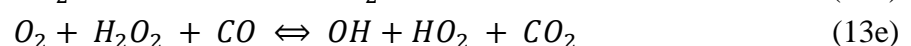
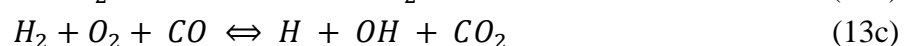
reversible reactions and 100 chemical species, and includes fuels from JP10 up to n-heptane. For the particular case of methane oxidation, a reduced subset from the entire San Diego mechanism can be used and has been extensively tested and validated for rich conditions [67] and general applications [68]. Another recent detailed scheme for methane combustion requiring 134 reversible reactions and 30 reactive species [69] was also developed by some of the authors.

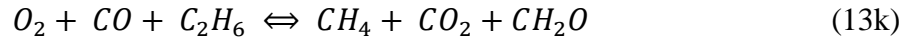
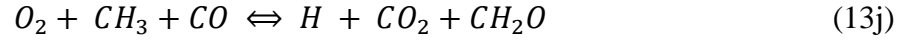
The Leeds mechanism has also been used to describe the chemical kinetics of methane combustion along with ethane and ethylene flames in the work by Hughes et al. [70]. This mechanism makes use of 351 chemical reactions with 37 species and the overall performance is rather similar to the GRI-Mech, although it uses different elementary reactions [59]. The mechanism proposed by Dagaut et al. [71] for methane combustion in a jet-stirred reactor has also been widely used in many combustion applications, so has been the mechanism by Davis et al. [72]. Ranzi et al. [73] also developed a detailed kinetic mechanism that has been successfully employed for the combustion of hydrocarbon fuels. This scheme provides detailed chemical data to the C₂ chemistry and comprises 70 species with 1600 reactions.

A more comprehensive analysis of detailed schemes can be found in the work by Westbrook and Dryer [56], and more recently by Simmie [59] and Renzi et al. [74] among many others. For brevity, the details of these models are not provided herein.

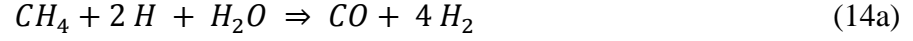
Reduced mechanisms are particularly valuable in CFD studies of reacting flows. Many reduced chemical schemes have been proposed in the literature to describe methane oxidation. These reduced schemes are usually required for CFD calculations on industrially relevant simulations in order to reduce the computing time of the chemical calculation. The reduction process can be achieved by assuming a limited range of operating conditions and assuming steady state of some intermediate species. From the early work of Westbrook and Dryer [56, 75], in which a compilation of one-step and two-step chemical schemes were presented for several fuels of interest, a large number of these schemes have appeared and continuously appear in the literature. This is a very active area of research, since the operating conditions of practical systems are constantly changing and advanced techniques for chemical reduction are developed.

Several reduced schemes from the GRI-Mech were proposed by Chen and co-workers [76, 77] for methane oxidation. These schemes include a 10-step, 12-step, 13-step, 15-step and 16-step reaction schemes that have been extensively used in the combustion research community. As an example, the 12-step scheme is given by:





Peters and co-workers [78] developed a broadly-used 4-step reduced scheme for methane oxidation accounting for C₁ and C₂ schemes.

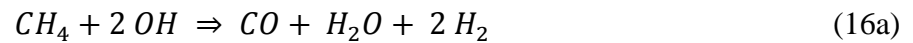


Jones and Lindsted [79] also developed a 4-step reaction scheme valid for methane oxidation given by the following global reactions:



The scheme reproduces the flame speed, species profiles and flame thickness with sufficient accuracy for standard equivalence ratios. However, it was shown that this well-known mechanism led to a severe over-prediction of the CO and H₂ concentration because of the simplified reaction path when it was used to predict the oxidation of natural gas in the MILD combustion regime [50].

Several reduction schemes for methane oxidation under general combustion conditions [80] and lean conditions [81] were also proposed based on steady state approximation of intermediate species. A 4-step reduction scheme was first proposed and then, further reduced to a 2-step mechanism for conditions relevant to gas turbine operations. The 4-step scheme is given by:



In the meantime, the 2-step mechanism is represented by the following two global reactions:



Reduced kinetic schemes for methane oxidation were also investigated by Bibrzycki and Poinot for methane/air and oxyfuel combustion [82]. The 2-step mechanism 2S-CM2 was

compared to the Jones and Lindsted mechanism [79] and then, adjusted to have better predictions for oxyfuel and rich conditions in combustion with air (2S-CM-JB1). Further corrections were made for lean methane flames (2S-CM-JB2) and better correlation with the reference GRI-Mech 3.0 was obtained. Other reduced mechanisms for methane oxidation have also been proposed, e.g. those by Lu and Law [83] or Wada et al. [84] and more recently by Nikolau et al. [85] for diluted mixtures with large water vapour content.

The applicability of these reduced schemes for oxidation of ultra-lean methane mixtures still has to be assessed as most of these mechanisms were developed for particular operating conditions. Some important aspects to be determined are the ignition delay time and flame propagation predicted by these schemes, since the reaction sets might not be appropriate when the radical pool of some species is rather low or the dilution overcomes certain values. This is an important topic that requires further investigation.

2.2.2 Chemical description of ultra-lean methane oxidation

While the chemical kinetics of most practical fuels under standard burning conditions is relatively well understood, as described before, the study of chemical kinetics of mixtures in unconventional burning conditions (e.g. highly diluted mixtures or ultra-lean conditions, low temperature and high pressure among others) still requires further research. In the case of ultra-lean mixtures, the combustion process is rather different from traditional flames.

The autoignition delay time, which can be defined as the time required for a well-mixed fuel and oxidiser mixture to ignite at certain steady temperature and pressure conditions, is found to be a key aspect to evaluate the burning characteristics of ultra-lean mixtures and some work has been devoted to this [86, 87]. The characteristics of the methane autoignition under atmospheric pressure and different preheating temperatures and diluents were investigated by Sabia et al. [88]. Their work showed different chemical kinetic pathways for methane autoignition in which the reactivity of the oxidation process changes. The local mixture temperature not only influences the reaction channels, but also the chemical kinetics governing the autoignition process. At the low temperature range ($T = 850\text{K}$), the main pathway of methane oxidation after dehydrogenation of CH_4 is the formation of CH_3O and CH_3O_2 that eventually leads to CH_2O , HCO and finally CO . At the intermediate temperature range ($T = 975\text{K}$), the reaction rates increase substantially with respect to the low temperature ignition and similar chemical pathways are observed, although alternative recombination routes to ethane and the formation of formaldehyde and OH radical also occur. At the high temperature range ($T = 1150\text{K}$), the weight of the chemical routes changes and the ignition occurs mainly due to the chain branching reaction $\text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O}$ and the thermal decomposition of CH_3O_2 . C_2 hydrocarbons are formed at such conditions.

As already mentioned, the concept of MILD combustion may help to understand the kinetics of burning ultra-lean mixtures. In MILD combustion, the oxidation process takes place by autoignition allowing low-calorific fuels to be easily oxidised [89]. The MILD regime occurs when the mixtures increase their flammability limit under preheating conditions [37], and are characterised by longer kinetic times governed by particular reaction paths different from conventional premixed or diffusion flames [87]. The chemical kinetics

can be represented by the fast kinetics for oxidative undiluted conditions and slow kinetics for low temperature self-ignition regime [37]. An important aspect of MILD combustion, which also relates to the oxidation of highly diluted mixtures, is that combustion can only be possible after preheating the reactants [37, 38]. The heat released after the oxidation is not sufficient to self-sustain the reaction process and without preheating the reactants, the combustion process slows down until quenching. A study of MILD combustion for methane rich mixtures was initially developed by de Joannon et al. [90], but more recent publications for lean conditions have also been reported in a one-dimensional flow reactor [86, 88]. The oxidation process is influenced by the heat losses to the surroundings and therefore, the characteristics of the experimental facilities where the measurements are performed must be taken into account [87, 91, 92]. The work by Sabia et al. [87] reported some interesting reactivity behaviours for the oxidation of methane under diluted conditions in the MILD regime named: slow combustion/pyrolysis, pyrolysis, transitional combustion, dynamic behaviour, combustion and slow combustion. It showed the existence of rather different chemical pathways for methane oxidation depending on the flow conditions. Maps of reactivity behaviour for C/O mixtures under different temperature and dilution levels at atmospheric pressure were reported and analysed.

Three main chemical pathways govern the methane oxidation process: oxidation, recombination and pyrolysis. For lean conditions, the oxidation is the principal chemical pathway and is promoted by the H_2-O_2 branching reactions. The recombination channel releases radicals that enhance the system reactivity at relatively low temperatures. As the mixture temperature increases, the pyrolytic channel is activated promoting the C_2 pathway and reducing the system reactivity. At ultra-lean conditions and elevated temperatures, the combustion regime shifts to “transitional combustion” requiring longer autoignition delay times [87]. The effect of dilution and low temperature gradients not only affects the competition of different chemical pathways usually hidden by large heat release [89], but also affects the validity of the scheme due to the different activation energies of some elementary reactions outside the range that the scheme was designed for [91, 92].

2.2.3 *Effects of catalysts*

Catalytic combustion of hydrocarbon fuels has been proven to be a promising approach to oxidise ultra-lean methane mixtures by extending the flammability limits and enhancing the kinetics associated to the oxidation process [15, 16, 19]. With the presence of catalysts, reactions may take place over the surfaces of the catalysts at lower temperatures. However, there are still challenges for catalytic oxidation/combustion of ultra-lean methane mixtures. In particular, the oxidation of methane becomes somehow more complex than higher order hydrocarbon fuels, since higher hydrocarbons allow initiation reactions at lower temperatures [93, 94, 95]. The catalytic conversion process depends on both temperature and catalyst type. In general, it undergoes the following steps: (1) oxidation takes place at low temperature and is controlled by surface kinetics, (2) in the intermediate temperature range, an exponential increase in conversion rate takes place and is mass transfer controlled, and (3) a further

increase in temperature leads to the maximum conversion rate (at maximum temperature) and the gas phase homogeneous reactions contribute to the overall reaction rates.

There are many types of catalysts used for combustion applications, but noble metal catalysts (Pt, Pd, Rh or combinations) are usually preferred over metal-oxide catalyst due to their enhanced conversion properties [16, 95]. There are several comprehensive review efforts in the literature summarising the state-of-the-art in the use of catalysts to enhance methane combustion [16, 95, 96], but none of them directly address their performance on the oxidation of ultra-lean methane mixtures. While it was found that Rh catalysts are better suited for methane partial oxidation [96], Pd and Pt catalysts are more appropriate for full oxidation because of the enhanced conversion of CH_4 to CO_2 on the catalyst surface [97]. Catalytic methane combustion is still an active area of research, to the authors' knowledge; no overall agreement is found about whether Pt or Pd catalysts perform better for methane catalytic conversion. The majority of the literature and data produced for those catalysts correspond to mixtures above 1% CH_4 [98], although Pd catalysts are preferred for lean conditions [99]. A comparison of the performance of such catalysts under dry and wet conditions, as well as for fresh or steam-aged conditions can be found in the work by Abbasi et al. [98]. The work suggested that catalyst performance is largely influenced by the ambient and operating conditions, and the expected conversion rate can be compromised during long-term steady operation or wet conditions. The support material also affects the overall conversion rate of the catalysts and a review paper on Pd-based catalysts from experiments addressed this issue in detail [100]. Further studies were also dedicated to examine the effect of support materials including the temperature range and material types [101]. Several initiatives leading to improved catalytic activities have also been addressed in the literature. It was recently found that ceria (CeO_2) could be used to increase the catalytic activity of Pd ($\text{Pd@CeO}_2/\text{H-Al}_2\text{O}_3$) providing thermal stability against sintering with outstanding catalytic performance [102]. The addition of cavities and fuel segmentation in catalytic reactors has also been investigated leading to enhanced conversion rates for certain fuels under particular conditions [103, 104]. It was found that cavities could be used for flame stabilization and a means of providing heat source to enhance chemical reactions. This is particularly relevant to porous burners for ultra-lean methane oxidation/combustion. New systematic reaction class based approaches are now being used for noble metals such as Pt [105, 106] as catalysts, which can potentially enhance the effective use of catalysts for ultra-lean combustion.

Most of the contributions and knowledge obtained about the performance of catalysts for combustion applications are based on experimental studies. From theoretical/modelling points of view, there are still many open questions about how accurate and appropriate the physicochemical models of catalytic combustion can be and how the predictions can be improved for practical applications. The modelling requires accounting for the gas phase kinetic and transport phenomena as well as the interactions between the reacting gas phase in the combustor and the catalyst surface. These interactions are rather complex and involve multicomponent transport processes that are chemically and thermally dependent at the interface. While the governing equations for the gas phase are already known (consisting of

conservations of mass, species and energy, Navier-Stokes momentum equations for chemically reactive flows, as well as possible equations for turbulence models [45-47], see Eqs.(1)-(4)), the equations governing the solid phase where the catalytic conversion takes place must be described. These equations include mass and energy balances over the catalytic surface and should include heterogeneous chemical reactions, diffusion, as well as convective, conductive and radiative energy transport with the resistive heating of the catalyst and the existence of chemical source terms on the surface [107]. Since the chemical reactions take place on a porous media, the porosity must be taken into account since it influences the lifetime and real performance of the catalyst. Another important requirement for the modelling of catalytic combustion is the surface chemistry. The gas phase chemistry involved in the oxidation process of hydrocarbon fuels is better understood as discussed previously, but the elementary steps of oxidation over the catalyst surface must also be taken into account. This is a complex research topic and the literature devoted to this problem is scarce. Elementary reactions in Arrhenius form have been proposed to account for surface chemistry, but these mechanisms are largely influenced by the catalyst type, shape, concentration, support material, operating conditions among many other aspects, therefore deviations are expected to occur when these mechanisms are used for general applications.

Mechanisms of surface chemistry for methane oxidation can be found in the literature. Deutschmann et al. [107] proposed a reaction scheme for the oxidation of methane, hydrogen and oxygen over polycrystalline platinum. It consists of 23 elementary reactions with temperature independent pre-exponential factors. For palladium catalysts, a correction of 13 steps can also be used. The schemes were compared against experimental data using simplified configurations and properties as well as two-dimensional calculations. The results indicated a certain level of correlation with the experiments and encouraged developing more sophisticated models. Chemical schemes for partial oxidation on Rh [108] and Ni have been developed [109]. A full set of a surface reaction scheme for C₁-C₃ alkanes on Rh was proposed by Schwiedernoch et al. [110] and then corrected with additional C₂- C₃- species [111]. Most of these schemes were designed for partial oxidation and particular catalyst type, therefore their use for ultra-lean methane combustion applications on possibly different combustor designs suggests a low applicability and the need to develop new surface chemical schemes capable of representing to a larger extent the combustion process over the catalyst surface.

2.2.4 Reduced chemical kinetics for ultra-lean methane oxidation

The oxidation process of highly diluted methane becomes complex not only from the chemical point of view, but also from the practical point of view when it comes to modelling the combustion process in practical burners. While general reduced schemes were developed for methane combustion under conventional operation conditions, much less has been done for ultra-lean conditions. This sub-section presents an overview of simplified and reduced chemical schemes specially developed to model the oxidation process of ultra-lean methane mixtures. Technological solutions will be discussed in section 3.

As not many reduced chemical schemes have been fully validated at ultra-lean conditions, this topic still remains open and requires further research. It is arguable that developing reduced schemes for ultra-lean CH_4 oxidation/combustion is somewhat premature, considering that chemical kinetics needs to be better understood. However, some preliminary efforts have already been devoted to this. Recent work [17, 91-93] has shown that simplifications of the mechanisms for ultra-lean methane oxidation can be developed by the constraint of considering the species that are measured experimentally in the combustion products. As the species in the final state of the combustion process correspond to CO , CO_2 and H_2O (even H_2 is not present), the mechanisms can be expressed in terms of those species only. In these studies, the authors gave more importance to the environment of the oxidation process such as characteristics of the reactors, materials, temperatures and type of monoliths than the chemical kinetics in multi-stage reaction kinetics. Gosiewski et al. [92] proposed three main reaction pathways for the homogenous combustion of methane under ultra-lean conditions: parallel, consecutive and parallel-consecutive, which are represented in Fig. 2. The chemical pathways are represented in Arrhenius form without including oxygen due to the large excess of O_2 present in the lean mixtures.

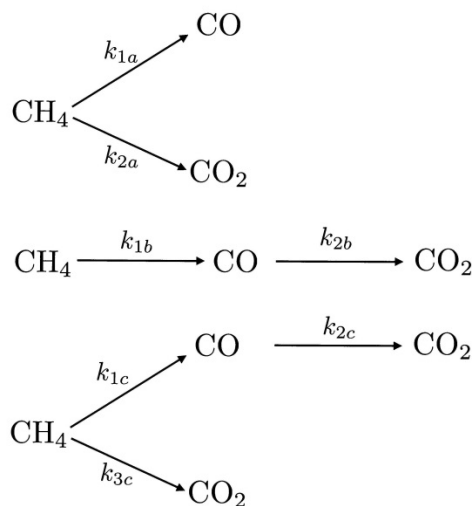


Fig. 2. Reaction pathways for the homogenous combustion of methane.

It was shown [92] that for certain temperature levels, the combustion of ultra-lean methane mixtures can be represented by a consecutive or parallel-consecutive reaction path, since CO_2 is only formed from CO at high temperatures. Kinetic reactions are determined for a free space, and type of monoliths reactors using two-stage and three-stage mechanisms. These results were consistent with the previous work by Slepterev et al. [93], in which the radical-chain termination reactions were investigated as functions of the reactor ceramic surface. In this work, two sets of reactions were proposed depending on temperature. For the low temperature range, the following two-step mechanism is proposed:



while for temperatures above 993K, the following scheme is proposed:



The work by Wang et al. [17] departed from the reaction pathways of Gosiewski et al. [92], where verification with thermal and catalytic reverse flow reactors was performed providing new reaction rates. This work also addressed effects of the ceramic beds on the ignition temperature and the stability of the combustion process. It was stated that the two-step consecutive mechanism could be considered to describe the combustion in a free reactor and with monolith under conditions of practical interest for the oxidation of ultra-lean methane mixtures. Abbasi et al. [98] also proposed reduced schemes for Pt and Pt-Pd catalysts including inhibition effect of water. Pt catalysts were modelled using an empirical power-law expression with orders one and zero for methane and water respectively. Stem-aged effects on Pt catalysts were found to be rather small and only small corrections on the pre-exponential factor and activation energy were required. The reaction kinetics for Pt-Pd required a more complex expression due to the sensitivity of the catalyst to water, so a Langmuir-Hinshelwood-Hougen-Watson type of rate equation was proposed.

Catalysts have been proven to be effective in extending the flammability limit for ultra-lean CH₄ oxidation/combustion. The presence of catalysts can change the chemical pathways. Fig. 3 shows an overall chemical mechanism for methane catalytic oxidation [16]. Relatively simple mechanisms like this are obviously advantageous in numerical simulations of combustion in large-scale industrial applications due to reduced computational costs associated with the simplified chemistry. However, the validity of such mechanisms depends on the relevant conditions including the detailed chemical pathways and the thermodynamic parameters of the reactions considered in the mechanism development.

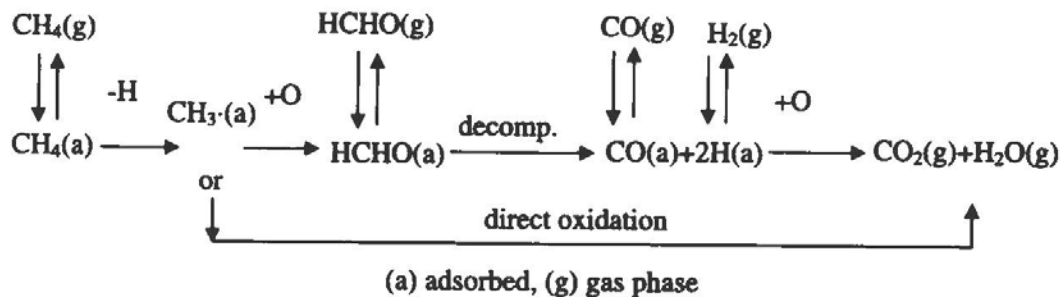


Fig. 3. A possible chemical mechanism for methane catalytic oxidation [16].

2.3 Development of chemical kinetic schemes

Development of the chemical kinetic scheme is an essential element for the modelling and simulation of ultra-lean methane oxidation/combustion. In chemical kinetics, the chemical pathways and the reaction rates dictate whether a specific reaction will take place or not, a new species will be observed or not, and how fast a species will be generated or destroyed for

the given conditions. Chemical pathways and reaction rates are not only influenced by local compositions, but also by environmental conditions such as pressure, temperature and heterogeneities. The presence of a plasma source or a catalyst also affects the chemical kinetics. Reaction rates strongly depend on concentrations of the reactants in most chemical reactions for combustion applications, which are also influenced by third-body reactions. Chemical schemes are currently developed for rich and lean conditions within the flammability limits of the mixtures, but are not adequately developed to describe the chemistry for unconventional conditions such as combustion under ultra-lean conditions. In this case, the chemical pathways might be different and new adjustments on the reaction rates will be required to account for the low concentration of the fuel. For industrial applications, the use of detailed schemes in advanced numerical simulations can become prohibitive when finite-rate chemistry approaches are used. Even with the massive increase in supercomputing power in the last decades, solving hundreds of species and reactions in CFD simulations such as LES of turbulent flames is still a challenge. Therefore, the development of skeletal and low-order reduced chemical schemes is essential to apply these simulations to practical systems operating with ultra-lean mixtures. However, understandings on detailed chemical pathways and reaction rates are the prerequisites for the development of these mechanisms. In the following, developments of chemical kinetic schemes for ultra-lean methane oxidation/combustion are briefly discussed.

Chemical kinetic schemes usually include information on chemical pathways or channels and reaction rates. For reaction rates, the influencing factors include the nature of the reactants and products, concentration of reacting species, temperature, as well as external agents such as catalysts. For ultra-lean methane oxidation, the individual steps in the mechanism are important as the mixture may not be able to ignite and the oxidation may not be sustainable. In chemical kinetics, the stoichiometric equation is the net results of any number of intermediate steps, where key information on the individual steps in the mechanism might have been lost. At ultra-lean conditions, an overall stoichiometric equation is unable to reveal the key stages in the reaction when the ignition and flame propagation with combustion instability are investigated. Fundamental studies are needed to understand the chemical kinetics for this extreme condition.

Although the chemistry of CH_4 oxidation/combustion is relatively well known at rich conditions, little is known about it at extremely diluted conditions. So far there is not a well-established detailed mechanism available for ultra-lean mixtures under ambient pressure conditions, nor skeletal/reduced mechanisms. Therefore there is a need to develop these schemes. The determination of parameters corresponding to the chemical reality is a complex task. Traditionally, it has been achieved in three different ways [112].

- 1) By designing experiments isolating some reactions in such a way that the model variables corresponding to the measurements can be expressed analytically as a function of parameters of interest. The optimal values can then be identified mathematically through a least-squares regression. For the understanding of chemical kinetics at ultra-lean conditions, well-designed experiments will be indispensable.

- 2) By using methods from theoretical chemistry such as density functional theory calculations coupled with transition state theory (TST). Depending on the involved assumptions and simplifications, some methods, especially semi-empirical techniques, can lead to great uncertainties with respect to the evaluated parameters.
- 3) By analogy with similar reactions with known rate coefficients. An unknown uncertainty is also introduced by this approach.

The elaboration of an accurate predictive reaction mechanism must surmount two major challenges: the detailed reaction mechanisms composed of numerous elementary reactions and the estimation of the kinetic and thermodynamic parameters of these elementary reactions. One fundamental approach to examine chemical kinetic mechanisms is to obtain insights from quantum mechanics, to explain the behaviour of matter and its interactions with energy on the scale of atoms and subatomic particles. In recent years, *ab initio* quantum chemical computations have been used in understanding the chemical kinetics of combustion [113]. In principle, quantum mechanical methods combined with chemical kinetic theory can provide accurate information on transition states and reaction rate constants for individual elementary reaction. However, these computational methods can be prohibitively expensive in providing detailed dynamical descriptions of complex oxidation reactions taking into account the effects of temperature and pressure on the reaction paths. For the foreseeable future, quantum chemistry is only expected to play a limited supporting role in the development of chemical kinetic schemes for very simple cases.

Molecular dynamics (MD) methods numerically simulate the physical movements of atoms and molecules, which are allowed to interact for a fixed period of time. In a MD simulation, the trajectories of atoms and molecules are usually determined by numerically solving Newton's equations of motion for a system of interacting particles. Forces between the particles and their potential energies are calculated using interatomic potentials or molecular mechanics force fields, so the results will give a view of the dynamical evolution of the system. However, conventional MD methods using the force fields with rigid connectivity cannot describe bond breaking, bond formation and chemical reactivity [114]. In order to overcome the deficiencies of conventional MD simulations and to retain nearly the accuracy of quantum mechanical calculations, reactive force field [115] was developed, but the application has been limited. Recently, a methodology for deducing quantitative reaction models from reactive molecular dynamics simulations by identifying, quantifying, and evaluating elementary reactions of classical trajectories was proposed [116]. In addition, a simple protocol allowing fully automated discovery of elementary chemical reaction steps was developed and applied to several single-molecule systems of combustion [117]. Nevertheless, the predictive tools need significant developments before they can be used for practical combustion applications since they currently cannot be easily used to predict reaction pathways and thermodynamic properties of multiple reaction steps under practical conditions including premixed combustion of methane at ultra-lean conditions.

Although improvements on theoretical kinetics and quantum chemistry have made fundamental theory an indispensable partner in reaction kinetics [113], chemical kinetic

schemes cannot be predicted at the fundamental level without empiricisms and simplifications at the present time. New experimental techniques are increasingly employed to investigate the fundamental reactions underlying oxidation/combustion in great details. For ultra-lean methane oxidation/combustion, quantum chemical computations and MD simulations may provide a useful tool in understanding the fundamentals of kinetics under highly diluted condition. However, the currently available theoretical/computational tools are not entirely deterministic and the computations can be far too expensive for the developments of chemical kinetic schemes. For the development of chemical kinetic schemes for ultra-lean CH₄ mixtures, concerted efforts from both experimentalists and modellers are called for.

Inevitably, uncertainties exist in developing chemical kinetic schemes for combustion applications due to the empiricisms and limitations/assumptions embedded in the available tools. To analyse the uncertainties in these schemes, uncertainty quantification (UQ) which tries to determine how likely certain outcomes are if some aspects of the system are not exactly known, is becoming increasingly important. The uncertainty quantification, propagation and minimization for the combustion kinetic models were recently systematically reviewed by Wang and Sheen [118], which detailed the sources of uncertainties and provided a classification for them. The application of UQ in highly complex, multi-parameter combustion chemistry problems has to be considered and treated as an integral part of the combustion chemistry development. When UQ is applied to combustion chemical kinetics, the main methods related to model and parameter evaluation employ probability-based approaches [112]. The standard sensitivity analysis for chemical kinetic schemes can be regarded as a consideration of UQ, which can aid the development of predictive kinetic models in different ways when treated as a Bayesian inference problem [118]. UQ is playing an increasingly important role in the development of chemical kinetic schemes, which is also essential for the development of the much needed chemical kinetic schemes for ultra-lean CH₄ oxidation/combustion.

Development of chemical kinetic schemes for ultra-lean CH₄ oxidation/combustion can be achieved through a combination of fundamental studies of reaction rates through well-defined and purposely designed experiments, ab initio theoretical calculations, and of analyses of global experimental measurements. These studies also need to be supplemented by UQ analyses, so that a measurable progress can be made over time. Catalytic oxidation is certainly a promising direction, where chemical mechanism for methane catalytic oxidation/combustion was developed [119] as shown in Fig. 3. However, further investigations are needed not only to assess the existing mechanisms, but also to develop schemes for new operating conditions such as different catalysts and different pressure and temperature conditions.

In computational modelling and numerical simulation of turbulent combustion, the chemical kinetic schemes are coupled with turbulent combustion modelling. Chemistry based on tabulation, e.g. [42, 120, 121], can provide significant reduction in computational costs. Recently, a turbulent combustion model was proposed [121] that extended a tabulated chemistry model to account for product gas dilution and heat-loss effects by introducing

simplified assumptions to reduce the model complexity. The turbulent closure model developed was based on a presumed PDF method to account for turbulence-chemistry coupling. The approach extended the flamelet/progress variable formulation by including information about the intensity of internal dilution rates and heat losses. In LES of ultra-lean combustion, the modelling ability in dealing with extinction and re-ignition is of great significance when one chooses the SGS models. In this regard, models such as the linear-eddy model (LEM), or the so-called one-dimensional turbulence (ODT) model [122], may be advantageous. Due to their formulations, the LEM or ODT type of SGS model has particular strengths in dealing with extinction and re-ignition problems, e.g. [123-126]. In this modelling concept, explicit distinction exists between molecular diffusion, turbulent advection (stirring), and chemical reaction, while all spatial and temporal scales are resolved down to the smallest turbulence scales for the transport of chemical species and the one-dimensional formulation makes small-scale resolution computationally affordable. Modelling/simulation of ultra-lean CH₄ combustion can benefit from developments in turbulent combustion modelling of other related applications, while the development of chemical kinetic schemes for ultra-lean conditions represents a unique challenge.

3 Technological challenges and perspectives

The technological challenges of combustion mitigation of ultra-lean CH₄ are significant, mainly because understanding on many of the scientific issues requires improvement. For example, plasma-assisted combustion is a promising technology to enhance low temperature fuel oxidation and processing, increase lean-burn flame stability and reduce emissions, but the area needs further investigation. Technical development of effective plasma discharges is still needed for operations in conventional combustion systems [25, 26]. For ultra-lean methane mitigation, tailor-made experimentations are essential to the development of the technology. To achieve effective combustion mitigation of ultra-lean CH₄, there are a number of important aspects. Firstly, the combustion of ultra-lean methane is highly sensitive to variations in concentration due to the previously described reaction sustainability issues; therefore, a combustion mitigation system has to be flexible in dealing with CH₄ concentration variations, as the CH₄ concentration often changes from case to case and also changes with the operating conditions for the same case [15]. A robust system must also be resistant to fuel variability. Secondly, contamination in the fuel stream can be important to the ignition and subsequent oxidation/combustion, where particulate matter and trace gases may have a detrimental effect on the catalysts or may even quench the process. Furthermore, the technology has to be cost-effective as a means of GHG mitigation with a view toward energy utilisation.

Among the possible technologies for combustion mitigation, a prominent common feature is recuperative combustion, where system heat and mass (often in the form of exhaust gas) are recirculated to improve the initial temperature for chemical reactions. The concept of recuperative combustion is not new, which is similar to the term “excess enthalpy combustion (EEC)” [127, 128], but the technology very much depends on the specific application involving optimisation for it to be effective. The starting point for the design of a system

using recuperative combustion or EEC is simply heat and mass balance equations. For practical applications, design optimisation is essential but it can be challenging as there are many interacting thermodynamic and chemical parameters involved. Flow and combustion control is the key to optimise ignition and sustain oxidation/combustion. Ideally the heat flow needs to be controlled as a function of the methane concentration. For low methane concentrations more heat is required to raise the temperature to the sustainable oxidation/combustion regime and as the methane concentration increases less heat is required because a lower temperature is needed for ignition and to maintain a sustainable reaction. In addition, combination of plasma ignition or catalysts with recuperative combustion may provide the best possible solution. However, there is currently a lack of study on these important technical issues.

Currently technologies that can be used for ultra-lean methane mitigation and utilization are not well established in general because of a wide range of technological issues. For ultra-lean methane oxidation/combustion, there has not been a full understanding on key aspects of reaction behaviour including ignition delay times and oxidation times as functions of working conditions such as concentration, temperature, pressure ranges of the mixture. This section discusses the technical aspects of ultra-lean CH₄ mitigation, where the focus is on one specific application only - VAM mitigation. Underground coal mining is a significant source of fugitive methane emissions, and most of coal mining related methane is emitted to the atmosphere through mine ventilation as VAM [129]. There is a certain uniqueness to mining operations that obviates the necessity of a technology with the flexibility of design to meet the requirements of a given mining project. Although the technology is only discussed for VAM in this section, some of the technical issues can be of general nature. Mitigation of CH₄ from gas and oil explorations may benefit from the technology for VAM mitigation. As the subject was reviewed by Su et al. [15] more than a decade ago, this section is mainly focussed on the recent development of the technology including some applications. In the following, VAM mitigation technical obstacles are discussed first, followed by overviews of primary fuel systems for VAM mitigation and ancillary use of low concentration methane.

3.1 VAM mitigation technical obstacles

VAM is a particularly intractable technological problem due to the low concentration of methane contained, infrequently near 2%, but typically 0.1% to 1%, within a high flow rate of ventilation air typically 100 m³/s to 300 m³/s [129, 130]. The variability of the methane concentration contained within the ventilation air flow presents operational and engineering challenges. Not only does the concentration vary due to operational changes such as conditions at the surface or variations in the methane concentration of the coal, but also is affected by the pressure at depth, the variations in atmospheric pressure and the presence of various other trace gases and particulate matters.

The methane contained in coal increases with both the depth and age of the coal seam [131]. The in-situ pressure increases with depth which reduces the permeability while

increasing the pore pressure. Under these conditions the methane is tightly bound to the coal and surrounding rock strata. Underground mining emits greater levels of methane than surface mining and deeper mines release more methane as the coal is crushed, consequently underground mines account for nearly 90% of methane emissions from the coal sector. As the depth increases, the air pressure at depth and the air density also increase with a corresponding increase of the pore pressure exerted on the coal surfaces exposed; however, this depth effect leads to an increase in the ability of the coal to contain methane, which results in higher concentrations of methane released as the depth of the mine increases.

Particulate matters and trace gases pose a potential issue in combustion or oxidation based mitigation systems due to the possibility of contamination of catalysts or quenching of the process [129, 130]. Depending on the concentrations, which are subject to variations, the chemical constituents of the flow can have a deleterious effect on the equipment or components. A recent study of the constituents of mine ventilation air was undertaken to provide an understanding of the potential effects on combustion based or catalytic oxidation systems. Using optical and scanning electron microscopy, energy dispersive X-ray analysis and micro gas chromatography to determine the particle morphology, mineral content and gas concentrations respectively, it was found that at an Australian mine with a methane concentration of about 1%, the CO₂, H₂S and SO₂ were all less than 1 ppm and the particulate matter ranged from 0.13 mg/m³ to 4.47 mg/m³ depending on the production activity in the mine [129]. Putting these values in the context of a typical flow rate of 300 m³/s to provide an engineering perspective, the range of particulate mass flow is 140 g/hr to 4800 g/hr. Considering the variability of particulate matter loading and that the particle size is in the 1 µm to 5 µm (which are very small and fall in the respirable particle range), as the particle size gets smaller the more difficult and expensive the filtration process becomes. Particulates of this size and the large flow rates present operational difficulties for processes that involve sensitive or exotic materials such as those used in catalytic, adsorptive and absorptive processes.

The low concentration of VAM leads to major difficulties in its mitigation. An effective mitigation strategy would be increasing its concentration. Concentrating the methane can be accomplished by membrane separation, absorption or adsorption. The engineering applications of membrane separation concepts have been considered as early as 1980 [132] when continuous membrane columns were studied as a means of methane enrichment. Membranes or nano-membranes are not currently viable as a means of separating a low methane concentration from the ventilation flows. Future development may provide commercially viable membrane separation systems, but presently the high costs of initial capital investment and membrane maintenance or replacement due to fouling are prohibitive.

Pressure swing adsorption (PSA) is a technology used to separate some gas species from a mixture of gases under pressure according to the molecular characteristics of the species and affinity for an adsorbent material. Since there are different affinities of gases for dissimilar surfaces, it is possible to separate a combination of gases by using different materials [24]. PSA is more effective for higher concentration methane flows such as mine methane gas,

which can typically be 50 % to 60% methane. A study of PSA showed that a 55.2 vol% methane concentration was enriched to 96–98 vol% methane [133]. Although the methane recovery efficiency reached 86–91%, the process is not yet available for low concentration high volumetric flow situations such as VAM. PSA may ultimately be less expensive than membrane technology; thus, a more attractive solution in future. The operational principles of adsorption require a flow of gas through vessels, which is difficult to accomplish at large diameters, but long reactors produce a significant pressure drop [15]. A petroleum pitch based honeycomb monolithic carbon fibre composite adsorbent [134] demonstrated a methane adsorption capacity, which corresponds to a micro-pore width of 2.14 nm, the optimum pore width generally considered to be ideal for methane adsorption [135].

Combustion based mitigation systems generally follow design imperatives that are balanced in terms of the fuel air ratios and the inlets are filtered to prevent extraneous particulates from entering the combustion chamber. Variations in fuel concentrations, particulate matter or various peripheral gaseous additions are not well tolerated in delicate systems, but do not present significant difficulties to large and rugged systems such as large diesel engines, power plants or rotary kilns.

Presently the availability of technology, combustion based or otherwise, to mitigate methane at the very low, but ubiquitous levels below 0.5%, without the use of an additional fuel is non-existent; thus, a forward focus on such technology would be of great benefit to the industry and provide a significant impact on the GHG emissions on a global scale [136]. There are two classes of combustion based systems in operation at present where the VAM is either used as a primary or secondary fuel. Other methods of methane mitigation that are not combustion based include biological action, concentration techniques and nano-membrane technology.

When VAM is the primary fuel in systems such as lean-burn or recuperative gas turbines, thermal or catalytic flow reversal reactors and regenerative thermal oxidation, the VAM is the only required fuel except in cases where the systems requires start-up energy or the methane concentration falls below the design specifications [7, 136]. When VAM is used as a secondary fuel a portion of the designed intake air is replaced with the air containing the VAM. The fuel value of the additional flow containing methane allows for a reduction of the fuel that would normally be injected, according to the design specifications of the device. This approach is employed more often in internal combustion engines due to the flexibility available with regard to locating the engines within proximity to the source of VAM. In the case of other systems, there are drawbacks such as the delicate operational aspects of the gas turbine or proximity issues with rotary kilns or coal fired power stations. There are often sources of methane at a much higher concentration such as drained sources. These are typically high concentration low volume sources and can be used to supplement the VAM flow to a higher methane concentration, making it easier to be used, such as being flared or sold to market if the quality of the gas is sufficient [7, 15].

One important issue for technological developments is the costing, which decides whether the technology can be commercially deployed. It was stated that the implementation of the methane mitigation plants is not economic without a carbon credit [15], where the major capital costs of established technologies including TFFR, CFFR and CMR were summarised. The recent developments have not led to significant drops in the costs as some of the technical elements such as the use of catalysts remains expensive. For the porous burner technology, there is still a lack of preliminary economic analysis. Costing is also an issue for many other mitigation/utilisation technologies. For example, concentrators to enrich methane levels to meet the requirements of a specific technology can be very useful if the costs can be further reduced.

3.2 Primary fuel systems for VAM mitigation

Principal uses of VAM involve combustion of the methane in ventilation air as a primary fuel. It should be noted that the definition of “primary fuel” is not exact for some technologies depending on the CH₄ concentration in air and the minimum CH₄ concentration for the operational requirement, particularly where a lot of supplementary high quality fuel is required when recovering energy to generate power. The operational mechanism of the technology can be thermal, catalytic and concentrating [15]. In practical applications, the system often employs the flow reversal principle to transfer methane’s heat of combustion, first to a solid medium, and then back to incoming air to raise its temperature to the ignition temperature of CH₄. The use of a catalyst can distinguish a specific technology with others. In the last decade, there have been a number of practical systems designed to burn VAM as a primary fuel. As the industrial designs always have commercial implications, not all the details are available. Therefore we only present some technical overviews of selected systems. Some examples on these practical systems will be mentioned.

The VAM RAB project (<http://www.corkys.net.au/vam-rab/>; accessed on 5 May 2016) in Australia exploits the principles of thermal oxidation. In 2011 some experimental work using a 1/40 pilot-scale system was performed to verify the safety aspects of the system at Centennial Coal’s Bloomfield operations. The scale of this demonstration project is a 1 m³/s flow rate with a design parameter to oxidise methane concentrations in the range of 0.35 to 1.1 %. The safety tests allowed the methane concentration in the 5% to 12% range, to simulate extreme conditions with a successful outcome. The VAM RAB is currently in the pre-commercial phase, but the scale-up designs are being prepared and discussions pertaining to a full-scale plant are ongoing. The principle of operation exploits a regenerative heat exchange between a gas flow and a stationary solid, with pore flow characteristics in the reaction zone. There are a few steps in the operation of the TFRR, the first is that the ventilation air enters one side, deposits combustion energy in the bed and exits the other side. At start up or at low fuel concentrations there is a need for additional fuel or heat, as the heat builds up the reaction becomes stable, requiring no additional fuel or heat. The heat in the bed will follow the flow; therefore, moves toward the exit of the reactor. This effect is countered

by reversing the flow at the appropriate time to keep the heat contained within the bed. One complete cycle is comprised of one flow reversal in each direction; thus, the flow is proceeding in the original direction after one cycle. Computer models are available to determine the optimal time of flow reversal, a time interval determined by the temperature profile, which are primarily used to design the systems for specific sites [19]. Since the flow direction reverses by the operation of valves, which are the main moving parts of the system, the system is a robust piece of equipment requiring minimal maintenance over the lifetime of operation.

In the United Kingdom, MEGTEC initially developed systems for the mitigation of volatile organic compounds. The MEGTEC VOCSIDIZER™ technology (http://www.megtec.com/documents/UK_Vocsidizer.pdf; accessed on 5 May 2016) is a regenerative thermal oxidiser and can supply a superheated steam or produce electricity using an ordinary steam turbine. The first testing of the VOCSIDIZER™ using methane was at the Thoresby Mine in 1994 in the UK. The positive results of that pilot plant verified the VOCSIDIZER™'s capability, which underwent a continuous methane oxidation reaction with a low susceptibility to the variations typical of methane in ventilation air. The first commercial installation of the VOCSIDIZER™ was at the Appin Colliery in Australia in 2001 - 2002, where heat recovery was demonstrated by the generation of steam for 12 months. In 2007 the Westvamp project began operation at 70 m³/s using CH₄ concentration maintained at 0.9% to produce power by driving steam through a 6 MWe turbine. The supplementation of the incoming ventilation air is possible by the addition of coal mine methane (CMM), the higher concentration methane taken from the mine by draining the coal seam. Although this is a convenient use of the CMM, this product is not always available and not necessarily inexpensive to acquire, which may lead to the need for an external fuel source should the system design be dependent on the CMM and supply is either exhausted or drainage is no longer required. The confidence generated by the trials has instigated the installation of a turnkey system for the Zhengzhou Coal Mining Group, Henan Province in China, which provides hot water from methane concentrations of 0.3 % to 0.7% at a flow rate 18 m³/s. MEGTEC now has over 800 VOCSIDIZER™ systems globally with many of them operating on methane. The regenerative thermal oxidiser is a proven technology for using VAM as a primary fuel with the capacity to produce various thermal products such as electricity or hot water, the efficiency of the system relies on the principles of flameless oxidation and a recirculation of heat from the combustion zone to pre-heat the incoming process air to oxidation temperatures.

A project underway at the Dafosi coal mine in China (<https://cdm.unfccc.int/Projects/DB/TUEV-SUED1236267273.45/view>; accessed on 5 May 2016) has demonstrated the use of both CMM and VAM combined together improved the operational stability by maintaining the methane concentration of the incoming fuel at 0.25% or greater. A preheating stage of 36 hrs is needed for the TFRR to become stably operating without any further fuel or heat additions. Electricity generation, by production of steam to drive a steam turbine, was possible only for the methane concentrations above 0.6% and the

thermal efficiency varied from 31.61% to 46.82%. The current power plant began operating in August 2012, at a capacity 83.3 m³/s (maintained at 0.9%-1.1% CH₄) to produce 1.2 MPa at 280 °C, which provides 4.5 MWe.

There are technologies based on using catalysts. The VAMCAT developed at Commonwealth Scientific and Industrial Research Organization (CSIRO) is a lean-burn catalytic gas turbine (<http://www.csiro.au/en/Research/EF/Areas/Coal-mining/Mining-safety-and-automation/VAMCAT>; accessed on 5 May 2016), which can operate at a methane concentration as low as 0.8%, but is designed for operation at 1% methane. The VAMCAT is comprised of a compressor, a catalytic combustor, a turbine and a recuperator. The thermal efficiency of a generic gas turbine system can be improved significantly if exhaust gas heat is recovered. The exhaust heat may be used for preheating the compressed air containing methane to improve the energy conversion efficiency. The VAMCAT uses a palladium catalyst supported on γ -alumina substrate, which has a maximum continuous service temperature of 850 °C [137]. The catalytic combustion gas turbine system oxidises methane while generating 25kWe electricity [138]. A power generator demonstration for the Huainan Coal Mining Group, China was undertaken in 2011. At the fuel concentration of 0.8%, the production of 25kWe of electrical power would require a gas flow of 0.25 m³/s to 0.3 m³/s; thus, for a VAM flow of 300 m³/s about 1200 VAMCAT™ units would be required to accommodate a single typical ventilation shaft. Although the catalytic technology for a gas turbine allows for lean fuel air mixtures it would not be cost-effective or practical to consider the use of such a large number of units to accommodate the flow from a typical mine; therefore, this technology is considered as conceptual and pre-commercial. A 1 MW design was reported to be in progress [138], but has not yet been completed. Should a 1 MW unit become available the supply air flow rate required would be much higher, which would reduce the number of units required to a more manageable number.

There is a catalytic combustion gas turbine system that operates on VAM supplemented by CMM, to produce a methane concentration approximately 2% [139]. The system is comprised of an electrical generator that uses the VAM, supplemented by CMM as fuel, and a VAM oxidation unit. The electrical generator is a regenerative gas turbine with a catalytic combustor, duct burner and power converter. The VAM is compressed and heated to about 430 °C in the recuperator, which increases the temperature sufficiently for oxidation by the catalyst combustor. In the VAM oxidation unit, VAM is heated to 280 °C by taking heat from gas turbine exhaust, which is then mixed into the gas turbine exhaust gas and conveyed to a catalyst layer for conversion to carbon dioxide. The catalytic combustion gas turbine generates 1 MWe for a 0.5% methane concentration VAM consumption of 6.4 m³/s. There are 1.2 MW of energy available for a 0.5% methane concentration, using 55 MJ/kg and a flow of 6.4 m³/s, but since the VAM is supplemented up to 2% the energy available is 4.8 MW so the electrical power generation efficiency is about 20%.

Catalytic thermal reverse reactors operate on similar principles as the TFRR but the addition of catalysts reduces the temperature at which oxidation occurs. There are many catalysts available; a partial list of common catalysts is Pd/Al₂O₃, Sr_{0.8}La_{0.2}MnAl₁₁O₁₉,

Pt/Al₂O₃, Co₃O₄, La_{0.5}Sr_{0.5}CoO₃, Cu/La/Al₂O₃, and LaCoO₃ which are characterised by their methane oxidation rate at atmospheric pressure for a given methane concentration at a given temperature. Note the expensive and exotic nature of the catalysts such as palladium, platinum or rare earth elements like lanthanum coupled with a high surface area oxide. The problem is that as the concentration of methane in ventilation air increases the heat generated also increases and for methane concentrations exceeding 1% even heat removal may be insufficient to protect the catalyst from degradation or destruction. Manganese is one of the least expensive catalyst metals, but the temperature of the catalyst bed can surpass 900 °C for methane concentrations over 0.8%, which is sufficiently high to cause the catalyst to undergo rapid destruction. Resorting to an expensive palladium catalyst to keep the temperature lower by about 100 °C also results in lower heat recovery and the cost of the palladium catalyst leads to a payback period of almost 7 years for an industrial plant [140]. The CH₄MIN employs a catalytic thermal oxidation process (https://www.globalmethane.org/documents/events_coal_120904_megtec.pdf; accessed on 5 May 2016), developed by CANMET, a Canadian government energy research organization that is part of Natural Resources Canada. It provides a great potential for the use of VAM as a principal fuel source because the technology is able to oxidise diluted methane in coal mine ventilation air and produce useable energy from heat exchangers operating at an optimal temperature.

Similar to TFRR, the CFRR technology requires a minimum methane concentration to maintain the reaction, which is more expensive from the point of initial capital expenditure and the potential need for replacement of the catalysts, either due to wear or fouling. There are three basic types of CFRR fluidized bed, packed bed and honeycomb monolith. The packed bed is comprised of ceramic beads coated with a catalyst; thus, only differs from packed bed TFRR by the addition of the catalyst, the introduction of a significant pressure drop is a drawback as an additional fan must be used to supply the energy to move the air through the reactor [7]. This extra electricity is in addition to supplemental fuel needed should the methane concentration fall below 0.4% to 0.45% or the temperature fall below the reduced autoignition temperature, typically 400 °C to 450 °C; thus, an extra expense and reduced efficiency compared to a TFRR. The fluidised bed introduced somewhat less of a pressure drop, but the flow must be high enough to entrain the beads in the flow in order to maintain the fluidisation. Monolith catalytic reactors are the most promising due to the strength inherent in the structure and the substantially reduced pressure drop [16]. It has been argued that a cut-off of 0.4% is the decision point that determines when a TFRR or CFRR is selected as the appropriate system [141]. Since the CFRR requires a methane concentration of at least 0.4% to maintain an auto-thermal reaction and the catalysts are prone to degradation or destruction at methane concentrations above 0.8% the TFRR is the reverse flow reactor of choice for both the high and low methane concentration extremes. Both the CFRR and TFRR are capable in the intermediate range, where other factors such as heat exchanger design, character of the ventilation flow in terms of contaminants and the desired operational temperatures become the influencing parameters.

Although there are a variety of industrial designs which can be quite different, the technological challenge of VAM mitigation remains the same – exploring the thermodynamic/aerodynamic limits, including minimising heat losses from the system, maximising fuel-air mixing for oxidation, and optimising the initial energy level to initiate the oxidation, so that the ultra-lean mixtures can be ignited, and once ignited, the oxidation/combustion will be sustainable.

3.3 Ancillary use of low concentration methane

Due to the low methane concentration, VAM can be used as part of the supply air for almost any combustion process. This is the ancillary use of low concentration methane. As mature technologies for energy conversion, both internal combustion engines and gas turbines can be used for this application. Internal combustion engines only require a medium quality gas, so they are an appropriate choice for using ambient air containing VAM to support the combustion processes. Diesel engines are routinely used to provide electricity to mines in remote locations and mining companies are well informed as to the capital costs and operating costs of these power plants, which can also be used to reduce the VAM emissions provided the installation is designed to avoid costs associated with transportation of the VAM [7]. The Appin Colliery in Australia is a significant and illustrative project, where 54 internal combustion engines power an electricity generation project in New South Wales and an additional 40 at the Tower location provide a total of 97 MWe from 94 Caterpillar 3516LE generators. The VAM and all the drained gas from the mine is used as a supplemental fuel, which contributes from four to ten percent of the required engine fuel while using about twenty percent of the ventilation discharged from the mine [15]. The total output is 654 GWe each year.

A gas turbine can be situated within reasonable proximity of the exhaust easé of the ventilation system fan enabling ventilation air to be drawn by the intake of the turbine to use the VAM as combustion air. Large gas turbines are required as a large supply of air has to be dealt with when attempting to use the mine ventilation as an air supply with a supplemental fuel. A typical simple gas turbine cycle requires about $0.003 \text{ m}^3/\text{s-kW}$, so a 10 MW turbine would need about $30 \text{ m}^3/\text{s}$ and the test case that employed a 2.5 MW Solar Centaur turbine, modified to accept an inlet air flow with 1.6% methane content would require about $7.5 \text{ m}^3/\text{s}$. As a test case the trials were suspended because of technical challenges pertaining to the operation of the gas turbine operation, the gas turbine suffered a failure to start suspected to be on account of the variations in composition of the inlet air. The failure of the trials is an indication of the difficulties involved with using sensitive equipment in conjunction with mine ventilation air and the requirement that typically $300 \text{ m}^3/\text{s}$ would need to be used suggests that about 40 2.5 MW turbines. Instead only two 50 MW turbines would be required to fully utilise the ventilation air. It is possible that the larger systems may be less susceptible to the contaminants in the mine air as considerable research has been undertaken by the

aviation industry to provide gas turbines that are capable of continuing operation upon encountering volcanic dust or flocks of birds.

Microturbine technology can also be employed for the ancillary use of low concentration methane. A FlexEnergy Microturbine, fitted with a catalytic combustor capable of operating on a wide range of fuels has been used for VAM mitigation (http://www3.epa.gov/cmop/docs/vam_technologies-12-2010.pdf; accessed on 5 May 2016). It was expected to achieve full power at a 1.5% methane concentration. The compressor-combustor is a compact module contained within turbine where hot compressed gases expand in the turbine to power the generator. The FlexEnergy turbine has been installed at the DCOR oil field near Santa Barbara, California, to consume oil field gas at concentrations ranging from 1.5 to 4.2 percent, and another is running on coal process waste gas at the Western Research Institute in Laramie, Wyoming.

Ventilation air used as part or all of the input air for a power station provides the required oxygen and the methane is oxidised readily by interaction with a high temperature combustion process. It may be used in power stations if VAM was appropriate as part of the required combustion airflow. The main difficulty with this concept is that the plant and the mine be located within reasonable distances to limit transportation issues so the possibilities are limited. The CSIRO has supported the research to design and build a 1.2 MW rotary kiln system that uses waste coal and VAM, burned in a rotating kiln, to generate electricity via an externally fired steam turbine system [142]. There are certainly technical potentials to use VAM for stationary power generation.

There are other technologies for the ancillary use of low concentration methane, e.g. fluidised bed. The essential description of a fluidised bed is that an upward flow suspends solids to create a turbulent mixing of any gases and solids that are contained or introduced. Using a fluidised bed with VAM would either involve a heat capturing solid, as in the design of TFRR and CFRR, capable of withstanding the ignition temperature of the methane combined with whatever fuel is also introduced. There are opportunities to reduce the pollutants by the addition of as limestone or dolomite to absorb sulphur compounds. The fuel can also be a solid that burns and ablates as the fuel is consumed. Numerous power plants currently burn unprocessed waste coal as long as the calorific value is 7 MJ/kg or higher when the minimum criterion for boilers is met [15]. The main issue with a fluidised bed is that it has been designed for purpose, which may not have included the inclusion of a premixed fuel as the inlet air, so the need for the system to at least operate at a minimum temperature capable of fully oxidising the methane is critical.

The potentials of technology development for the ancillary use of low concentration methane are substantial, as the thermodynamic/aerodynamic limits have not been fully explored. The burner design also needs to be optimised. The VamTurBurner© is a recently proposed methane mitigation system [130, 136] for the mitigation of VAM. The principles of flameless combustion for lean premixed fuels are exploited, such that a lean fuel air mixture will ignite and undergo flameless combustion in the presence of an ignition source given an

initial temperature that is reasonably close to the ignition temperature. The temperature of the ventilation air is elevated to a value that, depending on the concentration of methane, will undergo flameless combustion. Recirculating heat from the combustion either by a heat exchanger or mixing the combustion products increases the temperature of ventilation airflow in a similar manner as the regenerative thermal oxidiser. The preheated ventilation air stream is conditioned to ignite with very little further increase in temperature upon encountering the igniters to undergo flameless combustion and the heat generated by the ignition of the premixed fuel supports continued ignition. This system provides some flexibility in dealing with CH₄ concentration variability. The recirculation heat flow was intended to be controlled as a function of the methane concentration. At higher methane concentrations less recirculation heat is required so more energy is available as the high temperature gas transfers heat through exchange systems to produce steam to generate electricity and further energy transfer systems may create thermal products such as hot water.

As can be surmised from the technology review, the concept of ultra-lean combustion is at the foundation of the limitations of these technologies. By gaining a deeper understanding of ultra-lean methane combustion the opportunity for technological advancements for the mitigation of vast sources of methane becomes closer to a reality. Further to that the potential for energy capture from these new systems provides an added benefit and a potential cost reduction mechanism.

4 Concluding remarks

Although the largest source of anthropogenic greenhouse gas emissions is CO₂ from fossil fuel combustion, non-CO₂ sources are also important to the overall GHG impact [1, 11]. The two major non-CO₂ GHGs are methane and nitrous oxide. For N₂O, the co-existence of multi-sources including anthropogenic and natural sources makes the inventory estimates rather challenging. The atmospheric concentrations of N₂O is also affected by activities such as fossil fuel combustion, industrial processes, biomass burning and waste management release, but they are not the largest sources of N₂O emissions. Among the current anthropogenic N₂O emissions of 3.1±0.8 GtCO₂-eq per year [1], agricultural activities account for about 1.9 GtCO₂-eq per year and industrial processes including fossil fuel combustion account for about 0.8 GtCO₂-eq per year. The challenges of reducing the agricultural emissions of N₂O are mainly associated with controlling synthetic fertilizer use while maintaining the same levels of or even increasing crop production. N₂O emissions from stationary combustion are primarily a result of the usage of coal fluidised bed boilers in the electric power sector. N₂O is emitted directly from the combustion of the fuel with air at moderate temperatures. In general, the contribution of the stationary combustion to total N₂O emissions is not large, but the data uncertainty is high. The emission of N₂O is dependent on the temperature in the boilers. The emission rates are the highest when the combustion temperature ranges from 800K to 1200K, while the emissions are negligible below 800K and over 1200K. The mechanisms of N₂O chemistry are relatively well understood though the experimental data available are limited. In addition to anthropogenic emissions, N₂O has natural sources which are predominantly

terrestrial and these emissions are highest in the tropics. However, the exact contributions of natural sources remain difficult to identify for atmosphere-based, top-down inversion studies of emissions [143, 144] due to the co-existence of both anthropogenic and natural sources.

For N₂O emissions, agricultural activities are the dominant anthropogenic source, while other sources such as mobile source fuel combustion and stationary fuel combustion also contribute. Ozone depleting substance substitute emissions are the primary contributors to aggregate HFC emissions and partly to PFC emissions. PFC can also be emitted as a by-product of primary aluminium production and from semiconductor manufacturing. Electrical transmission and distribution systems accounted for most SF₆ emissions, while semiconductor manufacturing primarily led to NF₃ emissions. As HFCs are being phased out as the substitute for ODSs while PFC, HFC, SF₆, and NF₃ emissions can be controlled by coordinated efforts from the relevant manufacturing sectors, it is expected that the mitigation of these minor anthropogenic GHGs can be achieved without major obstacles.

Concerns on non-CO₂ GHGs are mainly associated with methane emissions, as the more active one of the two major non-CO₂ GHGs (in comparison with N₂O). CH₄ emissions, resulting primarily from agricultural activities including enteric fermentation associated with domestic livestock, natural gas systems, decomposition of wastes in landfills, coal mines and oil explorations etc., are the second largest GHG source. Methane is an important GHG with anthropogenic emissions accounting for about 20% of the total warming effects of all GHGs, where the emissions from the energy sector (fossil fuel exploitation) are one of the major sources. Reducing or mitigating CH₄ emissions while exploiting the potential utilisation of the thermal energy have brought up a wide range of scientific, technological and financial challenges. The adverse effect of CH₄ emissions can be potentially much larger because of the various positive feedback mechanisms between methane emissions and climate change. Accordingly mitigation of CH₄ emissions may have a profound impact on a wide range of areas.

It is worth noting that CH₄ emissions from agriculture could be larger than those from fossil fuel exploitation. Emissions from the agriculture sector are mostly attributable to enteric fermentation and manure management, representing non-point sources of methane emissions, e.g. ruminant animals like cattle and sheep are the major emitters of methane via enteric fermentation. The amount of methane emitted from enteric fermentation depends on the feed quality and amount of feed ingested by the animal. Usually it is not straightforward to cut the emissions from non-point sources as they are not concentrated and therefore difficult for technical solutions. Options to reduce methane emissions from enteric fermentation include improved animal productivity and feed management. Even in the energy sector, where emissions are often from point sources, capturing CH₄ represents a technical and economical challenge.

For CH₄ leakage from oil and gas systems, targeted collection can vastly reduce the GHG emissions, where the collected CH₄ can be flared off as carbon dioxide or used as an additional fuel source. Capturing or collecting the CH₄ is a difficult task with technical

difficulties and financial implications. Su et al. [15] summarised the four basic processes commonly used for gas purification activities and discussed their basic characteristics and differences, including solvent adsorption or selective absorption, pressure swing adsorption, cryogenic separation and membrane separation. The technologies can be used for rejecting nitrogen, carbon dioxide, oxygen and water etc., which can be used individually or combined together. In general, nitrogen rejection is the most critical and expensive component of any purification system. Although enrichment facilities have been used successfully for upgrading medium quality gas from natural gas wells to pipeline specifications, it is generally not economically viable to purify the mixture streams when CH₄ concentration is too low.

Energy-related activities are responsible for the anthropogenic emissions of CH₄ and N₂O. Although the mitigation of CH₄ in the form of VAM was the focal point in the context of this review, some of the issues discussed are of a general nature, which can be used in other areas such as the mitigation of CH₄ from gas and oil explorations, e.g. the chemical kinetics of ultra-lean methane mixture oxidation/combustion. This topic is summarised as follows and some promising research directions in the field are also briefly discussed.

4.1. Challenges in combustion mitigation of ultra-lean methane mixtures

Currently there are knowledge gaps in combustion mitigation of ultra-lean methane. The challenges are both scientific and technological, involving a number of physicochemical factors affecting the ignition and flame dynamics. Purposely designed experimentations can certainly help gain insights, which are still lacking. For the modelling of ultra-lean methane oxidation/combustion, chemical kinetics represents the largest challenge. Presently there is a lack of robust studies on ultra-lean CH₄ combustion chemistry and kinetic schemes that can be effectively used to describe the chemical process and to be employed in numerical simulations to design efficient combustion systems. There is a gap in the model availability for applications concerning diluted combustion with extremely low CH₄ concentrations.

Optimised chemical kinetic schemes especially reduced mechanisms that work effectively with CFD codes are needed for engineering applications. The development of these schemes depends on an in-depth understanding of the chemical reactions involved. Fundamental understanding on ultra-lean oxidation/combustion is still lacking. A combination of fundamental studies of chemical kinetics and reaction rates through well-defined and purposely designed experiments and *ab initio* theoretical calculations, and of analyses of global experimental measurements will play a major role in the further developments of chemical schemes for ultra-lean CH₄ oxidation/combustion. Validation of the schemes is also important. Systematic testing and validations also need to be supplemented by UQ analyses to ensure the applicability of the schemes. Systematic adjustments of kinetic parameters to experimental measurements need to be carried out, together with model and parameter evaluation. Chemical kinetic mechanisms need to be assessed at different operating conditions: pressure level and preheating effects on autoignition and flammability limits. Scheme optimisation, reduction and uncertainty quantification also need to be performed to

develop skeletal and reduced chemical schemes, to be integrated into the simulation codes used for design purposes. In addition, kinetics of catalytic combustion and plasma-assisted ignition certainly need a substantial amount of effort, as this is an area that may have huge technical potentials but the current understanding is rather limited.

It is worth noting that, apart from chemical kinetics, the thermodynamic/aerodynamic limits of burning ultra-lean methane in practical systems remain unexplored. Investigating the thermodynamic/aerodynamic limits would include minimising heat losses from the system, maximising fuel-air mixing for oxidation, and optimising the initial energy level to initiate the oxidation, which so far have not been systematically investigated. This represents an area requiring further research.

4.2. Promising research directions

Currently our understanding on non-CO₂ GHGs is still limited, where the inventory data are only estimates with inconsistencies. Our ability to quantify both natural and anthropogenic non-CO₂ GHG fluxes needs to be improved, so is our understanding on the interactions between natural and anthropogenic GHGs. Fundamental scientific understanding on anthropogenic non-CO₂ GHG emission mechanisms, sensitivities to and linkages with external factors need to be carried out, which could form the basis for treaty compliance, carbon-based trading markets and the initialisation of more accurate estimation techniques. Research activities should include enhancing observational networks and improving inverse modelling techniques to allow more accurate estimates of regional emissions. The stabilisation of climate forcing will be managed more effectively with scientific advances that enhance our understanding of non-CO₂ GHG emissions, the sensitivities of the emissions to external factors, the interactions between various non-CO₂ GHGs as well as those interactions with CO₂. With such advances, the overall effectiveness of mitigation efforts could be continuously assessed and optimised. Improved scientific capabilities could also increase our ability to reduce GHG emissions and may provide a better understanding of the precise cuts in anthropogenic emissions needed to stabilise climate forcing.

Further fundamental research needs to be carried out to address the effects of initial temperature and pressure on the flammability limits of ultra-lean methane combustion. Currently, there is a lack of in-depth understanding in a number of areas, e.g. the effects of system heat and mass transfer characteristics, plasma-assisted ignition and combustion, and the presence of catalysts on CH₄ ignition and oxidation/combustion. More specifically, questions need to be answered about under which concentration the mixture can be burned and under which conditions the oxidation/combustion can be sustainable and stable, with the effects of one or a combination of several of the influencing physicochemical factors.

On the technical side, breakthroughs are needed in several areas. For fugitive methane, effective capturing of the CH₄ represents a very significant challenge. The existing technologies need to be massively improved to become economical especially for low concentration emissions. For CH₄ emissions from non-point sources, there is currently no

large-scale technology available for targeted collection. Promising technologies such as the honeycomb monolithic carbon fibre composites have been used for VAM enrichment [145], where initial vacuum swing is a control step for the final methane concentration having 5 or 11 times the VAM enrichment by one-step adsorption and the mixture can be further enriched by second step adsorption to a higher concentration avoiding the methane explosive range of 5-15%. To further reduce the capturing costs and to scale up the technology are essential steps for these new technologies to be widely used.

Innovative methods will play a major part in the development of effective measures for cutting ultra-lean CH₄ emissions. For example, the mitigation of ultra-lean methane can be helped by plasma-assisted combustion. As a promising new technology, the application of plasma-assisted combustion to ultra-lean methane mitigation needs to be further investigated, both experimentally and theoretically/numerically. The utilisation of catalysts is playing a significant role in ultra-lean CH₄ mitigation and utilisation. The relevant progress in MILD combustion can potentially provide an opportunity for technical developments in this area, but the situation can be intriguing. The reduction of anthropogenic CH₄ emissions using combustion might also influence N₂O emissions. As the combustion temperature ranges from 800K to 1200K corresponding to the highest emission rates of N₂O, this temperature level may partially overlap with the temperature regime where MILD combustion or ultra-lean premixed combustion takes place. Although the combustion emissions of N₂O are believed to be insignificant, intriguing situations like this warrant further investigation. The advances in relevant areas will benefit ultra-lean methane mitigation in due course.

The need for robust technologies for the treatment of ultra-lean CH₄ air mixtures calls for further investigation and optimisation of recuperative combustion, involving flow and combustion control for sustainable oxidation/combustion. From a technological perspective, a combustion mitigation system has to provide some flexibility in dealing with methane concentration variations. It has to be resistant to changes in the concentration of methane when the heat flow is recirculated. Ideally the heat flow needs to be controlled as a function of methane concentration. For low methane concentrations more heat is required to raise the temperature to the sustainable oxidation/combustion regime and as the methane concentration increases less heat is required because a lower temperature is required for a sustainable reaction. For the ignition of ultra-lean mixtures, new technologies such as plasma-assisted ignition/combustion can be potentially utilised. At the same time, catalysts may be able to significantly enhance the ignition and oxidation/combustion performances of ultra-lean methane air mixtures.

Both scientific and technical advances are needed in our combat against global warming. The scientific advances should be able to identify the sources of non-CO₂ GHG emissions, to quantify the emissions, and to elucidate the parameters affecting their emissions. Meanwhile, technical advances should be able to provide economically viable mitigating measures to effectively cut the anthropogenic emissions of non-CO₂ GHGs.

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References

- [1] Montzka SA, Dlugokencky EJ, Butler JH. Non-CO₂ greenhouse gases and climate change. *Nature* 2011;476(7358):43-50. <http://dx.doi.org/10.1038/nature10322>.
- [2] Forster P, Ramaswamy V, Artaxo P, Berntsen T, Betts R, Fahey DW, Haywood J, Lean J, Lowe DC, Myhre G, Nganga J, Prinn R, Raga G, Schulz M, van Dorland R. Changes in atmospheric constituents and in radiative forcing. In: Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL, editors. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA; 2007. p. 129-234.
- [3] Galloway JN, Townsend AR, Erisman JW, Bekunda M, Cai Z, Freney JR, Martinelli LA, Seitzinger SP, Sutton MA. Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. *Science* 2008;320(5878):889–892. <http://dx.doi.org/10.1126/science.1136674>.
- [4] Vitousek PM, Naylor R, Crews T, David MB, Drinkwater LE, Holland E, Johnes PJ, Katzenberger J, Martinelli LA, Matson PA, Nziguheba G, Ojima D, Palm CA, Robertson GP, Sanchez PA, Townsend AR, Zhang FS. Nutrient imbalances in agricultural development. *Science* 2009;324(5934):1519–1520. <http://dx.doi.org/10.1126/science.1170261>.
- [5] Townsend AR, Howarth RW. Fixing the global nitrogen problem. *Scientific American* 2010;302(2):64–71. <http://dx.doi.org/10.1038/scientificamerican0210-64>.
- [6] Velders GJM, Andersen SO, Daniel JS, Fahey DW, McFarland M. The importance of the Montreal Protocol in protecting climate. *Proceedings of the National Academy of Sciences of the United States of America* 2007;104(12):4814–4819. <http://dx.doi.org/10.1073/pnas.0610328104>.
- [7] Karakurt I, Aydin G, Aydiner K. Mine ventilation air methane as a sustainable energy source. *Renewable and Sustainable Energy Reviews* 2011;15(2):1042–1049. <http://dx.doi.org/10.1016/j.rser.2010.11.030>.
- [8] Bousquet P, Ciais P, Miller JB, Dlugokencky EJ, Hauglustaine DA, Prigent C, van der Werf GR, Peylin P, Brunke E-G, Carouge C., Langenfelds RL, Lathière J, Papa F, Ramonet M, Schmidt M, Steele LP, Tyler SC, White J. Contribution of anthropogenic and natural sources to atmospheric methane variability. *Nature* 2006;443(7110):439–443. <http://dx.doi.org/10.1038/nature05132>.
- [9] Bergamaschi P, Frankenberg C, Meirink JF, Krol M, Dentener F, Wagner T, Platt U, Kaplan JO, Körner S, Heimann M, Dlugokencky EJ, Goede A. Satellite cartography of atmospheric methane from SCIAMACHY on board ENVISAT: 2. Evaluation based on inverse model simulations. *Journal of Geophysical Research* 2007;112(D2):D02304. <http://dx.doi.org/10.1029/2006JD007268>.
- [10] Shindell DT, Walter BP, Faluvegi G. Impacts of climate change on methane emissions from wetlands. *Geophysical Research Letters* 2004;31(21): L21202. <http://dx.doi.org/10.1029/2004GL021009>.
- [11] Whiteman G, Hope C, Wadhams P. Climate science: Vast costs of Arctic change. *Nature* 2013;499(7459):401–403. <http://dx.doi.org/10.1038/499401a>.
- [12] Spivakovsky CM, Logan JA, Montzka SA, Balkanski YJ, Foreman-Fowler M, Jones DBA, Horowitz LW, Fusco AC, Brenninkmeijer CAM, Prather MJ, Wofsy SC, McElroy MB. Three-dimensional climatological distribution of tropospheric OH: Update and evaluation. *Journal of Geophysical Research* 2000;105(D7):8931–8980. <http://dx.doi.org/10.1029/1999JD901006>.

- [13] Shindell DT, Faluvegi G, Koch DM, Schmidt GA, Unger N, Bauer SE. Improved attribution of climate forcing to emissions. *Science* 2009;326(5953):716–718. <http://dx.doi.org/10.1126/science.1174760>.
- [14] Cimino S, Pirone R, Russo G. Thermal stability of perovskite-based monolithic reactors in the catalytic combustion of methane. *Industrial & Engineering Chemistry Research* 2001;40(1):80-85. <http://dx.doi.org/10.1021/ie000392i>.
- [15] Su S, Beath A, Guo H, Mallett C. An assessment of mine methane mitigation and utilisation technologies. *Progress in Energy and Combustion Science* 2005;31(2):123-170. <http://dx.doi.org/10.1016/j.pecs.2004.11.001>.
- [16] Su S, Agnew J. Catalytic combustion of coal mine ventilation air methane. *Fuel* 2006;85(9):1201-1210. <http://dx.doi.org/10.1016/j.fuel.2005.11.010>.
- [17] Wang Y, Liu Y, Cao Q, Wang C, Che D. Homogeneous combustion of fuel ultra-lean methane/air mixtures: Experimental study and simplified reaction mechanism. *Energy & Fuels* 2011;25(8):3437-3445. <http://dx.doi.org/10.1021/ef200484c>.
- [18] Limbri H, Gunawan C, Rosche B, Scott J. Challenges to developing methane biofiltration for coal mine ventilation air: A review. *Water Air and Soil Pollution* 2013;224(6):1566. <http://dx.doi.org/10.1007/s11270-013-1566-5>.
- [19] Fernández J, Marín P, Díez FV, Ordóñez S. Coal mine ventilation air methane combustion in a catalytic reverse flow reactor: Influence of emission humidity. *Fuel Processing Technology* 2015;133:202–209. <http://dx.doi.org/10.1016/j.fuproc.2015.02.005>.
- [20] Mattus R, Källstrand Å. Fossil energy and ventilation air methane. In: Reay D, Smith P, van Amstel A, editors. *Methane and Climate Change*. Earthscan, London, United Kingdom and Washington, DC, USA; 2010. p. 201-210.
- [21] Howarth RW, Santoro R, Ingraffea A. Methane and the greenhouse-gas footprint of natural gas from shale formations. *Climatic Change* 2011;106(4):679–690. <http://dx.doi.org/10.1007/s10584-011-0061-5>.
- [22] Bracmort K, Ramseur JL, McCarthy JE, Folger P, Marples DJ. *Methane Capture: Options for Greenhouse Gas Emission Reduction*. CRS Report for Congress 7-5700, R40813, Congressional Research Service, USA; 2011.
- [23] Allen DT. Methane emissions from natural gas production and use: reconciling bottom-up and top-down measurements. *Current Opinion in Chemical Engineering* 2014;5:78–83. <http://dx.doi.org/10.1016/j.coche.2014.05.004>.
- [24] Karacan CÖ, Ruiz FA, Cotè M, Phipps S. Coal mine methane: A review of capture and utilization practices with benefits to mining safety and to greenhouse gas reduction. *International Journal of Coal Geology* 2011;86(2-3):121–156. <http://dx.doi.org/10.1016/j.coal.2011.02.009>.
- [25] Ju Y, Sun W. Plasma assisted combustion: Dynamics and chemistry. *Progress in Energy and Combustion Science* 2015;48:21-83. <http://dx.doi.org/10.1016/j.pecs.2014.12.002>.
- [26] Kim W, Snyder J, Cohen J. Plasma assisted combustor dynamics control. *Proceedings of the Combustion Institute* 2015;35(3):3479-3486. <http://dx.doi.org/10.1016/j.proci.2014.08.025>.
- [27] Wood S, Harris AT. Porous burners for lean-burn applications. *Progress in Energy and Combustion Science* 2008;34(5):667– 684. <http://dx.doi.org/10.1016/j.pecs.2008.04.003>.
- [28] Shi JR, Xie MZ, Li G, Liu H, Liu JT, Li HT. Approximate solutions of lean premixed combustion in porous media with reciprocating flow. *International Journal of Heat and Mass Transfer* 2009;52(3-4):702-708. <http://dx.doi.org/10.1016/j.ijheatmasstransfer.2008.08.002>.

- [29] Bubnovich V, Toledo M, Henriquez L, Rosas C, Romero J. Flame stabilization between two beds of alumina balls in a porous burner. *Applied Thermal Engineering* 2010;30(2-3):92-95. <http://dx.doi.org/10.1016/j.applthermaleng.2009.04.001>.
- [30] Pereira FM, Oliveira AAM, Fachini FF. Theoretical analysis of ultra-lean premixed flames in porous inert media. *Journal of Fluid Mechanics* 2010;657:285-307. <http://dx.doi.org/10.1017/S0022112010001461>.
- [31] Keramiotis C, Stelzner B, Trimis D, Founti M. Porous burners for low emission combustion: An experimental investigation. *Energy* 2012;45(1): 213-219. <http://dx.doi.org/10.1016/j.energy.2011.12.006>.
- [32] Robayo MD, Beaman B, Hughes B, Delose B, Orlovskaya N, Chen RH. Perovskite catalysts enhanced combustion on porous media. *Energy* 2014;76:477-486. <http://dx.doi.org/10.1016/j.energy.2014.08.045>.
- [33] Tierney C, Wood C, Harris AT, Fletcher DR. Computational fluid dynamics modelling of ultra-lean porous burners. *Progress in Computational fluid Dynamics* 2010;10(5-6): 352-365. <http://dx.doi.org/10.1504/PCFD.2010.035369>.
- [34] Jazbec M, Fletcher DF, Haynes BS. Simulation of the ignition of lean methane mixtures using CFD modelling and a reduced chemistry mechanism. *Applied Mathematical Modelling* 2000;24(8):689-696. [http://dx.doi.org/10.1016/S0307-904X\(00\)00012-3](http://dx.doi.org/10.1016/S0307-904X(00)00012-3).
- [35] Bromly JH, Barnes FJ, Muris S, You X, Haynes BS. Kinetic and thermodynamic sensitivity analysis of the NO-sensitized oxidation of methane. *Combustion Science and Technology* 1996;115(4-6):259-296. <http://dx.doi.org/10.1080/00102209608935532>.
- [36] Mira Martinez D, Cluff DL, Jiang X. Numerical investigation of the burning characteristics of ventilation air methane in a combustion based mitigation system. *Fuel* 2014;133:182–193. <http://dx.doi.org/10.1016/j.fuel.2014.05.022>.
- [37] Cavaliere A, de Joannon M. Mild combustion. *Progress in Energy and Combustion Science* 2004;30(4):329–366. <http://dx.doi.org/10.1016/j.pecs.2004.02.003>.
- [38] Sidey J, Mastorakos E, Gordon RL. Simulations of autoignition and laminar premixed flames in methane/air mixtures diluted with hot products. *Combustion Science and Technology* 2014;186(4-5):453–465. <http://dx.doi.org/10.1080/00102202.2014.883217>.
- [39] Goh KHH, Geipel P, Hampp F, Lindstedt RP. Regime transition from premixed to flameless oxidation in turbulent JP-10 flames. *Proceedings of the Combustion Institute* 2013;34(2):3311-3318. <http://dx.doi.org/10.1016/j.proci.2012.06.173>.
- [40] Goh KHH, Geipel P, Lindstedt RP. Lean premixed opposed jet flames in fractal grid generated multiscale turbulence. *Combustion and Flame* 2014;161(9):2419-2434. <http://dx.doi.org/10.1016/j.combustflame.2014.03.010>.
- [41] Pope SB. *Turbulent Flows*. Cambridge University Press, Cambridge, United Kingdom; 2000.
- [42] Lilleberg B, Christ D, Ertesvåg IS, Rian KE, Kneer R. Numerical simulation with an extinction database for use with the eddy dissipation concept for turbulent combustion. *Flow, Turbulence and Combustion* 2013;91(2):319–346. <http://dx.doi.org/10.1007/s10494-013-9463-y>.
- [43] Magnussen BF, Hjertager BH. On mathematical modeling of turbulent combustion with special emphasis on soot formation and combustion. *Proceedings of the Combustion Institute* 1977;16(1):719–729. [http://dx.doi.org/10.1016/S0082-0784\(77\)80366-4](http://dx.doi.org/10.1016/S0082-0784(77)80366-4).
- [44] Gran IR, Magnussen BF. A numerical study of a bluff-body stabilized diffusion flame. Part 2. Influence of combustion modeling and finite-rate chemistry. *Combustion Science and Technology* 1996;119(1-6)191–217. <http://dx.doi.org/10.1080/00102209608951999>.

- [45] Veynante D, Vervisch L. Turbulent combustion modeling. *Progress in Energy and Combustion Science* 2002;28(3):193–266. [http://dx.doi.org/10.1016/S0360-1285\(01\)00017-X](http://dx.doi.org/10.1016/S0360-1285(01)00017-X).
- [46] Pitsch H. Large-eddy simulation of turbulent combustion. *Annual Review of Fluid Mechanics* 2006;38:453-482. <http://dx.doi.org/10.1146/annurev.fluid.38.050304.092133>.
- [47] Gicquel LYM, Staffelbach G, Poinso T. Large eddy simulations of gaseous flames in gas turbine combustion chambers. *Progress in Energy and Combustion Science* 2012;38(6):782-817. <http://dx.doi.org/10.1016/j.pecs.2012.04.004>.
- [48] Haworth DC. Progress in probability density function methods for turbulent reacting flows. *Progress in Energy and Combustion Science* 2010;36(2):168–259. <http://dx.doi.org/10.1016/j.pecs.2009.09.003>.
- [49] Swaminathan N, Bray KNC, editors. *Turbulent Premixed Flames: Physics and Modelling*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA; 2011. p. 102-150.
- [50] Kim JP, Schnell U, Scheffknecht G. Comparison of different global reaction mechanisms for MILD combustion of natural gas. *Combustion Science and Technology* 2008;180(4):565–592. <http://dx.doi.org/10.1080/00102200701838735>.
- [51] Lindstedt RP, Milosavljevic VD, Persson M. Turbulent burning velocity predictions using transported PDF methods. *Proceedings of the Combustion Institute* 2011;33(1):1277-1284. <http://dx.doi.org/10.1016/j.proci.2010.05.092>.
- [52] Goktolga MU, van Oijen JA, de Goey LPH. 3D DNS of MILD combustion: A detailed analysis of heat loss effects, preferential diffusion, and flame formation mechanisms. *Fuel* 2015;159:784-795. <http://dx.doi.org/10.1016/j.fuel.2015.07.049>.
- [53] Minamoto Y, Swaminathan N. Subgrid scale modelling for MILD combustion. *Proceedings of the Combustion Institute* 2015;35(3):3529–3536. <http://dx.doi.org/10.1016/j.proci.2014.07.025>.
- [54] Bowman CT. Kinetics of pollutant formation and destruction in combustion. *Progress in Energy and Combustion Science* 1975;1(1):33-45. [http://dx.doi.org/10.1016/0360-1285\(75\)90005-2](http://dx.doi.org/10.1016/0360-1285(75)90005-2).
- [55] Heywood JB. Pollutant formation and control in spark-ignition engines. *Progress in Energy and Combustion Science* 1976;1(4):135–164. [http://dx.doi.org/10.1016/0360-1285\(76\)90012-5](http://dx.doi.org/10.1016/0360-1285(76)90012-5).
- [56] Westbrook CK, Dryer FL. Chemical kinetic modelling of hydrocarbon combustion. *Progress in Energy and Combustion Science* 1984;10(1):1-57. [http://dx.doi.org/10.1016/0360-1285\(84\)90118-7](http://dx.doi.org/10.1016/0360-1285(84)90118-7).
- [57] Warnatz J. The structure of laminar alkane-, alkene-, and acetylene flames. *Proceedings of the Combustion Institute* 1981;18(1):369-384. [http://dx.doi.org/10.1016/S0082-0784\(81\)80042-2](http://dx.doi.org/10.1016/S0082-0784(81)80042-2).
- [58] Warnatz J. Critical survey of elementary reaction rate coefficients in the C/H/O system. In: Gardiner WC, editor. *Combustion Chemistry*, Springer-Verlag, New York, USA; 1984. p. 197-360. http://dx.doi.org/10.1007/978-1-4684-0186-8_5.
- [59] Simmie JM. Detailed chemical kinetic models for the combustion of hydrocarbon fuels. *Progress in Energy and Combustion Science* 2003;29(6):599–634. [http://dx.doi.org/10.1016/S0360-1285\(03\)00060-1](http://dx.doi.org/10.1016/S0360-1285(03)00060-1).
- [60] Law CK. *Combustion Physics*, Cambridge University Press, Cambridge, UK; 2006. <http://dx.doi.org/10.1017/CBO9780511754517>.

- [61] Warnatz J, Mass U, Dibble RW. Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation, 4th edition, Springer-Verlag, Berlin, Germany; 2006. <http://dx.doi.org/10.1007/978-3-540-45363-5>.
- [62] Warnatz J. The mechanism of high temperature combustion of propane and butane. *Combustion Science and Technology* 1983;34(1-6):177-200. <http://dx.doi.org/10.1080/00102208308923692>.
- [63] Smooke MD, editor. Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane/Air Flames: A Topical Volume, Lecture Notes in Physics, Springer-Verlag, Berlin, Germany; 1991. <http://dx.doi.org/10.1007/BFb0035362>.
- [64] GRI-Mech 3.0 <http://combustion.berkeley.edu/gri-mech/version30/text30.html>. Accessed on 5 May 2016.
- [65] Petersen EL, Davidson DF, Hanson RK. Kinetics modeling of shock-induced ignition in low-dilution CH₄/O₂ mixtures at high pressures and intermediate temperatures. *Combustion and Flame* 1999;117(1-2):272-290. [http://dx.doi.org/10.1016/S0010-2180\(98\)00111-4](http://dx.doi.org/10.1016/S0010-2180(98)00111-4).
- [66] The San Diego Mechanism <http://web.eng.ucsd.edu/mae/groups/combustion/mechanism.html>. Accessed on 5 May 2016.
- [67] Li SC, Williams FA. NO_x formation in two-stage methane–air flames. *Combustion and Flame* 1999;118(3):399-414. [http://dx.doi.org/10.1016/S0010-2180\(99\)00002-4](http://dx.doi.org/10.1016/S0010-2180(99)00002-4).
- [68] Li SC, Williams FA. Reaction mechanisms for methane ignition. *Journal of Engineering for Gas Turbines and Power* 2002;124(3):471-480. <http://dx.doi.org/10.1115/1.1377871>.
- [69] Petrova MV, Williams FA. A small detailed chemical-kinetic mechanism for hydrocarbon combustion. *Combustion and Flame* 2006;144(3):526-544. <http://dx.doi.org/10.1016/j.combustflame.2005.07.016>.
- [70] Hughes KJ, Turányi T, Clague AR, Pilling MJ. Development and testing of a comprehensive chemical mechanism for the oxidation of methane. *International Journal of Chemical Kinetics* 2001;33(9):513–538. <http://dx.doi.org/10.1002/kin.1048>.
- [71] Dagaut P, Boettner J-C, Cathonnet M. Methane oxidation: experimental and kinetic modeling study. *Combustion Science and Technology* 1991;77(1-3):127-148. <http://dx.doi.org/10.1080/00102209108951723>.
- [72] Davis SG, Law CK. Determination of and fuel structure effects on laminar flame speeds of C1 to C8 hydrocarbons. *Combustion Science and Technology* 1998;140(1-6):427-449. <http://dx.doi.org/10.1080/00102209808915781>.
- [73] Ranzi E, Sogaro A, Gaffuri P, Pennati G, Faravelli T. A wide range modeling study of methane oxidation. *Combustion Science and Technology* 1994;96(4-6):279-325. <http://dx.doi.org/10.1080/00102209408935359>.
- [74] Ranzi E, Dente M, Goldaniga A, Bozzano G, Faravelli T. Lumping procedures in detailed kinetic modeling of gasification, pyrolysis, partial oxidation and combustion of hydrocarbon mixtures. *Progress in Energy and Combustion Science* 2001;27(1):99-139. [http://dx.doi.org/10.1016/S0360-1285\(00\)00013-7](http://dx.doi.org/10.1016/S0360-1285(00)00013-7).
- [75] Westbrook CK, Dryer FL. Simplified reaction mechanisms for the oxidation of hydrocarbon fuels in flames. *Combustion Science and Technology* 1981;27(1-2):31-43. <http://dx.doi.org/10.1080/00102208108946970>.
- [76] Sung CJ, Law CK, Chen J-Y. An augmented reduced mechanism for methane oxidation with comprehensive global parametric validation. *Proceedings of the Combustion Institute* 1998;27(1):295-304. [http://dx.doi.org/10.1016/S0082-0784\(98\)80416-5](http://dx.doi.org/10.1016/S0082-0784(98)80416-5).

- [77] Chen J-Y. Development of reduced mechanisms for numerical modelling of turbulent combustion. Workshop on “Numerical Aspects of Reduction in Chemical Kinetics”, CERMICS-ENPC Cite Descartes - Champ sur Marne, France; 1997.
- [78] Paczko G, Lefdal PM, Peters N. Reduced reaction schemes for methane, methanol and propane flames. *Proceedings of the Combustion Institute* 1988;21(1):739-748. [http://dx.doi.org/10.1016/S0082-0784\(88\)80306-0](http://dx.doi.org/10.1016/S0082-0784(88)80306-0).
- [79] Jones WP, Lindstedt RP. Global reaction schemes for hydrocarbon combustion. *Combustion and Flame* 1988;73(3):233-24. [http://dx.doi.org/10.1016/0010-2180\(88\)90021-1](http://dx.doi.org/10.1016/0010-2180(88)90021-1).
- [80] Fernández-Tarrazo E, Sánchez AL, Liñán A, Williams FA. A simple one-step chemistry model for partially premixed hydrocarbon combustion. *Combustion and Flame* 2006;147(1-2):32-38. <http://dx.doi.org/10.1016/j.combustflame.2006.08.001>.
- [81] Sánchez AL, Lépinette A, Bollig M, Liñán A, Lázaro B. The reduced kinetic description of lean premixed combustion. *Combustion and Flame* 2000;123(4):436-464. [http://dx.doi.org/10.1016/S0010-2180\(00\)00177-2](http://dx.doi.org/10.1016/S0010-2180(00)00177-2).
- [82] Bibrzycki J, Poinot T. Reduced chemical kinetic mechanisms for methane combustion in O_2/N_2 and O_2/CO_2 atmosphere. Working note ECCOMET WN/CFD/10/17, CERFACS, France; 2010.
- [83] Lu T, Law CK. A criterion based on computational singular perturbation for the identification of quasi steady state species: A reduced mechanism for methane oxidation with NO chemistry. *Combustion and Flame* 2008;154(4):761-774. <http://dx.doi.org/10.1016/j.combustflame.2008.04.025>.
- [84] Wada T, Jarmolowitz F, Abel D, Peters N. An instability of diluted lean methane/air combustion: Modeling and control. *Combustion Science and Technology* 2010;183(1):1-19. <http://dx.doi.org/10.1080/00102201003789147>.
- [85] Nikolaou ZM, Chen J-Y, Swaminathan N. A 5-step reduced mechanism for combustion of $CO/H_2/H_2O/CH_4/CO_2$ mixtures with low hydrogen/methane and high H_2O content. *Combustion and Flame* 2013;160(1):56-75. <http://dx.doi.org/10.1016/j.combustflame.2012.09.010>.
- [86] de Joannon M, Cavaliere A, Faravelli T, Ranzi E, Sabia P, Tregrossi A. Analysis of process parameters for steady operations in methane mild combustion technology. *Proceedings of the Combustion Institute* 2005;30(2):2605-2612. <http://dx.doi.org/10.1016/j.proci.2004.08.190>.
- [87] Sabia P, de Joannon M, Picarelli A, Ragucci R. Methane auto-ignition delay times and oxidation regimes in MILD combustion at atmospheric pressure. *Combustion and Flame* 2013;160(1):47-55. <http://dx.doi.org/10.1016/j.combustflame.2012.09.015>.
- [88] Sabia P, de Joannon M, Picarelli A, Chinnici A, Ragucci R. Modeling negative temperature coefficient region in methane oxidation. *Fuel* 2012;91(1):238-245. <http://dx.doi.org/10.1016/j.fuel.2011.07.026>.
- [89] Effuggi A, Gelosa D, Derudi M, Rota R. Mild combustion of methane-derived fuel mixtures: Natural gas and biogas. *Combustion Science and Technology* 2008;180(3):481-493. <http://dx.doi.org/10.1080/00102200701741368>.
- [90] de Joannon M, Saponaro A, Cavaliere A. Zero-dimensional analysis of methane diluted oxidation in rich conditions. *Proceedings of the Combustion Institute* 2000;28(2):1639-1646. [http://dx.doi.org/10.1016/S0082-0784\(00\)80562-7](http://dx.doi.org/10.1016/S0082-0784(00)80562-7).
- [91] Gosiewski K, Pawlaczyk A, Jaschik M. Thermal combustion of lean methane-air mixtures: Flow reversal research and demonstration reactor model and its validation.

- Chemical Engineering Journal 2012;207-208:76-84.
<http://dx.doi.org/10.1016/j.cej.2012.07.044>.
- [92] Gosiewski K, Pawlaczyk A, Warmuzinski K, Jaschik M. A study on thermal combustion of lean methane-air mixtures: simplified reaction mechanism and kinetic equations. Chemical Engineering Journal 2009;154(1-3):9-16.
<http://dx.doi.org/10.1016/j.cej.2009.03.045>.
- [93] Slepterev AA, Salnikov VS, Tsyrlunikov PG, Noskov AS, Tomilov VN, Chumakova NA, Zagoruiko AN. Homogeneous high-temperature oxidation of methane. Reaction Kinetics and Catalysis Letters 2007;91(2):273-282. <http://dx.doi.org/10.1007/s11144-007-5158-5>.
- [94] Lee JH, Trimm DL. Catalytic combustion of methane. Fuel Processing Technology 1995;42(2-3):339-359. [http://dx.doi.org/10.1016/0378-3820\(94\)00091-7](http://dx.doi.org/10.1016/0378-3820(94)00091-7).
- [95] Choudhary TV, Banerjee S, Choudhary VR. Catalysts for combustion of methane and lower alkanes. Applied Catalysts A: General 2002;234(1-2):1-23.
[http://dx.doi.org/10.1016/S0926-860X\(02\)00231-4](http://dx.doi.org/10.1016/S0926-860X(02)00231-4).
- [96] Enger BC, Lødeng R, Holmen A. A review of catalytic partial oxidation of methane to synthetic gas with emphasis on reaction mechanisms over transition metal catalysts. Applied Catalysts A: General 2008;346(1-2):1-27.
<http://dx.doi.org/10.1016/j.apcata.2008.05.018>.
- [97] Horn R, Williams KA, Degenstein NJ, Bitsch-Larsen A, Nogare DD, Tupy SA, Schmidt LD. Methane catalytic partial oxidation on autothermal Rh and Pt foam catalysts: Oxidation and reforming zones, transport effects, and approach to thermodynamic equilibrium. Journal of Catalysis 2007;249(2):380-393.
<http://dx.doi.org/10.1016/j.jcat.2007.05.011>.
- [98] Abbasi R, Wu L, Wanke SE, Hayes RE. Kinetics of methane combustion over Pt and Pt-Pd catalysts. Chemical Engineering Research and Design 2012;90(11):1930-1942.
<http://dx.doi.org/10.1016/j.cherd.2012.03.003>.
- [99] Schwartz WR, Ciuparu D, Pfefferle LD. Combustion of methane over Palladium-based catalysts: Catalytic deactivation and role of the support. The Journal of Physical Chemistry C 2012;116(15):8587-8593. <http://dx.doi.org/10.1021/jp212236e>.
- [100] Ciuparu D, Lyubovsky MR, Altman E, Pfefferle LD, Datye A. Catalytic combustion of methane over palladium-based catalysts. Catalysis Reviews: Science and Engineering 2002;44(4):593-649. <http://dx.doi.org/10.1081/CR-120015482>.
- [101] Persson K, Ersson A, Colussi S, Trovarelli A, Järås SG. Catalytic combustion of methane over bimetallic Pd-Pt catalysts: the influence of support materials. Applied Catalysts B: Environmental 2006;66(3-4):175-185. <http://dx.doi.org/10.1016/j.apcatb.2006.03.010>.
- [102] Cargnello M, Delgado Jaén JJ, Hernández Garrido JC, Bakhmutsky K, Montini T, Calvino Gámez JJ, Gorte RJ, Fornasiero P. Exceptional activity for methane combustion over modular Pd@CeO₂ subunits on functionalized Al₂O₃. Science 2012;337(6095):713-717.
<http://dx.doi.org/10.1126/science.1222887>.
- [103] Li Y-H, Chen G-B, Wu F-H, Cheng T-S, Chao Y-C. Enhancement of methane combustion in microchannels: effects of catalyst segmentation and cavities. Chemical Engineering Journal 2010;160(2):715-722. <http://dx.doi.org/10.1016/j.cej.2010.03.057>.
- [104] Li Y-H, Chen G-B, Wu F-H, Cheng T-S, Chao Y-C. Effects of catalyst segmentation with cavities on combustion enhancement of blended fuels in a micro channel. Combustion and Flame 2012;159(4):1644-1651. <http://dx.doi.org/10.1016/j.combustflame.2011.11.017>.
- [105] Vincent RS, Lindstedt RP, Malik NA, Reid IAB, Messenger BE. The chemistry of ethane dehydrogenation over a supported platinum catalyst. Journal of Catalysis 2008;260(1):37-64. <http://dx.doi.org/10.1016/j.jcat.2008.08.014>.

- [106] Vincent RS, Lindstedt RP, Malik NA, Reid IAB, Messenger BE. The dynamics of partial oxidation of ethane over platinum. *Proceedings of the Combustion Institute* 2011;33(2):1809-1817. <http://dx.doi.org/10.1016/j.proci.2010.05.034>.
- [107] Deutschmann O, Schmidt R, Behrendt F, Warnatz J. Numerical modelling of catalytic ignition. *Proceedings of the Combustion Institute* 1996;26(1):1747-1754. [http://dx.doi.org/10.1016/S0082-0784\(96\)80400-0](http://dx.doi.org/10.1016/S0082-0784(96)80400-0).
- [108] Deutschmann O, Schwiedernoch R, Maier LI, Chatterjee D. Natural gas conversion in monolithic catalysts: Interaction of chemical reactions and transport phenomena. *Studies in Surface Science and Catalysis - Natural Gas Conversion VI* 2001;136:251-258. [http://dx.doi.org/10.1016/S0167-2991\(01\)80312-8](http://dx.doi.org/10.1016/S0167-2991(01)80312-8).
- [109] Hecht E, Gupta GK, Zhu H, Dean AM, Kee RJ, Maier L, Deutschmann O. Methane reforming kinetics within a Ni-YSZ SOFC anode support. *Applied Catalysis A: General* 2005;295(1):40-51. <http://dx.doi.org/10.1016/j.apcata.2005.08.003>.
- [110] Schwiedernoch R, Tischer S, Correa S, Deutschmann O. Experimental and numerical study on the transient behavior of partial oxidation of methane in a catalytic monolith. *Chemical Engineering Science* 2003;58(3-6):633-642. [http://dx.doi.org/10.1016/S0009-2509\(02\)00589-4](http://dx.doi.org/10.1016/S0009-2509(02)00589-4).
- [111] Hartmann M, Maier L, Minh HD, Deutschmann O. Catalytic partial oxidation of iso-octane over rhodium catalysts: An experimental, modeling, and simulation study. *Combustion and Flame* 2010;157(9):1771-1782. <http://dx.doi.org/10.1016/j.combustflame.2010.03.005>.
- [112] Fischer M, Jiang X. Numerical optimisation for model evaluation in combustion kinetics. *Applied Energy* 2015;156:793–803. <http://dx.doi.org/10.1016/j.apenergy.2015.05.002>.
- [113] Zador J, Taatjes CA, Fernandes RX. Kinetics of elementary reactions in low-temperature autoignition chemistry. *Progress in Energy and Combustion Science* 2011;37(4):371-421. <http://dx.doi.org/10.1016/j.pecs.2010.06.006>.
- [114] Wang QD, Wang JB, Li JQ, Tan NX, Li XY. Reactive molecular dynamics simulation and chemical kinetic modeling of pyrolysis and combustion of n-dodecane. *Combustion and Flame* 2011;158(2):217-226. <http://dx.doi.org/10.1016/j.combustflame.2010.08.010>.
- [115] van Duin ACT, Dasgupta S, Lorant F, Goddard III WA. ReaxFF: A reactive force field for hydrocarbons. *Journal of Physical Chemistry A* 2001;105(41):9396-9409 <http://dx.doi.org/10.1021/jp004368u>.
- [116] Döntgen M, Przybylski-Freund M-D, Kröger LC, Kopp WA, Ismail AE, Leonhard K. Automated discovery of reaction pathways, rate constants, and transition states using reactive molecular dynamics simulations. *Journal of Chemical Theory and Computation* 2015;11(6): 2517-2524. <http://dx.doi.org/10.1021/acs.jctc.5b00201>.
- [117] Suleimanov YV, Green WH. Automated discovery of elementary chemical reaction steps using freezing string and Berny optimization methods. *Journal of Chemical Theory and Computation* 2015;11(9):4248–4259. <http://dx.doi.org/10.1021/acs.jctc.5b00407>.
- [118] Wang H, Sheen, DA. Combustion kinetic model uncertainty quantification, propagation and minimization. *Progress in Energy and Combustion Science* 2015;47:1-31. <http://dx.doi.org/10.1016/j.pecs.2014.10.002>.
- [119] Oh SH, Mitchell PJ, Siewert RM. Methane oxidation over alumina-supported noble metal catalysts with and without cerium additives. *Journal of Catalysis* 1991;132(2):287-301. [http://dx.doi.org/10.1016/0021-9517\(91\)90149-X](http://dx.doi.org/10.1016/0021-9517(91)90149-X).
- [120] Gövert S, Mira Martinez D, Kok JBW, Vázquez M, Houzeaux G. Turbulent combustion modelling of a confined premixed jet flame including heat loss effects using tabulated

- chemistry. *Applied Energy* 2015;156:804–815.
<http://dx.doi.org/10.1016/j.apenergy.2015.06.031>.
- [121] Lamouroux J, Ihme M, Fiorina B, Gicquel O. Tabulated chemistry approach for diluted combustion regimes with internal recirculation and heat losses. *Combustion and Flame* 2014;161(8):2120-2136. <http://dx.doi.org/10.1016/j.combustflame.2014.01.015>.
- [122] Kerstein AR. One-dimensional turbulence: model formulation and application to homogeneous turbulence, shear flows, and buoyant stratified flows. *Journal of Fluid Mechanics* 1999;392:277-334. <http://dx.doi.org/10.1017/S0022112099005376>.
- [123] Echehki T, Kerstein AR, Dreeben TD, Chen JY. One-dimensional turbulence' simulation of turbulent jet diffusion flames: model formulation and illustrative applications. *Combustion and Flame* 2001;125(3):1083–1105. [http://dx.doi.org/10.1016/S0010-2180\(01\)00228-0](http://dx.doi.org/10.1016/S0010-2180(01)00228-0).
- [124] Ranganath B, Echehki T. One-dimensional turbulence-based closure with extinction and reignition. *Combustion and Flame* 2008;154(1-2):23–46.
<http://dx.doi.org/10.1016/j.combustflame.2008.03.020>.
- [125] Gupta KG, Echehki T. One-dimensional turbulence model simulations of autoignition of hydrogen/carbon monoxide fuel mixtures in a turbulent jet. *Combustion and Flame* 2011;158(2):327–344. <http://dx.doi.org/10.1016/j.combustflame.2010.09.003>.
- [126] Punati N, Sutherland JC, Kerstein AR, Hawkes ER, Chen JH. 2011. An evaluation of the one-dimensional turbulence model: comparison with direct numerical simulations of CO/H₂ jets with extinction and reignition. *Proceedings of the Combustion Institute* 2011;33(1):1515–1522. <http://dx.doi.org/10.1016/j.proci.2010.06.127>.
- [127] Weinberg FJ. Combustion temperatures: The future? *Nature* 1971;233(5317):239–241.
<http://dx.doi.org/10.1038/233239a0>.
- [128] Hardesty DR, Weinberg FJ. Burners producing large excess enthalpies. *Combustion Science and Technology* 1973;8(5-6):201–214.
<http://dx.doi.org/10.1080/00102207308946644>.
- [129] Su S, Chen H, Teakle P, Xue S. Characteristics of coal mine ventilation air flows. *Journal of Environmental Management* 2008;86(1):44–62.
<http://dx.doi.org/10.1016/j.jenvman.2006.11.025>.
- [130] Cluff DL. Concepts in Coalmine Ventilation and Development of the VamTurBurner© for Extraction of Thermal Energy from Underground Ventilation Air Methane. PhD Dissertation, University of Exeter, United Kingdom; 2014.
- [131] Karakurt I, Aydin G, Aydiner K. Sources and mitigation of methane emissions by sectors: A critical review. *Renewable Energy* 2012;39(1):40–48.
<http://dx.doi.org/10.1016/j.renene.2011.09.006>.
- [132] Hwang ST, Thorman JM. The continuous membrane column. *AIChE Journal* 1980;26(4):558-566. <http://dx.doi.org/10.1002/aic.690260406>.
- [133] Olajossy A, Gawdzik A, Budner Z, Dula J. Methane separation from coal mine methane gas by vacuum pressure swing adsorption. *Chemical Engineering Research and Design* 2003;81(4):474–482. <http://dx.doi.org/10.1205/026387603765173736>.
- [134] Thiruvengkatachari R, Su S, Yu XX. Carbon fibre composite for ventilation air methane (VAM) capture. *Journal of Hazardous Materials* 2009;172(2–3):1505–1511.
<http://dx.doi.org/10.1016/j.jhazmat.2009.08.020>.
- [135] Burchell TD, Judkins RR. A novel carbon fiber based material and separation technology. *Energy Conversion and Management* 1997;38(Supplement):S99–S104.
[http://dx.doi.org/10.1016/S0196-8904\(96\)00253-1](http://dx.doi.org/10.1016/S0196-8904(96)00253-1).

- [136] Cluff DL, Kennedy GA, Bennett JG, Foster PJ. Capturing energy from ventilation air methane a preliminary design for a new approach. *Applied Thermal Engineering* 2015;90:1151–1163. <http://dx.doi.org/10.1016/j.applthermaleng.2015.05.013>.
- [137] Yin J, Su S, Yu XX, Weng Y. Thermodynamic characteristics of a low concentration methane catalytic combustion gas turbine. *Applied Energy* 2010;87(6):2102–2108. <http://dx.doi.org/10.1016/j.apenergy.2009.12.011>.
- [138] Somers JM, Schultz HL. Coal mine ventilation air emissions: project development planning and mitigation technologies. 13th United States/North American Mine Ventilation Symposium, 2010 – Hardcastle & McKinnon (Editors), ©2010, MIRARCO - Mining Innovation, Canada; 2010.
- [139] Tanaka K, Yoshino Y, Kashihara H, Kajita S. Utilization and mitigation of VAM/CMM emissions by a catalytic combustion gas turbine. In: Qi H, Zhao B, editors. *Cleaner Combustion and Sustainable World*, Springer-Verlag Berlin Heidelberg and Tsinghua University Press; 2013. p. 401-406. http://dx.doi.org/10.1007/978-3-642-30445-3_56.
- [140] Warmuzinski K. Harnessing methane emissions from coal mining. *Process Safety and Environmental Protection* 2008;86(5):315–320. <http://dx.doi.org/10.1016/j.psep.2008.04.003>.
- [141] Gosiewski K, Pawlaczyk A. Catalytic or thermal reversed flow combustion of coal mine ventilation air methane: What is better choice and when? *Chemical Engineering Journal* 2014;238:78–85. <http://dx.doi.org/10.1016/j.cej.2013.07.039>.
- [142] Schultz K. Coal mine-ventilation air methane mitigation: Technologies to harness an energy and environmental resource. Center for Applied Energy Research, University of Kentucky, USA. *Energeia* 2003;14(5):1-6.
- [143] Hirsch AI, Michalak AM, Bruhwiler LM, Peters W, Dlugokencky EJ, Tans PP. Inverse modeling estimates of the global nitrous oxide surface flux from 1998–2001. *Global Biogeochemical Cycles* 2006;20(1):GB1008. <http://dx.doi.org/10.1029/2004GB002443>.
- [144] Huang J, Golombek A, Prinn R, Weiss R, Fraser P, Simmonds P, Dlugokencky EJ, Hall B, Elkins J, Steele P, Langenfelds R, Krummel P, Dutton G, Porter L. Estimation of regional emissions of nitrous oxide from 1997 to 2005 using multinet network measurements, a chemical transport model, and an inverse method. *Journal of Geophysical Research* 2008;113(D17):D17313. <http://dx.doi.org/10.1029/2007JD009381>.
- [145] Bae JS, Su S, Yu XX. Enrichment of ventilation air methane (VAM) with carbon fiber composites. *Environmental Science & Technology* 2014;48(10):6043-6049. <http://dx.doi.org/10.1021/es500025c>.