

MILD Combustion and Biofuels: A Minireview

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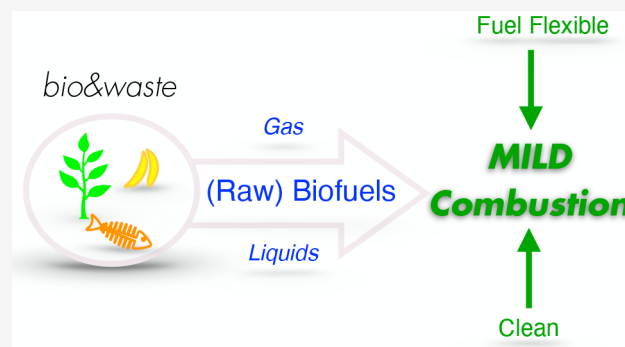
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ABSTRACT: Even in the presence of the formidable growth of renewable energy sources, advanced combustion processes have and will continue to have an irreplaceable role as a driving force for energy market. This is indeed motivated by the same huge amount of energy that can be conveniently stored in the form of energy carriers, made available from the renewable sources. The coupling of the appropriate combustion conversion technology with locally available biofuels certainly is among the most effective solutions, now on the table, to face the decarbonization challenge. In this framework, moderate or intense low oxygen dilution (MILD) combustion is among the best candidates to support the transition toward the net zero emission target. Indeed, due to its inherent features, it is highly fuel flexible and efficient, allowing for the utilization of whatever energy carrier can be considered in the decarbonization strategy. It is also characterized by an inherent low or absent pollutant emission. The novelty of this minireview is to highlight the relevance of the kinetics involved in MILD combustion processes with particular focus on biofuels, identifying invariant temperatures, relevant for process stabilization for any energy carrier. A critical evaluation of advantages and drawbacks of the use of raw bioliquids in MILD combustion conditions is reported. Then, challenges, open questions, and future perspectives on the use of biofuel in MILD combustion are discussed.



1. INTRODUCTION

Liquid and gaseous fuels derived from biomass are pivotal tiles in the pathway to the decarbonization of the combustion-based energy sector.¹ For this reason, massive attempts for development and optimization of the biomass value chain for production are on the table. The composition and the calorific value of biofuels mainly depends on both biomass feedstock and the process used for their production.^{2,3} As a consequence, their properties, and the combustion relevant properties indeed, may significantly differ from each other, requiring further processing to transform them in a standard marketable product. Remarkably, the most common strategy is to standardize them, by suitable chemical and physical treatments, in order to meet as much as possible the calorific value, rheological features, ignition times, and burning velocity of traditional fuels.^{1,4–7} The basic idea is thus to modify the fuel supply chain while reducing to a minimum the modification of the existing combustion-based plants retaining a reasonably high combustion efficiency and minimizing the investment of the final users while moving toward the net zero emission target.

The dual approach is to directly use raw biofuels, retaining their initial composition and limiting to a minimum or avoiding upgrading processes.^{1,8} This approach has to face the need of redesigning, even in part the end users plants (by either changing conversion processes and/or technologies). However, the direct

use of “raw” biofuels has the advantages of reducing or strongly cutting production chain transformation and fuel upgrading costs. This implies a possible reduction in the operating expenses and a reduced environmental impact⁹ that may compensate for the increased capital expenditure. In dependence on application to be considered, this strategy appears to be more straightforwardly usable and likewise effective for biogas. In the case of liquid biofuels, an additional degree of difficulty comes from their peculiar physical characteristics and the corresponding need to modify the feeding and mixing systems.^{1,2}

It is important to stress here that whatever is the used strategy, the availability of fuel-flexible combustion processes is a key enabling factor. In the case of mimicking fuels, this is mostly related to the inevitable variation of fuel properties to ensure the economical sustainability of the production chain, and in the case of “raw” biofuels, this is required to ensure a sustainable efficiency of the whole chain. In both cases, the fuel flexibility

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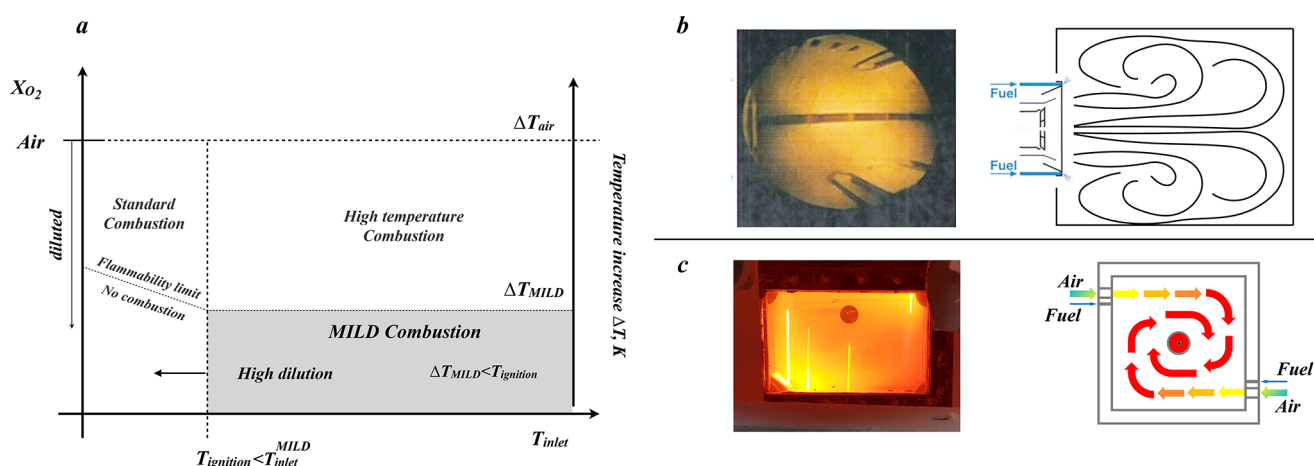


Figure 1. (a) X_{O_2} - T_{in} plan for MILD combustion. (b, c) Typical fluid-dynamic configuration for MILD combustion applications.^{20,36,37}

concept must include the eco-sustainability of the fuel conversion processes.

Among advanced combustion processes and technologies nowadays attracting attention in the field of research and applications, moderate or intense low oxygen dilution (MILD) combustion¹⁰ has been proven to be intrinsically fuel flexible. Indeed, it is very effective with gaseous,^{11,12} liquid fossil,^{13,14} and solid fuels^{15,16} but also with energy carriers such as biofuels,¹⁷ alcohols,¹⁸ and ammonia.^{19,20} For this reason and for its inherent low emissions and high efficiency, it is straightforward to consider MILD combustion as a preferential conversion technology of raw and upgraded biofuels in the general effort toward energy decarbonization.

The aim of this review is to give a concise overview of assessed potentials and possible perspectives of utilization of gaseous and liquid fuels derived from biomasses and waste treatments by means of transformation processes possibly integrated with renewable energy sources, coupled with MILD combustion.

MILD combustion of biomasses is also an interesting and challenging topic and is already a subject of a dedicated review available in the literature,²¹ and therefore, it will be not considered here. It has to be clarified that the relatively few results available in the literature obtained with different biomasses^{16,21,22} do not yet allow a comprehensive view of the conversion process nor to identify characteristic behavior beyond the ones very well assessed for MILD combustion.

In the literature, there are several papers reviewing MILD combustion in terms of possible definitions,^{10,23} reactive structures,²⁴ numerical models,^{25,26} burner configurations,^{27,28} and biomasses.²¹ In this panorama, this review has the novelty to highlight the relevance of the kinetics involved in MILD combustion processes with particular focus on biofuels. Taking the cue from behaviors of specific molecules reacting in MILD combustion conditions, inherent overall features, relevant for any tested energy carrier reacting in this condition, are brought into focus. Thus, invariant temperatures, related to the reactions which constitute the backbone of combustion kinetics common to all hydrogen containing molecules, are identified as threshold values to be locally reached to stabilize a MILD combustion process, independently on the fluid-dynamic configuration of the system. This analysis paves the way for an easy identification of operational conditions where MILD combustion can occur also for energy carriers not yet extensively analyzed, such as raw bioliquids. Very limited information is available in the literature on direct use of raw bioliquids, and there is a scarcity of

accessible data for reference bioliquids as alcohols. In an attempt to compensate for these deficiencies, potentials and possible drawbacks related to their direct use in MILD combustion have been critically discussed for the first time, with also a look at the influence of this condition on subprocesses associated with fuel feeding, such as injection as well as droplet atomization and evaporation.

Then, the content of this review can be summarized as follows. After a short description of MILD combustion features, this review first discusses the main findings on the use of biogas in MILD combustion conditions, analyzing the behavior of the main components and then the effects of minor species on the process. Afterward, igni-diffusive structures are shortly reviewed discussing the asymptotic steady case, exemplifying the local formation of reactive kernels. Then, the behaviors of bioliquids in MILD combustion have been discussed. The review closes with a discussion of challenges and perspectives of utilization of gaseous and liquid fuels derived from biomasses and waste treatments by means of transformation processes possibly integrated with renewable energy sources, coupled with MILD combustion.

2. MILD COMBUSTION: FEATURES AND POTENTIALS

In an energy decarbonization scenario, MILD combustion processes and systems are among the few advanced combustion technologies able to inherently satisfy the general criteria of sustainability, fuel flexibility, and readiness level required to promptly support the energy transition toward net zero carbon emission.^{10,23} Since its formal definition by Cavaliere and de Joannon,¹⁰ MILD combustion (also identified as colorless, flameless, distributed combustion^{29,30}) attracted the attention of scientists and industrial partners in several fields. Many different applications have been proposed, optimized, and marketed. Among them, there are domestic and industrial boilers,³¹ furnaces for intensive industries,^{32,33} stationary gas turbines, and even aviation combustors.³⁴

On the basis of the canonical definition of MILD combustion,¹⁰ it occurs when the local initial temperature of reactants (T_{in}) is higher than their ignition temperature (T_{ign}), and the dilution is as high as to keep the temperature increase during combustion (ΔT) below T_{ign} ($\Delta T < T_{ign}$). This definition of MILD combustion is summarized in Figure 1a where the regions corresponding to the different combustion regimes were identified on a qualitative oxygen molar fraction (X_{O_2}) vs inlet

temperature (T_{in}) plan. In the plot in Figure 1a, MILD combustion corresponds to the gray region lying below the oxygen molar fraction corresponding to a reactant dilution capable of limiting the temperature increase below the T_{ign} value for the specific case. It is straightforward to point out that the gray region in Figure 1a corresponds to the occurrence of a local composition of a reactant mixture falling outside the flammability limits for $T_{in} > T_{ign}$.

Because of the local highly diluted and preheated conditions in which the fuel conversion develops, the process evolves through peculiar distributed spontaneous ignitions that have been identified in literature as igni-diffusive structures.^{24,35} Igni-diffusive structures do not rely on heat and mass feedback from the reacting region but on spontaneous ignition of reactant mixtures. Hence, they are very different from those occurring in conventional premixed and diffusion flames.^{24,35} This implies that flame propagative structures, with very thin reactive regions and strong gradients, that are the common features of standard combustion processes, give the way to igni-diffusive pockets almost uniformly distributed over the whole combustion chamber volume. The direct consequence of this peculiar feature is the absence of a visible flame which makes MILD combustion a flameless and colorless process. As a matter of fact, the internal appearance of combustion chambers where MILD combustion is occurring looks like the pictures reported in Figure 1b and c.

Distributed spontaneous ignition guarantees high resilience to the extinction as well as a solid fuel flexibility. Indeed, as it is discussed in the next paragraph, the chemical evolution of the fuel oxidation is essentially dominated by the branching reactions of the H_2/O_2 mechanism which are not strictly linked to the fuel molecule structure making MILD combustion a highly fuel-flexible process. This characteristic makes the process truly fuel flexible with respect to conventional combustion methodologies which, instead, are strictly related to the combustion characteristics of single molecules. In addition, the relatively low temperature increase leads to a reduction of main pollutant species, whose formation mechanisms is strongly tied to the occurrence of high temperature regions and/or relevant spatial unevenness. In MILD combustion it is quite common to reach one digit level of NO_x (i.e., concentration at the exhaust of the combustion chamber below 10 ppm at 15% O_2) and a substantial soot absence.¹⁰

The possibility of stabilizing MILD combustion process for a wide palette of energy carriers has been demonstrated,^{11,18,20,38} from standard carbon-based fuels to biogas, alcohols, ammonia, and mixtures surrogating industrial gaseous waste streams. This is generally explained by the fact that in MILD combustion an additional degree of freedom is the possibility of modulating the amount of dilution/recirculation in the reactor (as is shown in the following) and hence of the autoignition temperature and oxygen molar fraction. This allows one to attain the stable self-ignition condition best suited for the specific fuel and to tailor the operational temperature in a wide range of values, provided that the crossover temperature of high temperature radical branching is locally achieved. This outstanding feature turns the concept of "combustion process" into "thermochemical conversion process" to stress that in these kinds of processes the output conditions can be easily tuned based on end-use needs.

The high dilution level and preheating of reactants can be reached locally or imposed as inlet conditions. In the first case,

local conditions are obtained with a suitable recirculation level inside the combustion chamber through tailored internal flow features. This is the most common solution in actual devices, not relying on regenerative systems. The two main strategies followed in the design of MILD combustion chambers with internal recirculation are summarized in the two sketches and related pictures reported in Figure 1b and c. Figure 1b represents the typical configuration where a reverse flow is generated by means of the fluid-dynamic flow field which is established due to a very high inlet air jet velocity and appropriate aspect ratio of the combustion chamber.^{39–45} Very often, the configuration of this typology has the gas exit section on the same side of fuel and air inlet.^{39,45}

On the other hand, Figure 1c shows a cyclonic flow burner^{37,46} which can be schematized as a confined highly recirculated flow field. It is representative of a second category of MILD combustion burner configuration. Along with the jet-in-hot-coflow,^{47,48} the cyclonic burner of Figure 1c represents a canonical reference configuration for MILD combustion studies. In this case, the cyclonic burner in Figure 1c can be considered a scale bridging configuration between model reactors and real systems. Indeed, it has been used for fundamental MILD combustion studies representing a recirculation region inside a full scale burner, but it can be also considered itself a full scale burner for small scale applications.

In both cases, the pictures of Figure 1b and c show the interior of combustion chambers of related configurations where no flame structures but only the luminosity from the burner's walls (and thermocouples for local measurement in the case of cyclonic configuration) are visible.

Apart from the above-described macroscopic features of MILD combustion, there are some inherent microscopic characteristics of the reactive process that are worth stressing. The local igni-diffusive structures depend on particular mixing conditions realized between fuel and oxidizer streams. Indeed, a hot and/or diluted fuel can mix with a hot and/or diluted oxidant flow. Consequently, these structures may be classified as hot oxidant, diluted oxidant, hot fuel, and diluted fuel^{35,49–52} as needed in relation to the local initial conditions of the reactants streams. They were thoroughly discussed in the literature in their different combinations. The one of major interest in the case of biogas is the hot oxidant (and possibly diluted oxidant) diluted fuel⁵⁰ configuration which is described in the following section in relation to biogas and bioliquids.

Dilution and preheating of reactants lead to three main emergent features which unambiguously identify igni-diffusive structures.⁵⁰ They are wider than the typical reaction zone of a diffusion flame; the region of the maximum heat release not correspondent to the stoichiometric condition and the pyrolytic region, typically present in a standard diffusion flame, is absent. Results were also confirmed by DNS analysis carried out by Swaminathan and coworkers.^{53–55}

Due to very different characteristics from a conventional combustion process, MILD combustion may be considered a true paradigm shift in the field of "combustion" processes. As such, some critical issues were evidenced that make it difficult to accurately model the process. These issues mainly concern chemical kinetics and kinetic/turbulence interactions. The increase of characteristic times of fuel oxidation made new features and unexpected behavior of kinetic conversion emerge which are reproduced with difficulty by available kinetic models, optimized on the basis of experimental results mainly collected in standard conditions. In addition, the high characteristic

reaction times make MILD combustion related to low Da (<1). This requires the review of assumptions and models used for reactive fluid-dynamic modeling of these processes.^{26,56,57}

The numerical modeling of such a regime must carefully consider the turbulence/chemistry interaction, and detailed kinetic mechanisms must be used. The adoption of primitive-variable-based methods (such as tabulated chemistry approaches) or reactor-based models (EDC or PaSR) were reported in the literature as the optimal ones to treat the previous issues related to MILD reactive structure modeling.^{56,58}

In addition, the internal gas recirculation configuration, used for several MILD reactors, implies high contents of absorbing and emitting species (H_2O and CO_2) recirculating in the combustion chamber, which leads to a nontrivial modeling of the radiative heat transfer as well.²⁵ These features make the modeling of MILD combustion even more challenging and interesting for the scientific community.

Despite the lower maximum temperature and higher residence times than the ones of conventional combustion processes, the effectiveness of MILD combustion in a wide range of power and power density is guaranteed, as discussed in reviews^{14,27,59} and archival papers^{8,34,43,60} as well as in the outcomes of international research projects funded by international entities.⁶¹ This is also confirmed by its utilization in gas turbine (e.g., sequential combustion)⁵⁹ or reheating furnaces³² as a small set of examples. Indeed, in conventional combustion processes, the maximum temperature is obtained in the section of the combustion chamber where the heat release occurs, which is a small fraction of the entire volume of the combustion chamber. Differently, in MILD combustion, the lower temperature and heat release occur nearly homogeneously in the whole combustion chamber.

A few more comments have to be devoted to the NO_x kinetic mechanism. In MILD combustion conditions, the main flame-based system NO_x route (NO_x thermal) is drastically reduced due to diminished temperature peaks and a uniform low temperature field within the combustion chamber.^{62–64} Many authors refer to NO emissions as mainly attributable to the prompt mechanism,⁶⁵ that instead is responsible for about 5% of the NO_x formation in a conventional flame.⁶⁶ However, in MILD combustion, N_2O - and NNH -intermediate mechanisms⁶⁴ (relevant for temperatures below 1800 K) become significant for NO production. In particular, the N_2O -intermediate pathway plays an essential role in fuel-lean and high pressure conditions, while the NNH pathway becomes relevant under hydrogen-enriched fuel mixtures. Therefore, the integration of these submechanisms is essential to model the NO formation under MILD conditions.^{67–69}

For fuels containing N species, the N-fuel route to NO cannot be avoided, given the scarce dependence on the system temperature, while it can be controlled modulating the local mixture equivalence ratio toward fuel-rich conditions.^{62–65}

Nonetheless, many authors claimed under MILD operating conditions that NO reburning chemistry gains relevance with respect to conventional combustion systems. In particular, Nicolle and Dagaut⁷⁰ pointed out a relevant reburning chemistry during the reactants mixing process prior autoignition, with NO reconverted back to $HCN-NH_3$ reacting with CH_i radicals.

The presence of H_2O and CO_2 from recirculated exhaust gas may modify the temperature field to more uniform and homogeneous conditions through enhanced radiation and higher thermal capacities with respect to N_2 . It can

simultaneously alter the radicals pool with a net chemical inhibiting effect of NO production routes relevant in MILD condition. It has to be underlined that H_2O has a more effective thermal/chemical impact on the NO_x route with respect to CO_2 .⁷¹

Furthermore, NH_2 radicals in recirculated flows, derived from prompt/fuel- NO_x routes, may promote further De- NO_x chemistries⁶⁴ through reactions $NH_2 + NO$. On the other hand, many works suggest that N radicals, conventionally involved in NO_x thermal routes at elevated temperatures, may act as NO reversion to N_2 at lower temperatures.⁷²

Indeed, MILD combustion operating temperature falls in a typical temperature window compatible with NO_x selective noncatalytic reduction as a conventional postcombustion treatment, with an enhanced role of recirculated H_2O that may extend the characteristic De- NO_x range.^{64,73}

3. BIOGAS CONVERSION IN MILD COMBUSTION

Plenty of papers in the literature are focused on biogas compositions and their dependence on the process and raw feedstock used for their production.^{6,74–76} Typical compositions from different biogas sources are summarized in Table 1. Their

Table 1. Example of Typical Compositions of Biogas in Dependence of Their Derivation^{74–77}

Species		Anaerobic digestion	Landfill biogas	Biomass pyrolysis
CH_4	vol%	53–70	30–65	10–30
CO_2	vol%	30–50	25–47	35–40
CO	vol%			15–30
N_2	vol%	2–6	<1–17	
O_2	vol%	0–5	<1–3	NA
H_2	vol%	NA	0–3	1–10%
Higher hydrocarbon	vol%	NA	NA	1–3
H_2S	ppm	0–2000	30–500	<1000
NH_3	ppm	<100	0–5	NA
Siloxane	$\mu g/g$ -dry	<0.08–0.5	<0.3–36	NA

common feature is the high content of diluents, such as CO_2 and N_2 , that strongly reduces the biogas calorific value, not enabling for their direct use in standard combustion processes. Low calorific values lead to unstable behaviors which do not allow for effectively sustaining premixed nor diffusion flames. Therefore, biogas composition is directly related to combustion efficiency.

One of the issues that triggered the development of the MILD combustion concept was the need for providing the market with efficient technologies for low calorific value fuels, due to the increasing lack of traditional resources.^{10,78}

Looking at the literature available on MILD combustion, it is evident that biogas compositions meet the requirement for their use in MILD combustion applications. Indeed, the high CO_2 and N_2 content makes the fuel react where local conditions reach high levels of dilution.

In the following, key findings on biogas and surrogate mixtures reported in the literature are used to point out the controlling kinetics in MILD combustion which is responsible for comprehensive features of this combustion regime, taking also into account the presence of minor species. In addition, the effect of the high concentration of diluent species on local reaction kernels has been discussed by means of the analysis of a steady asymptotic reactive structure.

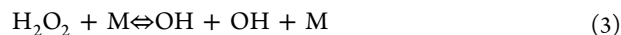
3.1. Biogas Kinetics in Diluted Conditions. Looking at biogas where the main components are CH_4 and N_2 , results obtained by de Joannon and coworkers^{79–83} can be considered as references to highlight the possible characteristics of fuel conversion in MILD combustion conditions. Indeed, they studied the oxidation kinetic of methane in the presence of high dilution levels both in 0D^{81–83} and 1D^{80,84} configurations using several gases as diluents.

What was demonstrated is that in complex kinetic mechanisms, where several kinetic pathways are active at the same time and compete each other, such competitions are stressed, as a consequence of the overall slower reaction rates caused by high amounts of diluents. Interestingly, such a competition leads to very characteristic dependences of fundamental combustion parameters, such as ignition delay or steady combustion limits, on process variables.

A typical example of the peculiarity of these working conditions is the dependence of ignition delay (t_{ign}) of CH_4 on T_{in} .

As shown in Figure 2, t_{ign} shows a dependence on T which resembles the negative temperature coefficient dependence

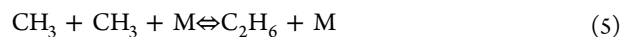
route leads to the formation of a methoxy radical derived from the oxidation of a methyl radical. At this temperature, the radical branching mechanism relies on the following reactions:



At temperatures higher than 1100 K, the typical branching reaction is



In the temperature range corresponding to the invariance of t_{ign} with T , two main effects occur in the diluted case. The production of OH radicals by means of reaction channels (1–3) decreases in rate while the OH high temperature channel is not fully active yet. The net effect is a reduction of the OH radical available for fuel oxidation despite the inlet temperature increase. At the same time, the CH_3 recombination channel (reaction 5) gains relevance and subtracts radicals from the oxidation channel, acting as a sink for CH_3 .



Of course the range where t_{ign} is independent of temperature depends on the operative condition considered. Indeed, by identifying the mechanism responsible for such peculiar behavior, it is important to point out the effect of process variables on the reactivity and kinetics in the intermediate T region. For example, the equivalence ratio has a small relevance in fuel-lean conditions, whereas a stronger effect has been recently evidenced in fuel-rich conditions.⁸⁵

In relation to the potential composition of biogas, it is worth noting that also the presence of other species influences the observed behavior. More specifically, the presence of other diluent species, namely, CO_2 and H_2O , has a significant impact on the oxidation kinetics both for their role as colliders in three-body reactions and for their direct involvement in chemical reactions.^{83,84} Elaborating on a large database of experimental evidence collected in controlled conditions in elementary reactors, Sabia et al. thoroughly discussed the relevant role of such species in branching reactions of hydrogen⁸⁶ and hydrocarbon oxidation.^{79,84,87} They showed that, in the intermediate T range, the ignition delay varies on the basis of diluent molecules in the reacting mixture. More specifically, as shown in Figure 2, CO_2 and H_2O have a third body efficiency higher than those competing to other species, such as N_2 , both for reactions 1 and 5, thus further delaying the shift to high temperature branching. In addition, in the case of CO_2 , its high concentration enhances the depletion of the H radical in the high temperature range through reaction 6



H_2O has an even higher impact. Indeed, its third body efficiency in reaction 1 is generally considered six times higher than the CO_2 efficiency which becomes relevant also at high temperatures. A high third body efficiency is also recognized for reaction 5. Moreover, at high temperature, also the reaction



contributes to the depletion of H radicals, inducing a further increase of the ignition delay in the intermediate temperature range.

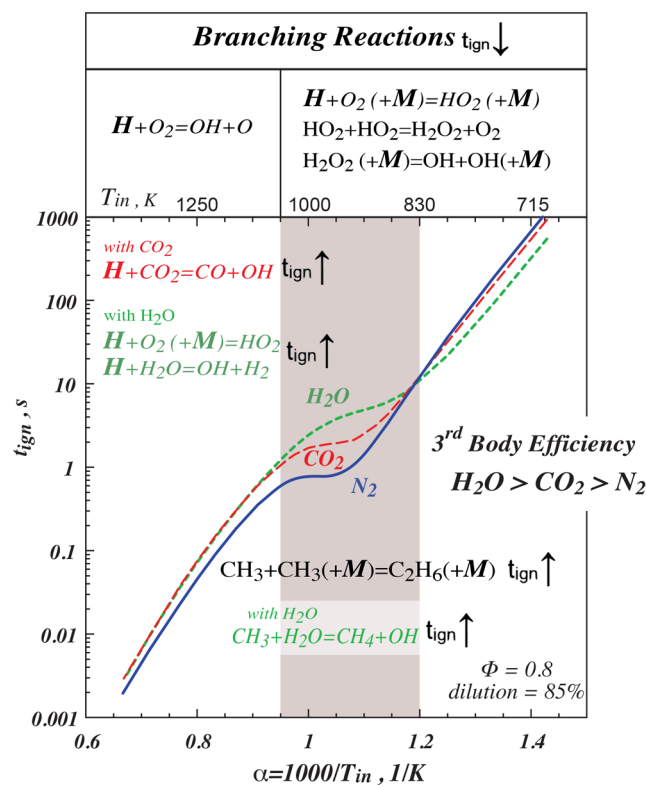


Figure 2. CH_4 ignition delay evaluated at $p = 1$ atm for different diluents.

typical of linear hydrocarbons with a number of carbon atoms higher than 5. This behavior, predicted only by few kinetic models,⁸⁰ was also experimentally detected by Sabia et al.⁷⁹ It is well explained in Figure 2 where the key reactions for each temperature range are reported.

Before and after the region of negative temperature coefficient, even though the relative weight of reactions are different from standard case, the branching is related to the same set of reactions active in the standard case. Thus, for temperatures lower than 830 K, the main methane oxidation

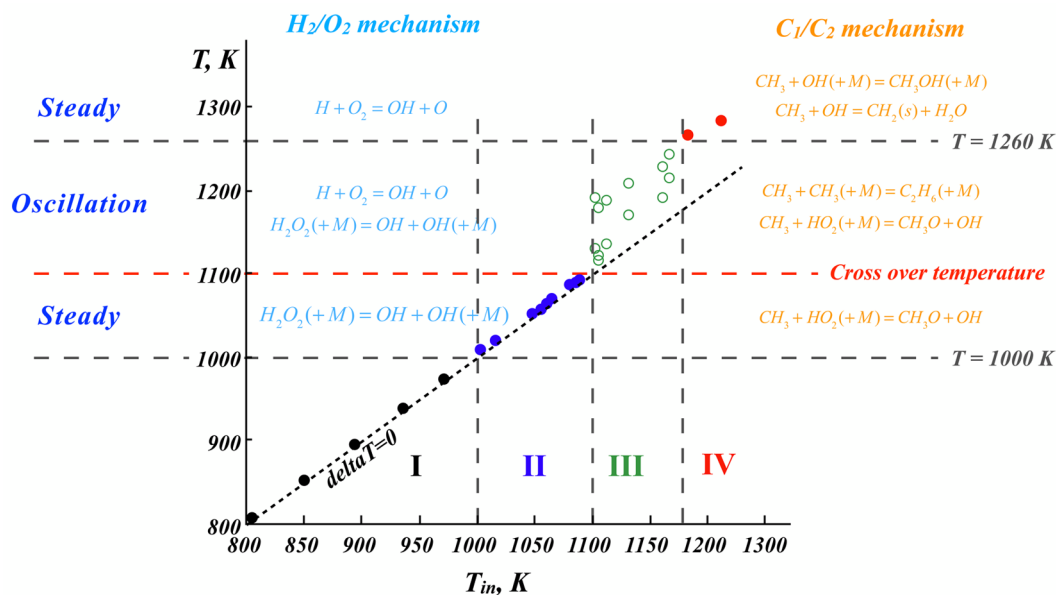


Figure 3. JSFR reactor temperature vs T_{in} for methane at dilution level of 90% and stoichiometric equivalence ratio⁸⁷

The competition among the different kinetic channels also affects the typology of ignition and the combustion regime that can be stabilized. Sabia et al.⁷⁹ experimentally measured temperature profiles in tubular flow reactors evidencing and confirming the effect of competing mechanisms that have been discussed before. They identified, among the others, a slow combustion regime featuring a very low temperature increase. In this case, the system reactivity is dampened by a sink of methyl radicals in the recombination channel, forming C_2 species. This is what happens also in the first part of a temperature rise occurring in a standard fully developed combustion regime.

In the case of biogas derived from the pyrolysis process of biomass, the presence of other reactive species, such as small hydrocarbons and H_2 , affects the behaviors discussed so far. Indeed, studying the oxidation of a biogas, composed of C_2H_4 , C_2H_6 , CH_4 , CO , and CO_2 , Sabia et al.⁸³ pointed out that the presence of C_2H_6 and C_2H_4 enlarges the region of the stable combustion regime, because these species support the establishment of high temperature reaction channels. This was also shown by Vasavan et al.⁸⁸ that evaluated the ignition delay in MILD combustion conditions of methane in the presence of higher molecular weight hydrocarbons and CO_2 about 10% lower than the one evaluated for the pure methane. Also in this case, Sabia et al.⁸³ highlighted that the kinetic mechanisms were not able to reproduce the experimental data and that the discrepancy increases when CO_2 and H_2O are used as diluents.

The peculiar effects induced by the presence of massive amounts of third body species and the role of higher molecular weight species in the reactive pool during reaction onset have been identified as key issues over the years, since the fundamental studies on MILD combustion began, and so far, they are not yet definitively clarified. Indeed, in several papers, Sabia and coworkers discussed the need of improving the kinetic models starting from the simplest building blocks of oxidation kinetics, such as H_2 oxidation,⁸⁶ which are not able to reproduce the experimental data when the oxidation occurs in the presence of a huge amount of diluent, typical of MILD combustion. More specifically the authors underlined how the presence of high amount of diluents, which are mainly involved in three-body

reactions, makes the weakness of third body efficiency modeling emerge.⁸²

Fürst et al.,⁸⁹ applying a methodology based on uncertainty quantification of kinetic parameters identified by means of an impact factor ranking of reactions, strongly improved the prediction of the data set of Sabia and coworkers, not taking into account the third body efficiency aspect.

As expected, the presence of H_2 in the biogas affects the balance of branching reactions shifting the high temperature branching to lower temperatures, thus reducing the negative temperature coefficient (NTC) region with respect to the one of methane. Similar results were found by Ning et al.⁹⁰ in their studies on ignition delay of syngas. In their paper, the authors confirmed the effect of CO_2 as a third body in the branching reaction of H_2/O_2 kinetic schemes.

3.2. Dynamic Behavior in Biogas Combustion. The concurrent effect of H_2/O_2 branching mechanisms and CH_3 recombination channel is also responsible for dynamic behaviors related to thermo-kinetic oscillation detected in a continuous flow reactor which represents a clear example of very peculiar behavior emerging in diluted combustion. The first observation of this dynamical behavior was reported in 2005 by de Joannon et al.⁸²

To describe the role of different kinetic oxidation pathways in these processes, as shown in Figure 3, the operative temperature measured in the reactor has been reported as a function of the inlet temperature of premixed reactants T_{in} . Four peculiar T_{in} regions were identified on the diagram. They help in the identification of controlling kinetics.⁸⁷ In most of the T_{in} range, a unique steady state operative temperature is reached (regions I, II, and IV). Instead, region III delimits a temperature range where oxidation instabilities occur. In this region, two reaction temperatures, the minimum and the maximum value measured during oscillation, have been reported for each T_{in} . After the thorough experimental and numerical analysis carried out on simple 0D and 1D configurations already discussed so far, it was possible to definitely assess that dynamic behaviors are related to the kinetic competition between the two main reaction routes of

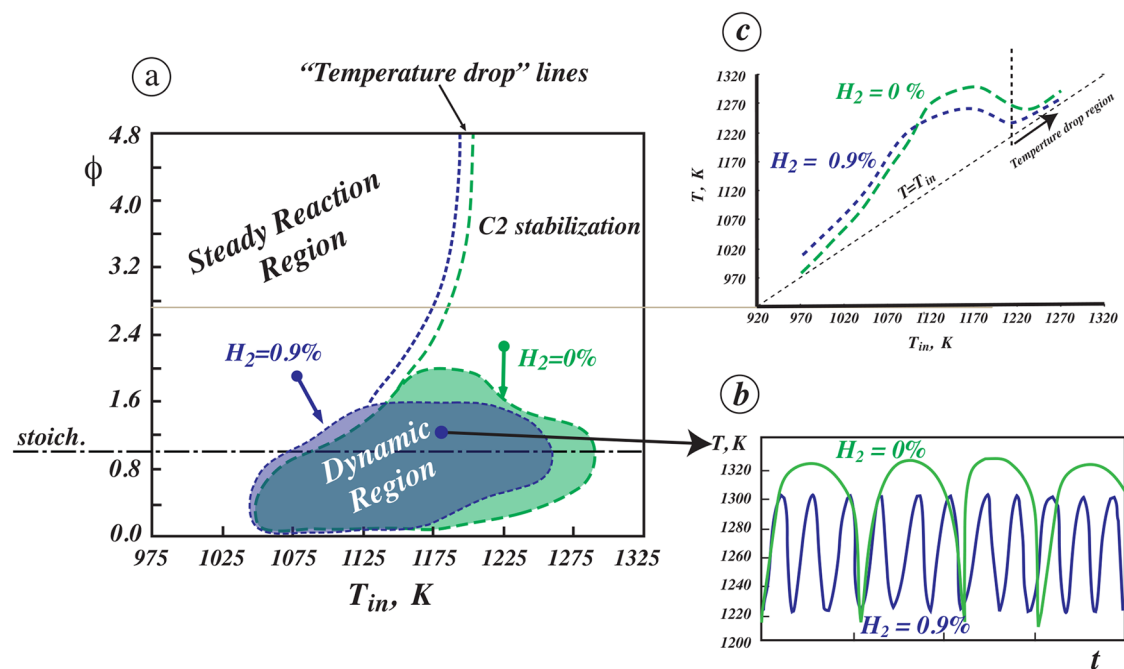


Figure 4. (a) T_{in} vs ϕ map of behavior for diluted methane miming biogas with H_2 (blue) and without H_2 (green). (b) Example of temporal temperature profiles during oscillations collected in conditions. (c) Reactor temperature vs T_{in} at $\phi = 2.8$.

hydrogen and carbon chemistries already identified as responsible for the NTC behavior observed in the ignition delay

The main competing reactions of H and C species are summarized in Figure 3, on the left and on the right side of the experimental points, respectively. Also in this case, dynamic behavior arises in the temperature range which corresponds to the transition from intermediate to high temperature mechanisms both for H and C oxidation routes. More specifically they start when the intermediate and high temperature branching reactions of the H_2/O_2 system are both active, and their rates are of the same order of magnitude. Nevertheless, production rates are limited by the availability of radicals which, in turn, should derive from the C chemical channel through the CH_4/CH_3 dehydrogenation/oxidation. On the other hand, in this temperature range, CH_3 partially sinks in recombination species. Consequently, a radical subtraction occurs limiting the temperature increase needed for the establishment of a stable oxidation regime based on high temperature branching. Depending on the presence of a suitable heat sink, the consequent temperature decrease may open the C_2 oxidation channel thus leading to another temperature increase and giving rise to a temperature oscillation event.

It is very important to point out here that, in the standard combustion condition, the cross over temperature (Figure 3) identifies the condition where the high temperature branching overcomes the slower intermediate temperature radical branching, via H_2O_2 dissociation.

Sabia and coworkers^{81,82,91} demonstrated that the oscillation region extends in a relatively wide range of temperature and mixture composition as well described by the T/ϕ maps reported in Figure 4a (green color refers to pure methane as fuel molecule). Figure 4b reports one of the temperature oscillation typologies identified by the authors. Only lately, Stagni et al.⁹² were able to experimentally reproduce these dynamic behaviors confirming the role of carbon and hydrogen kinetics in these processes by means of time-resolved chemical sampling.

A further peculiarity highlighted on the map, which supports the attribution of controlling kinetic mechanism, is the existence of the temperature drop line in the region above the dynamic area. As shown in Figure 4c, for a fixed equivalence ratio above the dynamic region, the reactor temperature increases with T_{in} up to a specific T_{in} value that is called the temperature drop value. At inlet temperatures higher than this drop value, the reactor temperature increase drops to a low, nearly constant value, independent of T_{in} in the temperature range explored by the authors. The profile of the temperature drop values vs ϕ identifies a temperature drop boundary. The authors demonstrated that above this boundary the temperature increase is damped by the methane recombination channel, which leads to the stabilization of C_2 species.⁸²

The understanding of the chemical and physical underpinnings of such a dynamic behavior is very relevant both to foresee possible occurrences and to find effective solutions to avoid unwanted and potentially dangerous instabilities in combustion systems. On the basis of data summarized so far, Li et al.⁹³ carried out a numerical analysis identifying the potential loop mechanism among chemical kinetics, heat transfer, and acoustic oscillation responsible for combustion instabilities in full scale systems.

It is interesting to consider the effect of trace species present in biogas, like hydrogen, on the competing mechanisms, also responsible for dynamic behavior. In Figure 4, the results collected in the presence of H_2 were reported.⁸¹ It is possible to see that the presence of a small amount of H_2 in the order of 1% sensibly narrows the dynamic occurrence region. More specifically, the presence of H_2 changes the balance between H and C channels which is reflected in a reduction of the dynamic region of high temperature and fuel lean condition bound. Accordingly, the temperature drop boundary slightly shifts toward lower temperature, and the oscillation frequency increases in the presence of H_2 (Figure 4a, b).

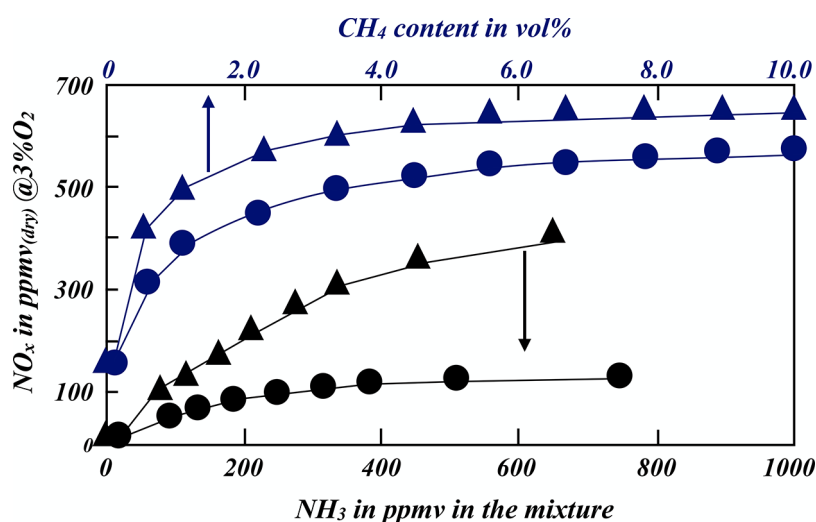


Figure 5. NO_x emission in MILD combustion of biogas in the presence of ammonia as impurities in dependence of ammonia concentration (black symbols) and in dependence of CH₄ concentration.^{100,102}

3.3. Effect of Minor Species in Biogas: NH₃, H₂S, Siloxane. One of the major issues in the direct use of raw biogases is the presence of minor undesired species that can negatively affect combustion efficiency, such as NH₃, H₂S, and siloxanes.^{6,74,97} Their presence is critical because they can lead to the formation of pollutants species that are dangerous not only for the environmental impact but also for the combustion apparatus itself.

Ammonia is currently under the attention of the combustion community as a potential hydrogen carrier and, therefore, one of most relevant and intriguing candidates as a future carbon-free fuel.⁹⁸ Of course, the amount of NH₃ in biogas is limited from tens to hundreds of ppm, and it has to be considered not for its energy content but only as a potential source of NO_x. Indeed, the main drawback of ammonia combustion is the formation of NO_x, so that downstream systems for their abatement are often taken into account. MILD combustion of pure ammonia has been proven to be very effective in terms of NO_x formation.^{19,20} In these studies, the formation of NO_x in the MILD combustion regime is lower than 100 ppm for stoichiometric conditions and decrease even to less than 10 ppm toward fuel-rich conditions, depending on the operating conditions. NO_x concentration further decreases in the presence of water.⁹⁹ However, in the case of ammonia in biogas, interactions among C and N kinetics have to be taken into account to have a reliable prediction of NO_x yield. Although experimental data in the literature is exponentially increasing, interactions of these two kinetics are not completely disentangled, especially in the temperature range typical of MILD combustion. Indeed, if available kinetic models are acceptable to reproduce the high temperature oxidation of ammonia, they fail in modeling experimental data in the low temperature range, while this interval is gaining even more relevance in many industrial applications.

The effect of a few ppm of ammonia on NO_x formation during oxidation of biogas, natural gas, and syngas was explored by Zieba and coworkers^{100,101} and Slefarski¹⁰² in a flameless burner. Results by these authors are summarized in Figure 5, where NO_x concentration measured in the flues gases of a flameless burner have been reported. In the case of a fixed biogas composition, containing 6.5% of CH₄ in volume and lean conditions (black symbols), they pointed out that even a very low concentration of NH₃ in biogas makes NO_x suddenly increase. Then, the slope of

the curve strongly decreases, and NO_x slightly increases with a further increase of ammonia concentration. They also identified the same behavior by increasing the CH₄ concentration for a fixed initial ammonia concentration of 700 ppm (Figure 5, blue symbols). In this case, it was also shown that the presence of CO and H₂ slightly affects ammonia conversion to NO_x. In a very recent work by Sorrentino et al.,¹⁰³ the same trend has been obtained studying MILD combustion in methane/ammonia in a cyclonic burner in a wider range of NH₃ (from 0% to 100%). A kinetic analysis carried out on available models highlighted that the main backbone of the C and N oxidation mechanism proceed independently from each other and only compete for radicals.^{100,103}

As is well known, the presence of H₂S in biogas represents a serious problem due to its toxicity and its oxidation to SO₂ and SO₃ during the combustion process in standard conditions, which are highly corrosive for appliances and have a high environmental impact. H₂S is also present in natural gas in small quantities and is one of the main component of sour gases, where the concentration reaches levels as high as 30%. Therefore, despite the few experimental data present in literature, oxidation and pyrolysis mechanisms have been developed for identifying the conditions for minimizing the undesired species. On the other hand, due to the need of widening the fuel palettes, the attention has been raised on the conversion of H₂S to H₂ and S₂ in sour gases for energy conversion application. Gupta et al.¹⁰⁴ proposed an optimized Claus process where the thermal step was replaced with a flameless/MILD burner, whose fluid-dynamic and thermodynamic characteristics make the H₂S conversion to S₂ and water very efficient for lean H₂S concentrations lower than 15%. Indeed, low and nearly homogeneous temperatures of a MILD combustion burner was demonstrated to favor S₂ formation.^{104,105} Even though the concentration of H₂S in biogas is much lower than such a value, their use in MILD combustion has the potential to reduce the impact of sulfur undesired compounds. The challenge of the research in this field is to find the optimal condition to operate MILD combustion burners for minimizing the formation of pollutant species taking advantage of staged combustion which often occurs in MILD combustion burners of long residence time and in the presence of CO₂ in

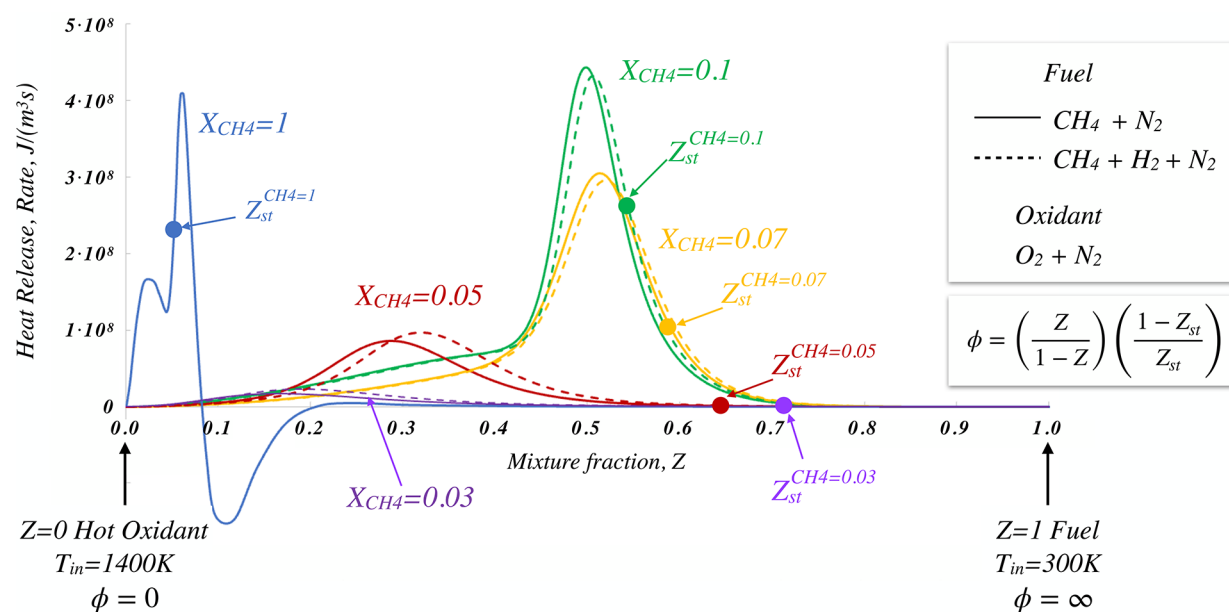


Figure 6. Heat release profiles in a steady mixing layer highlighting igni-diffusive structure characteristic of MILD combustion.

biogases that can further favor the formation of H_2 when it is present in a certain amount.

Siloxanes represent a category of Si compounds present in biogas derived from landfill and wastewater treatment processes¹⁰⁶ that are very critical for combustion systems because they suddenly decompose, leading to the formation of silica particulates which, in turn, deposit on the walls of combustion chambers, on sensors, and on possible electric devices causing serious problems.^{107–110} In addition, particulates emitted in the atmosphere can have severe impact on the environment and human health.¹¹⁰ Due to all these issues, the major indication coming from the literature is to remove siloxanes from biogases prior to their use. There are no studies carried out on the fate of siloxanes in MILD combustion, but some comments can be done on the basis of information available from standard combustion processes. Siloxanes affect the ignition time of CO/ H_2 mixtures and of methane. Indeed, it was proved that 100 ppm makes the ignition delay of syngas and hydrogen decrease.¹¹¹ As a consequence, they can support an easier stabilization of MILD combustion. However, the characteristic temperatures of MILD combustion favor the formation of condensed SiO_2 , in respect to gaseous SiO , which is instead present above 2000 K, due to equilibrium established with SiO_2 at such a high temperature.¹⁰⁸ The presence of dilution could reduce the dimensions of SiO_2 aggregates¹¹⁰ which are responsible of deposition, leading to a potential lower tendency to deposit thus limiting the related criticalities in terms of thermal efficiency reduction and operational safety of combustion chambers. Moreover, in order to avoid their emission in the atmosphere, the high H_2O content generally present in the flue gases of MILD combustion can be used to eliminate them by means of a water condensation abatement technique, as was shown in the literature in relation to other particulate matters present in flue gases.^{112–114}

3.4. Effect on Elementary Reactive Structures. The analyses of reactive structures stabilized in diluted and preheated conditions in a steady diffusive mixing layer as asymptotic cases are very useful to understand the very peculiar behavior of MILD combustion. Indeed, in the literature, these reactive structures

became reference cases for classification of possible typologies of local structures in MILD combustion processes.^{35,49,50,52,54,115}

Moreover, they can be used as canonical structures to represent the thermochemical state in tabulated chemistry models where steady diffusion flamelets are no longer valid.^{56,116}

The preheating and dilution of reactant flows locally impinging led to very peculiar reactive structures, exhibiting the three emerging features discussed in Section 2: (1) They widen with respect to the standard case. (2) They show an uncorrelation between heat release and stoichiometric mixture fraction and an absence of pyrolytic regions. This is very clear from Figure 6 that reports the heat release rate profiles versus mixture fraction (Z) occurring in a steady mixing layer, where undiluted and diluted methane mixes with a hot oxidant stream at $T_{in} = 1400$ K.⁴⁹ Profiles obtained without and with 5% of H_2 added to the methane stream are reported with solid and dotted lines, respectively. The relation between Z and ϕ has been also reported in the figure to make easily identifiable relevant ϕ values.

Analyzing the solid lines, i.e., in the absence of hydrogen, the typical profile for the undiluted conditions, on the left of the diagram, shows the maximum of heat release in the region where the maximum heat release takes place. As expected, fuel dilution shifts Z_{st} toward the fuel side ($Z = 1$) at increasing fuel dilution (i.e., at decreasing X_{CH_4}). Heat release initially follows the same trend, but from $X_{CH_4} = 0.1$, the position of the maximum of heat release (Z_{max}) shifts in the opposite direction with respect to the Z_{st} , i.e. toward the oxidant side ($Z = 0$). This behavior is a typical marker of the igni-diffusive structure that characterizes MILD combustion. As can be expected, the uncorrelation between Z_{max} and Z_{st} was also shown for the condition where the oxidant flows are preheated and diluted.⁹⁴ Furthermore, the presence of CO_2 in place of N_2 in the fuel does not significantly affect the reactive structures both in the steady and igniting mixing layers, as shown by Vasavan et al.⁸⁸

The presence of a small amount of hydrogen in biogas does not significantly affect the overall behavior of the reactive structure, just slightly reducing the displacement between Z_{max} and Z_{st} . This is well shown by the dashed lines in Figure 5 which

refer to a biogas mixture containing different concentrations of CH_4 and 5% H_2 . Different effects were identified considering the temporal evolution of the igniting mixing layer. Indeed, also in MILD combustion, differential diffusion of hydrogen and hydrogen-derived radicals can have a significant impact of the evolution of heat release in the mixing layer even though such effects emerge for H_2 concentrations higher than 10%.⁸⁸ Therefore, it has to be taken carefully into account in the transport equation along with an appropriate evaluation of the Schmidt number.⁹⁵ As the overall effect, Mardani and Tabejamaat⁹⁶ numerically showed that in a jet-in hot coflow configuration in turbulent conditions increasing H_2 up to 20%, the reaction volume reduces and increases the turbulence decay. However, such a hydrogen concentration in methane refers to a hydrogen-enriched biogas and not to a raw biogas.

4. BIODERIVED COMBUSTIBLE LIQUIDS

A wide category of bioderived liquid combustible products, deriving from different sources and produced by consolidated and newly developed technologies,¹ is now available. However, despite the different feedstocks and processes, in general, biogases are constituted by a limited number of chemical species present in different proportions; this is not the case of these liquid products whose chemical compositions strongly varies among fuels and includes many, often hardly identifiable, compounds (for example, bio-oils obtained by pyrolysis are constituted by organic acids, alcohols, aldehydes, ketones, furans, pyrans, sugars, and other minor species). Following the categorization reported by Seljak et al.,¹ liquid produced by means of a thermal, chemical, or biochemical process can be divided in two main categories: biofuels and bioliquids. The first class refers to liquid products upgraded to meet the requirements of specific applications and are generally direct substitutes for traditional liquid fuels. In contrast, the second class refer to liquids used as they are produced. They often require the adaptation of existing technologies and plants to the specific bioliquid rheological and chemical characteristics unless a suitable truly fuel-flexible technology is in use.

Biofuels have the advantage of being mostly transparent to final users. However, the need for an energy-demanding complex transformation process, that also adds an inherent degree of inefficiency (along with an effective or equivalent emission of GHG), partly hinders environmental benefits. Therefore, as in the case of biogas, the direct use of raw bioliquids would have significant advantages in terms of environmental impact and in terms of their usage. Therefore, in the following, attention is given to bioliquids behaviors and their requirements for MILD combustion, showing potentials and perspectives. Biofuels, with particular regard to alcohols, are also discussed in relation to the results already present in the literature.

Highly variable and complex chemical compositions of bioliquids not only strongly affects their combustion, both in terms of overall efficiency and pollutants emissions, but also their chemical–physical characteristics. Possible differences in viscosity, surface tension, and boiling temperature may heavily impact the atomization process and subsequent evaporation and mixing stages. Optimization of these strongly entwined subprocesses represents one of the major challenges in bioliquid utilization in combustion.¹¹⁷ This is why a short analysis of atomization and evaporation issues of bioliquids in MILD combustion has been reported in the following.

Despite the limited number of papers available in the literature on the use of biofuels with MILD combustion, the proof of the effectiveness of the process is well demonstrated, with particular regard to the use of alcohols.^{13,18} Very scarce are the works carried out on bioliquids, even though, due to its now well assessed characteristics, MILD combustion is among the technologies which are considered to have great potentials in easily spreading their use in energy and power.

4.1. Impact on Atomization and Droplet Evaporation.

The use of bioderived combustible liquid presents in MILD combustion the same possible corrosion phenomena as in traditional combustion systems operated with bioliquids. In addition, the higher viscosity of bioliquids with respect to the ones of traditional (fossil) liquid fuels may create additional atomization issues. Indeed, higher viscosities are associated with greater average dimensions of the liquid droplets, both for a greater stability of the liquid column, leading to a delayed primary breakup process. On top of that, even a moderate increase in viscosity strongly reduces significantly secondary atomization processes.

Lehto et al.¹¹⁸ reported that typically viscosity and surface tension of fast pyrolysis bio-oils are 50 times and 30% higher than those of light oil (#2 oil) leading to a Sauter mean diameter (SMD) of the resulting spray at least twice that of a fossil light oil. In this respect, the atomization process is a crucial point for a successful deployment of biofuels, regardless of combustion mode, MILD or traditional. In the case of MILD combustion, as mentioned before, both the peculiar reacting conditions and the absence of high temperature concentrated reaction zones relax in some respect the criticality of atomization and mixing stages.

Different strategies can be used to reduce the viscosity thus improving the dispersion of fuel in the oxidant stream, such as fuel preheating. Such a procedure may, on the other hand, favor the formation of deposits and other heavy species that may result in a degradation of the atomization process and/or a greater pollutant emission.^{119,120} In general, the heating of the fuel before its injection is a costly operation and, in the case of this particular class of liquids, may lead to results difficult to predict due to their variable compositions. For all these reasons, it is generally suggested to use air-assisted processes (or air blast nozzles) to atomize them. Indeed, it is well known^{121,122} that air-assisted nozzles are the most tolerant injectors to the variability of liquid properties and that they ensure a good atomization quality (i.e., a low SMD) in a wide range of operating conditions. Internal and external mixing air blast atomizers have been suggested as a suitable means of injecting, with good efficiency, bioderived combustible liquid.¹²⁰ Airblast systems are preferable because they do not require a high pressure air stream and may be used also in smaller scale applications.¹²² It is worthwhile to note that in internal combustion engines, with the exception of gas turbines, the use of such injectors is not easy.

Internal mixing injectors, based on the “flow blurring” atomization concept proposed by Simmons and Agrawal,¹²³ have been suggested as a suitable choice for the injection of bioliquids and biofuels. The main characteristics of this type of injector is the absence of narrow passages and an orthogonal impact geometry of the air and fuel streams that ensures a strong interaction among them and promotes the fragmentation of the liquid column. In addition, the possibility to regulate independently the two streams permits operation with good performance in a wide range of liquid flow rate and ability to adjust the atomization process to the liquid characteristics.

Gonçalves de Azevedo et al.^{124,125} showed that using a flow blurry injector an almost uniform droplet size distribution could be achieved. They successfully tested an injector developed according to the flow blurry concept, comparing soy biodiesel and hydrous ethanol combustion performances in a compact flameless combustion chamber.

Overall, however, even the presence of larger droplets and lower temperatures in the combustion chamber is overcome by the residence time characteristics of MILD combustion, of the order of seconds, which are longer than droplet lifetime, which are on the order of tenths of milliseconds.^{126,127} In addition, the low temperature gradient makes the evaporation process change from an onion peeling to distillative mechanism.¹⁰ Indeed, the characteristic times of the process allow for molecular diffusion inside the droplet itself thus inducing differential evaporation of different components according to their volatility. This mechanism may be detrimental in a standard combustion process where the release of fuel from the droplets has to occur rapidly and in a well-specified region with respect to the reaction zone to avoid a massive formation of particulates and of other partial-oxidation species. On the contrary, a distillative evaporation does not alter the efficiency of the combustion process in MILD conditions due to highly diluted and preheated local conditions which promote a distributed autoignition that is substantially independent of available fuel. Instead, major issues could arise from the formation of carbonaceous particulates during droplet evaporation, as was shown by thermogravimetric analysis by Ramachandran et al.¹²⁸ studying pyrolysis oil oxidation. However, the authors showed that the higher the temperature (up to 850 °C) was, the lower the char yield was. Differently from standard combustion, due to an almost uniform temperature field in a MILD combustion chamber, droplets less likely experience the low temperature regions which promote char formation. Moreover, carbonaceous particulates possibly formed during evaporation can be more easily oxidized due to long residence times and the virtual absence of “cold spots”. This points out again the “clean/clearing” feature of MILD combustion.¹⁰

4.2. Alcohols. As it is well known, alcohols are a particular class of bio-derived liquids since they have been largely used in traditional combustion systems, and there is vast literature on the physical and chemical underpinnings of their combustion processes. On the other hand, the literature on alcohol behavior in MILD combustion is rather limited, in particular, for practical application. As a general indication, fundamental studies on alcohol behavior in MILD conditions confirmed the main outcomes obtained for gaseous fuels, when prevaporized fuels were considered. Remarkably, also in this case, it was possible to identify the critical temperature needed for the stabilization of MILD combustion.¹⁸

Following the same approach used for biogas, the analysis of ignition delay evaluated in diluted conditions points out different dependencies on T_{in} in relation to the range of T_{in} considered. This is clearly shown in Figure 7 where ignition delays evaluated in stoichiometric and adiabatic conditions as function of T_{in} have been reported for methanol, ethanol, and butanol alcohols.

The dependence of t_{ign} on T_{in} highlights the different oxidation pathways in the different temperature ranges. Ignition delays of ethanol and butanol show a negative temperature coefficient behavior in the range between 950 and 1100 K. In the same temperature range, t_{ign} of methanol shows a drastic change in slope. Even though this aspect is only briefly discussed in the

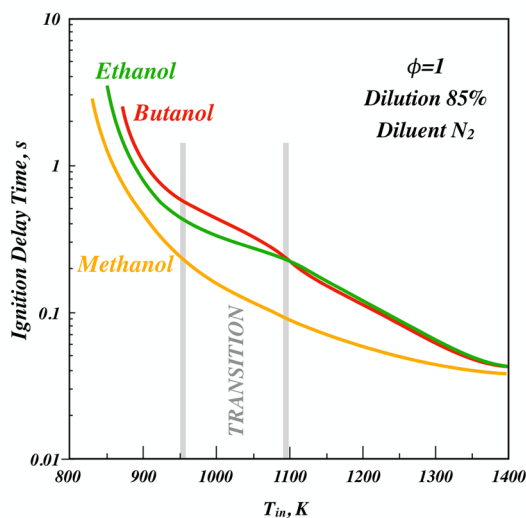


Figure 7. Ignition delay time of methanol, ethanol, and butanol evaluated in MILD combustion conditions.

literature for alcohols, because it is not relevant for standard combustion conditions, it can be commented on for the basis of the analogous trend found for small hydrocarbons in MILD conditions. Indeed, in accordance with what happens for hydrocarbons and discussed before for the biogas, this temperature range corresponds to a transition from low/intermediate to high temperature kinetics, where the competition of C species and H_2/O_2 kinetic routes is strongly stressed in MILD combustion conditions.

Also in the case of alcohols, this competition affects and “modulates” in some extent the branching routes, highlighting the existence of regions where a lighter dependence on temperature is present. This effect is emphasized by the peculiar operational conditions.

Moreover, despite that C species reaction routes are different for different categories of molecules, the branching mechanism mainly relies on the H_2/O_2 oxidation pathway, and in this temperature range, the intermediate temperature branching through H_2O_2 decomposition gives way to the high temperature branching reaction $H + O_2 = OH + O$. As it occurs for hydrocarbons, in this temperature range, thermo-kinetic oscillations can be numerically identified in temporal temperature profiles evaluated in a premixed reactor. Ariemma et al.¹⁸ presented the first exhaustive experimental and numerical analysis on MILD combustion of methanol, ethanol, and butanol carried out in a cyclonic burner shown in Figure 1, they discussed in detail this pivotal issue.¹⁸ More specifically, they experimentally identified the minimum temperature for the stabilization of the process that corresponds to about 1100 K for the three alcohols studied both in premixed and nonpremixed conditions. By means of numerical analysis, they showed that the stabilization temperature corresponds to the crossover temperature. Before reaching such a temperature, instabilities occur that lead to the extinction of the oxidation process. Overall, Ariemma et al.¹⁸ showed that methanol, ethanol, and butanol have similar behaviors in MILD combustion in term of efficiency and pollutant formation. NO_x levels fall in the 1-digit range for the most of the conditions the authors explored, following the molecular weight of the reference alcohol. Analogously, CO levels are below 10 ppm almost in the whole equivalence ratio range and are also independent of considered alcohols.

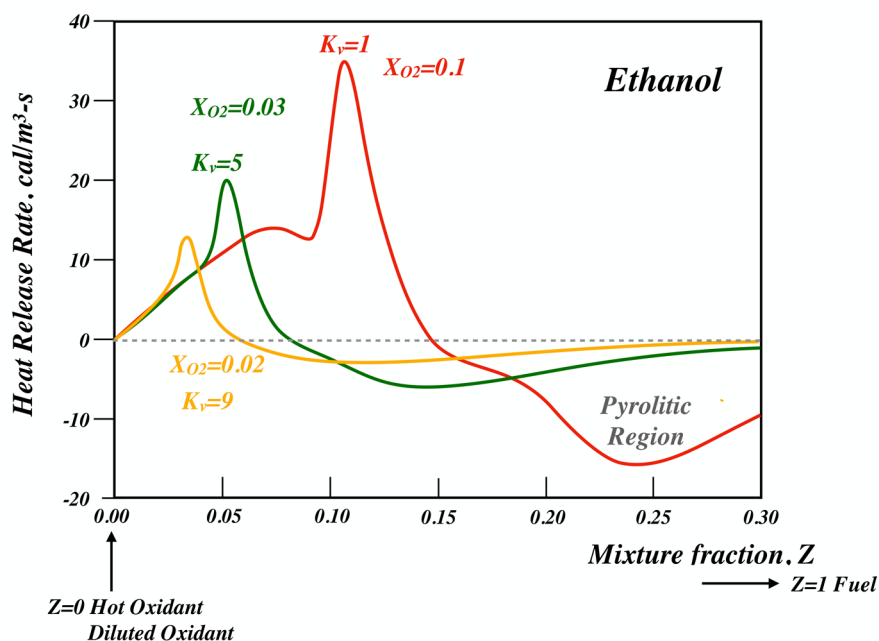


Figure 8. Heat release profile as a function of mixture fraction in a 1D steady diffusive layer for ethanol oxidation.¹³¹

It is worth noting that by adding naphthalene to ethanol in order to increase the heating value of ethanol of about 9%, Gupta et al.¹²⁹ demonstrated that neither NO_x nor CO are affected in the MILD condition, keeping their very low overall values. The same outcome was pointed out in the cases of heptane/ethanol and kerosene/ethanol mixtures.¹³

The analysis of the MILD combustion reactive structures on liquid fossil fuels were carried out for the first time by de Joannon et al.¹³⁰ Differently from the case considered for biogas, where the presence of diluent was considered on the fuel side, the structures of interest are also those deriving from strong local mixing of heat and mass recirculation of exhaust gases and undiluted fuel, generally identified as a hot oxidant diluted oxidant configuration.⁵² Cha et al.¹³¹ reported the numerical analysis of a reacting 1D mixing layer of ethanol and vitiated air at different levels of recirculation ratios and initial temperatures. They showed that the resulting heat release profiles, reported in Figure 8, widen, decrease in intensity, and lose the pyrolytic part when MILD combustion conditions are reached, confirming the peculiar characteristics of the reactive structure occurring in this combustion regime. Despite in this feeding configuration (HODO) both Z_{st} and Z_{hmax} shift toward the oxidant side, the displacement between them is still present. The same conclusions were reached by Ariemma et al.¹⁸ evaluating the reacting 1D mixing layer for methanol, ethanol, and butanol.

The widening and disappearing of the pyrolytic region, typical of MILD combustion, was experimentally and numerically verified in the case of prevaporized ethanol in a jet-in-hot-coflow configuration also by Medwell et al.,¹³² i.e., in time-dependent reactive structures. Interestingly, the authors also pointed out that the Lift-Off Height (LOH) is independent of the fuel used when the system attains a MILD combustion regime. In contrast, LOH is quite sensitive to the fuel composition outside this regime. This behavior was related to the different kinetics controlling the stabilization process in the two different cases. Indeed, the authors affirm that while in the standard case the stabilization of the reactive structure depends on the chemical kinetics directly involving the fuel molecule, in the case of the

MILD combustion regime it relies on the H_2/O_2 mechanism, thus confirming the relevance of hydrogen high temperature branching in the stabilization of the process.

So far, indication of possible behavior in MILD combustion of pure alcohols has been considered. However, hydrous alcohols are the primary product of the alcohol production chain with about 8% of water.⁸ There are no specific studies on elementary structures in the case of hydrous alcohols, but it is easy to extend the considerations reported so far also in the presence of diluent species such as H_2O in the fuel. Indeed, the overall behavior is certainly kept while the temperature ranges where the different regimes prevail may slightly change. Looking at the effect of heating value reduction on MILD combustion regime of ethanol, Karimi et al.¹³³ studied the effect of water addition on ethanol oxidation. They pointed out that the presence of up to 5% of water in ethanol favors the establishment of MILD combustion conditions. The authors affirm that this is due to the reaction $\text{O} + \text{H}_2\text{O} \rightarrow 2 \text{OH}$, where OH favors CO oxidation. A higher water content would make the MILD combustion region too narrow due to the prevailing physical and kinetic third body effects of water.

Findings, discussed so far, refer to alcohols which were prevaporized before their injection in the combustion chamber. In practical applications, liquid fuels are generally fed as spray, and the presence of droplets can very likely alter the reactive structures, in particular, if the oxidation occurs in a spatial region where fuel droplets are not yet fully evaporated.

In the case of alcohols, the high volatility of the fuel coupled with increased radiative heat transfer produces droplet lifetimes of the same order of magnitude (few ms), with only a moderate increase, despite the lower temperatures, with respect to those of standard combustion processes.¹²⁴

The presence of droplets in ethanol oxidation in the jet-in-hot-coflow configuration leads to a multistructured reaction zone with outer and inner regions,¹³⁴ this latter due to vaporization of the fuel droplet and mixing of fuel and coflow which entrains along the lift-off height. In the inner reaction zone, fuel reacts in hot and rich conditions which leads to

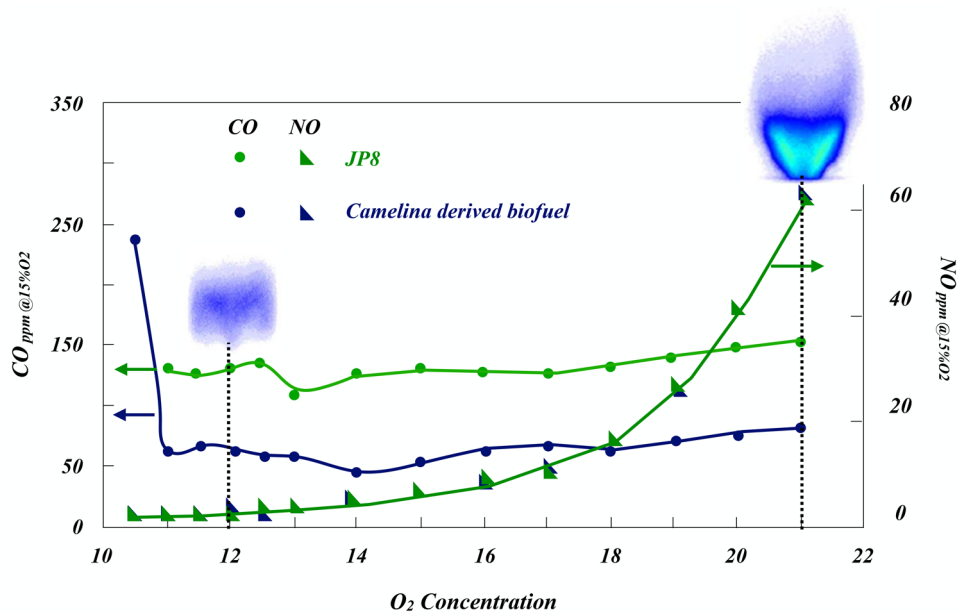


Figure 9. CO and NO_x emissions measured in a swirl burner working in MILD combustion conditions for JP8 and camelina-derived biofuels.¹⁷

intermediate species that oxidize in the outer reaction zone. The presence of swirler¹³³ as well as the use of combustion chamber geometry that allow very high recirculation ratios make the differences in inner and outer flame regions to almost disappear, as can be seen in the combustion region detected in the swirl burner by Gupta and coworkers^{29,129} and Kumar et al.¹³⁵ both working in MILD combustion conditions.

4.3. Other Biofuel and Bioliquids Use in MILD Combustion. So far, there is a very limited number of works carried out on bioliquids in MILD combustion systems. This lack is even more evident when burners working in almost realistic conditions, i.e., preserving at least in part the complexity of real systems, are considered.

However, with respect to the fundamental chemical issues of the bioliquids combustion, some general indications may be derived using existing knowledge. As it has been deeply discussed so far, MILD combustion relies on local autoignition of fuel/oxidant mixtures derived from the high velocity flow field, responsible for gas recirculation. This makes the process dependent on branching reactions of a H₂/O₂ mechanism which is not strictly linked to the fuel molecule structure. Previous behaviors explain the high fuel flexibility of MILD combustion systems. Due to the high variability and complex composition of bioliquid, MILD combustion and, in general, exhaust gas recirculation (EGR)⁸ can be considered among the best technologies for a wide use of this category of fuels.

One of the leading research groups dealing with bioliquids studied the beneficial effect of exhaust gas recirculation,⁸ showing the decrease of NO_x, CO, and soot formed during combustion of glycerol, as representative of highly oxygenated waste-derived fuels, in an experimental gas turbine. The authors verified that in correspondence of 18% of exhaust gases recirculated, with respect to the fresh reactants stream, all the concentrations of monitored noxious species halve.

The benefits of EGR were also studied by Singh and Lear¹³⁶ which numerically pointed out the effect of EGR in lowering the NO_x and CO levels during combustion of rapeseed methyl ester.

Kumar et al.¹³⁵ studied the combustion of biodiesel in truly MILD/flameless conditions in a combustor developed and

tested with gaseous and liquid fuels. They evidenced that using an asymmetric fuel injection strategy, with respect to the symmetric injection geometry they used along the years, a significant improvement of the combustion characteristics of biodiesel can be achieved. Indeed, they were able to stabilize the MILD combustion of biodiesel also for very lean conditions corresponding to an equivalence ratio of 0.2. The best condition was found for an equivalence ratio of 0.9 which however corresponds to high CO and NO_x emissions. The authors attributed this undesired behavior to the atomization and evaporation of biodiesel.

Excellent results were obtained by Gupta et al.¹⁷ by using prevaporized camelina-derived biofuel compared with JP8, and analyzing the reactive process from standard to colorless distributed combustion/MILD conditions in a swirl burner.

As shown in Figure 9, both CO and NO_x are within the allowed limit. More specifically, NO_x for JP8 and camelina coincides and decreases up to a 1-digit range by decreasing the O₂ concentration and shifting to MILD combustion, as shown by the OH* chemiluminescence images reported in the figure. CO measured for the biofuel is even lower than that measured for JP8 almost in the whole O₂ range explored. It only increases for O₂ lower than 11% probably due to the rising of process instability.

5. CHALLENGES AND PERSPECTIVES

It is undeniable that advanced combustion technologies and alternative fuels will play fundamental roles in sustaining the energy transition toward the net zero emission scenario. MILD combustion, together with biofuels, can be effective candidates to participate in this critical transition.

Indeed, the high fuel flexibility, already very well assessed in the literature, along with its characteristic to be a very clean process, makes MILD combustion perfectly meet the requirement to be part of technologies contributing to the energy mix. On the other hand, biofuels are part of the circular streams for energy and material recoveries, considered essential approaches to reach the net zero emission target.

The synergistic use of MILD combustion and biofuels can be extremely advantageous, coupling the potential use of whatever carrier is derived from waste and biomasses, produced using many different processes having variable composition and features according to the production chain and to seasonal and geographical variability, with efficiency.

The critical overview reported in previous paragraphs has shown that the use of biogas and liquid biofuels in MILD combustion systems can be considered a well-assessed process. In this case, the main challenge, which can be considered a crucial point in any combustion process, is the need of the kinetic models to take a step forward in reproducing the fuel conversion in nonconventional systems. Further considerations have to be added in the case of raw bioliquids, whose complex compositions are responsible for their limited direct application in whatever combustion system.

However, large scale deployment of biofuels MILD combustion still requires additional research efforts. In particular, the following issues and challenges will have to be faced in the near future:

- MILD combustion processes are essentially distributed autoignition processes. A lack of knowledge on the actual behavior of the many components of the raw fuels and of their interactions during combustion does exist. A significant research effort is still needed to define the chemical kinetics of components of raw fuels, in particular, in temperature ranges characterizing MILD combustion. As a matter of fact, the high level of dilution and the strong velocity gradients used to ensure a good mixing between the recirculated flows and the fresh reactants correspond to a low Damköhler number. This is the main reason for the onset of distributed combustion. However, this also entails a very strong entanglement of chemical and physical subprocesses and a further degree of complexity with respect to standard combustion processes. This is even more relevant in the case of biofuels since their chemical composition may be significantly different from the traditional fossil fuels, and it is, typically, associated to lower reactivity.
- As discussed, the modeling of third body efficiency in kinetic mechanisms is still an open issue that affects results especially in MILD combustion. It becomes even more challenging in the case of bioliquids. Indeed, they are constituted by molecules characterized by high polarity. Sabia et al.¹³⁷ demonstrated that molecules with higher polarity have higher third body efficiency, strongly affecting the onset of the oxidation process in the temperature range of interest of MILD combustion. Even if this is not limited to the MILD combustion case, in this case, being the reaction stabilization mechanism essentially due to the autoignition onset, a stronger third body effect may even more reduce the fuel reactivity and extend the residence time needed for fuel conversion. Therefore, a strong effort in modeling the third body efficiency is required and would have a significant impact on combustion kinetic mechanism modeling efficiency.
- MILD combustion has been also used in large scale burner and furnaces (up to tens of MW for single burner). However, it requires proper modifications of the overall plant design and a thorough redesign of the burner geometry. Many new concepts to attain the proper burning conditions in a wide range of operating

conditions (in wide working load ranges) have been proposed and demonstrated. However, the actual experience of MILD combustion of biofuels is relatively modest, and a research and development effort is still required to define geometries and flow configurations capable of ensuring a satisfying load flexibility at large scale plants.

- One final comment concerns the assessment of emission performances of MILD combustion plants using biofuels (either raw or upgraded ones). It is well known that MILD burners have very low NO_x emissions and particulate emissions in the submicrometer size range that are much lower than traditional combustion ones. However, a clear description of the complex relationships between pollutant emissions and biofuel composition, operating conditions, and thermal load is far from being available.
- On the basis of the peculiarity of MILD combustion, its utilization with biofuels can also be evaluated in other processes or from a different point of view, as new perspectives.
- It has been said that raw biofuels are subject to significant oxidation/degradation processes, and their storage is not recommended. In addition, they are typically corrosive, due to their acidity, and this poses materials problems both for their storage and feeding to the combustion devices. The inherent fuel flexibility and the tolerance to the inert species present in the inlet streams to a MILD combustion burner, provided that a proper level of recirculation of enthalpy and exhausts is ensured, enable to envisage a direct coupling of thermal treatment of biomass and waste processes to the MILD combustion burner itself. This may represent an optimal configuration allowing a direct use of gaseous and vaporized products with several beneficial effects. First, the enthalpy content of the stream from the thermal treatment stage can be totally recovered and used to help attain MILD combustion conditions. Moreover, there will be reduced fouling issues and no need for condensation/post-treatment stages and, furthermore, no need for condensed liquid pumping and atomization systems.
- MILD combustion reactors may be regarded as “temperature-tailored” reactors in that their internal temperature, that is almost constant across the reactor itself, is essentially determined by the stoichiometry of the oxidation reaction.^{20,37} This peculiar feature paves the way for the possibility to use a MILD combustion reactor as an in-flux noncatalytic thermal reformer to produce hydrogen from gaseous and vapor fractions of thermal biomass degradation processes. The concept may be even improved designing the burner as a two-stage reactor aimed at separating the fuel reforming stage and the oxidation of reformed fuel. In this way, the possible production of high molecular weight products, potentially leading to the eventual formation of pollutants, may be significantly reduced.

6. CONCLUDING REMARKS

MILD combustion is an ideal thermo-chemical conversion process to produce heat and power from a wide variety of gases and liquids produced starting from biomasses and wastes, also in their raw conditions.

This is possible due to the inherent peculiar microstructures that are realized in MILD combustion reactive processes, characterized by a distributed diffusion-controlled local auto-ignition (named ignidiffusion). They reveal unconventional features of the oxidation region when high dilution and preheating levels of the reactants are achieved. Such distinctive aspects are not dependent on the fuel nature and were confirmed also for several types of biofuels. This structure corresponds to the apparent macroscopic uniformity of the process and gives rise to a highly stable reacting process. Strongly related to the previous mentioned characteristics, there is a kinetic common feature of a MILD combustion regime that emerges from the results reported in this review. The chemical evolution of fuel oxidation is essentially dominated by the branching reactions of the H_2/O_2 mechanism which are not strictly linked to the fuel molecule structure making MILD combustion a highly fuel-flexible process. This characteristic makes the process truly fuel flexible with respect to conventional combustion methodologies which, instead, are strictly related to the combustion characteristics of single molecules.

Oxidation process stability, pollutant emissions, and overall performances achievable in MILD combustion conditions are independent of the used fuel in a wide range of reactant compositions and thermal loads. Several results, from both the fundamental and practical points of view, are available for utilization of biogas and alcohols. On the contrary, very few data are still available on bioliquids. However, it emerges that the specific conditions occurring in MILD combustion may be also beneficial for bioliquid combustion, not only for the inherent fuel flexibility but also for the occurrence of distributed reactions that relaxes the need for an optimal coupling between the liquid atomization process and flame front location. In the future, a significant effort is required in such directions.

Finally, it is worthwhile to stress that there are several open questions and possibly very interesting perspectives in the use of biofuels in MILD combustion which solicit the interest of researchers. The outcomes of future research on this topic can open excellent opportunities to effectively support and facilitate the energy transition to meet a net zero emission target.

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Notes

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