

Combustion characteristics of small alkanes on noble metal surfaces in pre-mixed homogeneous-heterogeneous hybrid systems

Junjie Chen

Department of Energy and Power Engineering, School of Mechanical and Power Engineering, Henan Polytechnic University, Jiaozuo, Henan, 454000, P.R. China

* Corresponding author, E-mail address: jchengn@163.com, <https://orcid.org/0000-0001-6708-071X>

Abstract

In conventional thermal combustion fuel and air in inflammable proportions are contacted with an ignition source to ignite the mixture which will then continue to burn. Flammable mixtures of most fuels are normally burned at relatively high temperatures, which inherently results in the formation of substantial emissions of nitrogen oxides. In purely catalytic combustion systems, there is little or no nitrogen oxides formed in a system which burns the fuel at relatively low temperatures. The present study is focused primarily upon the combustion characteristics of small alkanes on noble metal surfaces in pre-mixed homogeneous-heterogeneous hybrid systems. The homogeneous-heterogeneous combustion characteristics small alkanes on noble metal surfaces are investigated to gain a greater understanding of the mechanisms of flame stabilization and to gain new insights into how to design pre-mixed combustors with improved stability and robustness. The essential factors for design considerations are determined with improved combustion characteristics. The primary mechanisms responsible for the loss of flame stability are discussed. The present study aims to explore how to effectively operate catalytically stabilized combustion. Particular emphasis is placed upon the catalytic combustion characteristics of small alkanes in the pre-mixed hybrid systems. The results indicate that the combustion effluent is characterized by high thermal energy and typically by low nitrogen oxides content. Precise tuning of the combustion process is needed to establish a balance between stable combustion and low emissions. Simply changing the combustor geometry to maintain near-stoichiometric ratios will not avoid nitrogen oxides formation. The catalytic reactor oxidizes substantially all of the ingested fuel and produces thermal energy. Adiabatic combustion systems, from a practical standpoint, have relatively low heat losses, thus substantially all of the heat released from the combustion zone of such systems appears in the effluent gases as thermal energy for producing power. Catalytic oxidation has the disadvantage that the physical reaction surface which must be supplied for complete oxidation of the fuel increases exponentially with decreasing inlet temperatures, which greatly increases the cost of the combustor and complicates the overall design. The operating temperature is determined by the theoretical adiabatic flame temperature of the fuel-air admixture passed to the combustor and thus is dependent on the initial temperature of the air as well as the amount of fuel contained therein. The temperature of the catalyst zone is controlled by adjusting the composition and initial temperature of the fuel-air admixture as well as the uniformity of the mixture.

Keywords: Combustion; metals; Designs; Fuels; Alkanes; Oxidation

1. Introduction

All flames can be classified either as premixed flames or as flames that burn without premixing. A widely applied thermal theory, one of the first flame propagation theories, implies that combustion proceeds primarily at temperatures close to the maximum the flame can achieve [1, 2]. A set of differential equations developed for thermal conductivity and diffusion is reduced to one equation that

yields the burning velocity value [3, 4]. Further development of the theory has been made, and computers now make most simplifications unnecessary [5, 6]. According to thermal theories, flame propagation is accounted for by heat energy transport from the combustion zone to the unburned mixture, which raises the temperature of the mixture [7, 8]. Diffusion theory assumes that thermodynamic equilibrium sets in behind the flame front at a maximum temperature and that radicals produced in this zone diffuse into the unburned mixture and ignite it [9, 10]. Both heat transport and diffusion of active particles must be considered essential for ignition. Industrial flames, including those activated in furnaces, belong to the type of turbulent diffusion [11, 12]. However, the theory of diffusion flames, is less advanced than that of premixed flames. Since gas intermixing is mainly responsible for the structure and the features of diffusion flames, the theory of diffusion flames operates more in terms of thermodynamics and physics than chemical reactions.

Combustion, with rare exceptions, is a complex chemical process involving many steps that depend on the properties of the combustible substance. It is initiated by external factors. The lean, pre-mixed combustor is a combustor in which fuel is premixed with air prior to combustion to form a largely homogeneous fuel lean admixture having an adiabatic flame temperature less than about 1700 °C. This differs from a diffusion flame combustor where the fuel is injected directly into the combustion zone and mixed with air during combustion [13, 14]. As a result, combustion is essentially at the stoichiometric fuel air ratio with combustion flame front temperatures as high as 2200 °C. Unlike diffusion flame combustors, lean, pre-mixed combustors avoid stoichiometric combustion and are able to inherently achieve lower nitrogen oxides emission levels. In both approaches the combustion products are modified by dilution air to achieve the desired turbine inlet temperature, however lower amounts are required in the premixed system [15, 16]. To achieve single digit nitrogen oxides emission levels in a lean, pre-mixed combustor requires operating at a flame temperature of the fuel and air admixture no higher than about 1600 °C. Unfortunately, as the flame temperature of a fuel and air admixture is decreased to little more than 1500 °C, typically combustion becomes unstable and high carbon monoxide emissions are generated [17, 18]. Thus, legal compliance requirements placed on both nitrogen oxides and carbon monoxide make the operating window for a lean, premixed combustor quite limited, even operating at rich enough conditions where nitrogen oxides levels are as high as 20 milligrams per cubic meter. Accordingly, various types of independently controlled pilots are employed in lean, pre-mixed combustors to extend the stable operating window below 1500 °C to minimize nitrogen oxides emissions [19, 20]. However, if the pilot is a flame some nitrogen oxides are produced by it and often there is little or no corresponding improvement in overall carbon monoxide emissions [21, 22]. Consequently, there is a very small operating window in which both nitrogen oxides and carbon dioxide emissions meet environmental regulations.

Physical processes that transfer energy and mass by convection or diffusion occur in gaseous combustion. In the absence of external forces, the rate of component diffusion depends upon the concentration of the constituents, pressure, and temperature changes, and on diffusion coefficients, which are a measure of the speed of diffusion. The lean, pre-mixed combustor is familiar with staging of combustion to achieve low emissions over a wide engine operating range where lower turbine inlet temperatures are required. However, staging has practical limits both in terms of its ultimate ability to reduce emissions as well as the level of complexity introduced into the design of the combustor system [23, 24]. Even with this complexity, most lean, premixed combustors cannot reliably achieve ever lower standards for carbon monoxide and nitrogen oxides emissions, for example below 20 milligrams per cubic meter. The lean, pre-mixed combustor is also familiar with the use of catalysts to both improve combustion stability and reduce emissions in combustors [25, 26]. A catalyst is applied to the inner surface of a diffusion flame combustor for the purposes of flame stabilization. In the event that the primary combustion zone is extinguished, a re-ignition of the combustor can be achieved if the rich

fuel-air mixture can contact a sufficiently hot catalytic surface [27, 28]. The catalytic surface must be non-continuous so that the flame created by the contact of the rich fuel and air mixture to it will leave the liner wall and ignite the bulk combustor flow [29, 30]. The discontinuity in the catalyst coating is identified in those regions where film cooling of the combustor would be non-existent, the surfaces prior to or directly over the film cooling air inlets [31, 32]. A catalyst applied to a diffusion flame combustor should also tend to reduce unburned hydrocarbons and carbon monoxide emissions [33, 34]. The combustor is completely film cooled, due to the temperature of combustion, and that the flame, or reactants, contact the catalytic surface [35, 36]. It is therefore necessary to allow achievement of both lower nitrogen oxides emissions and lower carbon monoxide emissions in lean, pre-mixed combustors. These reductions are possible in a lean, premixed combustor both with and without open flame pilots [37, 38]. It is also therefore necessary to provide a means to operate at leaner conditions if carbon monoxide emissions are the limiting factor in the design, allowing lower firing temperatures and the associated incremental reduction of nitrogen oxides.

In conventional thermal combustion, fuel and air in inflammable proportions are contacted with an ignition source to ignite the mixture which will then continue to burn. Flammable mixtures of most fuels are normally burned at relatively high temperatures, which inherently results in the formation of substantial emissions of nitrogen oxides. In purely catalytic combustion systems, there is little or no nitrogen oxides formed in a system which burns the fuel at relatively low temperatures. The present study is focused primarily upon the combustion characteristics of small alkanes on noble metal surfaces in pre-mixed homogeneous-heterogeneous hybrid systems. The homogeneous-heterogeneous combustion characteristics small alkanes on noble metal surfaces are investigated to gain a greater understanding of the mechanisms of flame stabilization and to gain new insights into how to design pre-mixed combustors with improved stability and robustness. The essential factors for design considerations are determined with improved combustion characteristics and flame stability. The primary mechanisms responsible for the loss of flame stability are discussed. The present study aims to explore how to effectively operate catalytically supported thermal combustion. Particular emphasis is placed upon the catalytic combustion characteristics of small alkanes on noble metal surfaces in pre-mixed homogeneous-heterogeneous hybrid systems.

2. Methods

Recent studies on gas-phase micro-burners and hydrogen production using homogeneous combustion as an energy supply route have revealed the feasibility of such an operation, on the one hand, but the susceptibility of gaseous flames to radical and thermal quenching, on the other, arising from confining flames in small devices [39, 40]. The high temperatures associated with homogeneous combustion also limit the choice of materials for device fabrication. Given the small scales of these devices and the large surface-area-to-volume ratios, catalytic combustion appears to be a promising alternative to gaseous combustion. Elimination of flames makes integration into compact devices easier. The lower temperatures, compared to those in homogeneous combustion, generated via catalytic combustion can significantly widen the operating window of these micro-devices [41, 42]. Fuel-lean catalytic operation can eliminate carbon monoxide formation, without coking of the catalyst. Even though catalytic combustion has been studied intensively, both experimentally and theoretically accurate and reliable rate expressions for the combustion of alkanes are not readily available, but are highly desirable for design and optimization studies of microchemical devices and possible homogeneous-heterogeneous hybrid systems, namely thermally stabilized combustion [43, 44]. Surface reaction rates have traditionally been modeled with one-step rate expressions of a power-law form [45, 46]. Such rate expressions provide no insight into the physics and their regime of applicability is ill defined [47, 48]. As a result, the wide scatter in the parameters is not surprising, making the usefulness

of power-law rate expressions questionable.

Langmuir-Hinshelwood type kinetic rate expressions are used to describe reaction rates. An advantage of a Langmuir-Hinshelwood type kinetic rate expression is that reaction orders could vary from positive to negative as operating conditions change. The assumptions made in Langmuir-Hinshelwood models rely mainly on intuition or at best on limited knowledge of reaction energetics. Adequate description of experimental data via a Langmuir-Hinshelwood model is typically considered as validation of the assumptions made. If the model fails to describe data, a different set of assumptions is made and the process is repeated. This methodology does not necessarily guarantee that the underlying assumptions are correct and that the derived rate expression captures the physics of the reaction mechanism over a broad range of conditions, which is typically delimited by the available experimental data. Since the coverages of surface species vary considerably with operating conditions and within the reactor itself, so do the rate-determining step conditions. Microkinetic models that describe all relevant elementary reaction pathways are needed to overcome the limitations discussed above and provide insights into the mechanistic pathways. A number of microkinetic models are available for simple fuels on noble metal catalyst surfaces. The foremost challenge in microkinetic model development is the estimation of kinetic parameters. Computational fluid dynamics simulations using microkinetic models for design and optimization are a central processing unit-intensive task. Hence, reduced kinetic models and one-step rate expressions for the combustion of small alkanes on noble metal surfaces are desirable. The quest for better and more efficient catalysts for commercial processes is an ongoing journey for the chemical industry. Tools such as high-throughput screening using microreactors are being developed to this end, but analysis of data from such experiments is challenging. A simple theoretical model with a few catalyst-based parameters, which can be estimated from first principles calculations or simple experiments, can be valuable for catalyst screening.

The combustor pressure in this work is assumed to be constant. This greatly simplifies the calculations because it means that the momentum equation does not have to be solved. As a result, a relatively large number of combustor configurations can be investigated in a reasonable amount of time. While pressure loss in micro-channels can be an important performance parameter because of its impact on the efficiency of thermodynamic cycles, the losses associated with the optimum combustor configurations identified here are less than a few percent. Note, however, that pressure losses for combustor configurations away from the optimum combustor configurations can be much larger and their accurate determination will require inclusion of the momentum equation. The use of silicon as a combustor material imposes two additional constraints on the simulation. The first is that the equivalence ratio be less than or equal to 0.6 so that the adiabatic flame temperature remains below the melting point of silicon. The second is that the temperature dependence of silicon's thermal conductivity be included. Silicon's thermal conductivity changes by more than a factor of 6 over the expected range of temperatures and is computed using a power law fit to tabulated data. Six million evenly spaced cells are used to discretize the gas flow path and structure. The cells are numerous enough to capture gradients accurately no matter where the flame is stabilized in the passage. The number of computational cells is kept constant as the length of the combustor is reduced. Adequate resolution is verified by checking that doubling the mesh size does not influence the results of the computations. The reference length scale used here is the reaction zone thickness associated with a freely propagating flame that does not interact with a structure. The temperature profile used to compute the reference length scale is determined by setting the Nusselt number for heat transfer between the gas and the structure equal to zero. The reference velocity is the laminar flame speed associated with a freely propagating flame. It is also computed by setting the Nusselt number equal to zero. Thermal coupling between the reacting gas and the structure has important implications for the design of efficient, high power density combustors. The overall efficiency of a micro-channel

combustor can be written as the product of a chemical efficiency and a thermal efficiency.

The chemical efficiency is defined as the ratio of the total heat evolved in the reaction to the total heat available if the reaction is to go to completion. In this work, this is equivalent to the fraction of the fuel that gets consumed before the mixture exits the micro-channel. The thermal efficiency is defined as the ratio of the total heat actually delivered to the flow exiting the channel divided by the total heat evolved by the reaction. This is computed from the axial temperature profile through the micro-channel, the heat loss to the environment, and the mass flow rate. The power density is defined the energy release rate due to combustion divided by the combustor volume. A catalyst is deposited on the inner surfaces of the combustor with particular attention to the areas of highest interaction with combustion gases, not the flame or reactants. For catalyst effectiveness, it is important that the catalyst be located within the combustion zone on the combustor wall in areas that are not blanketed by film cooling air. As the combustion zone and film cooling within the combustion zone are altered due to different operational conditions, it may be necessary to coat the entire combustor to assure that the catalyst at any given time is in an effective area. Backside cooled liner walls are preferred since such systems do not flow significant cool air on the flame tube side of the wall where the catalyst is applied. While a lean, pre-mixed combustor that does not utilize film cooling is ideal for this design, a total elimination of film cooling is not required. It is critical that if film cooling is employed, that the operational non-film cooled area, that is the area of the combustor not film cooled at an operational condition where nitrogen oxides or carbon monoxide reduction is desired. In addition, it is critical to this design that catalyst cooling, generally accomplished by backside cooling of the combustor wall onto which the catalyst is applied, be engineered such that the catalyst is maintained at an effective operating temperature. This temperature is at a minimum the threshold light-off temperature for the particular catalyst interacting with the particular fuel. Typical precious metal catalysts have minimum operating temperatures of approximately 400 °C. Thus, with metal liners it is desirable to place the catalyst on a thermal barrier inner coating which lines the inner surfaces of the flame tube or combustor liner. The catalyst can be applied directly to ceramic combustor liners if so equipped.

Catalytically-supported thermal combustion is achieved by contacting at least a portion of the carbonaceous fuel intimately admixed with air with a solid oxidation catalyst having an operating temperature substantially above the instantaneous auto-ignition temperature of the fuel-air admixture. At least a portion of the fuel is combusted under essentially adiabatic conditions. Combustion is characterized by the use of a fuel-air admixture having an adiabatic flame temperature substantially above the instantaneous auto-ignition temperature of the admixture but below a temperature that would result in any substantial formation of oxides of nitrogen. The adiabatic flame temperature is determined at catalyst inlet conditions. The resulting effluent is characterized by high thermal energy useful for generating power and by low amounts of atmospheric pollutants. Where desired, combustible fuel components, for example, un-combusted fuel or intermediate combustion products contained in the effluent from the catalytic zone, or fuel-air admixture which has not passed through a catalytic zone, may be combusted in a thermal zone following the catalytic zone. Sustained catalytically-supported, thermal combustion occurs at a substantially lower temperature than in conventional adiabatic thermal combustion and therefore it is possible to operate without formation of significant amounts of nitrogen oxides. Combustion is no longer limited by mass transfer as in the case of conventional catalytic combustion, and at the specified operating temperatures the reaction rate is substantially increased beyond the mass transfer limitation. Such high reaction rates permit high fuel space velocities which normally are not obtainable in catalytic reactions. The adiabatic flame temperature of fuel-air admixtures at any set of conditions is established by the ratio of fuel to air. The admixtures utilized are generally within the inflammable range or are fuel-lean outside of the inflammable range, but there may be instances of a fuel-air admixture having no clearly defined inflammable range but nevertheless

having a theoretical adiabatic flame temperature within the operating conditions. The proportions of the fuel and air charged to the combustion zone are typically such that there is a stoichiometric excess of oxygen based on complete conversion of the fuel to carbon dioxide and water. The term instantaneous auto-ignition temperature for a fuel-air admixture as used herein is defined to mean that the temperature at which the ignition lag of the fuel-air mixture entering the catalyst is negligible relative to the residence time in the combustion zone of the mixture undergoing combustion. The catalyst surface and the gas layer near the catalyst surface are above a temperature at which thermal combustion occurs at a rate higher than the catalytic rate, and the temperature of the catalyst surface is above the instantaneous autoignition temperature of the fuel-air admixture. The fuel molecules entering this layer spontaneously burn without transport to the catalyst surface. As combustion progresses, the layer becomes deeper. The total gas is ultimately raised to a temperature at which thermal reactions occur in the entire gas stream rather than only near the surface of the catalyst.

3. Results and discussion

The enthalpy contour plots in the pre-mixed homogeneous-heterogeneous hybrid system are illustrated in Figure 1 with combustion of small alkanes on noble metal surfaces. The term thermal combustion, as used herein, is understood to mean a homogeneous combustion reaction which proceeds without the aid of a catalyst. The combustion is conducted by utilizing a selectively controlled fuel-to-air ratio to achieve an approximately constant combustion temperature which is substantially above the instantaneous auto-ignition temperature of the fuel-air admixture but preferably is below a temperature that would result in the substantial formation of oxides of nitrogen. Subsequently, additional, selectively controlled air can be combined with the products or effluent from the combustion of the fuel-air admixture. The combustion effluent is characterized by high thermal energy and typically by low nitrogen oxides content. The method and apparatus thus provide for highly efficient turbine operation and quick response to changes in operation of the system with relatively little atmospheric pollution. Broadly, intake air is compressed and at least a portion of the compressed air is intimately admixed with a carbonaceous fuel [49, 50]. The resulting admixture is then passed to a temperature-controlled combustion or primary zone where it is combusted above the instantaneous auto-ignition temperature at an approximately constant temperature advantageously over a period of turbine operation in which the amount of fuel charged to the combustion zone is varied in response to power demand on the turbine [51, 52]. The fuel-to-air volume ratio is adjusted, taking into account the temperature of the gas entering the combustion zone, so that the theoretical adiabatic flame temperature of the mixture remains about constant over a wide range of fuel inputs. The effluent from the combustion zone is combined in a secondary zone with at least a portion and preferably most of the remaining compressed air charged to the turbine system. The power obtained from the gas turbine can thus be controlled without changing the temperature in the combustion zone by adjusting the overall volume of fuel-air mixture to the combustion zone and the volume of additional or bypass air or gas combined with the combustion effluent. These adjustments regulate the temperature of the gas entering the turbine and thus the power produced thereby. Since the temperature of the combustor effluent-bypass air mixture is primarily dependent on the temperature and relative amounts of combustor effluent and bypass air, it is possible to obtain a quick response of the gas turbine system to different power requirements by varying the amount of additional or bypass air combined with the combustion effluent. Further, even at low turbine inlet temperatures, low combustion temperatures can be avoided. Thus, the combustor need not operate at low temperatures which might impair performance with possible flame-out and also might result in an effluent having a high content of carbon monoxide and hydrocarbons. Similarly, avoidance of combustion temperatures significantly in excess of about 1800 °C avoids the formation of excessive amounts of nitrogen oxides during combustion.

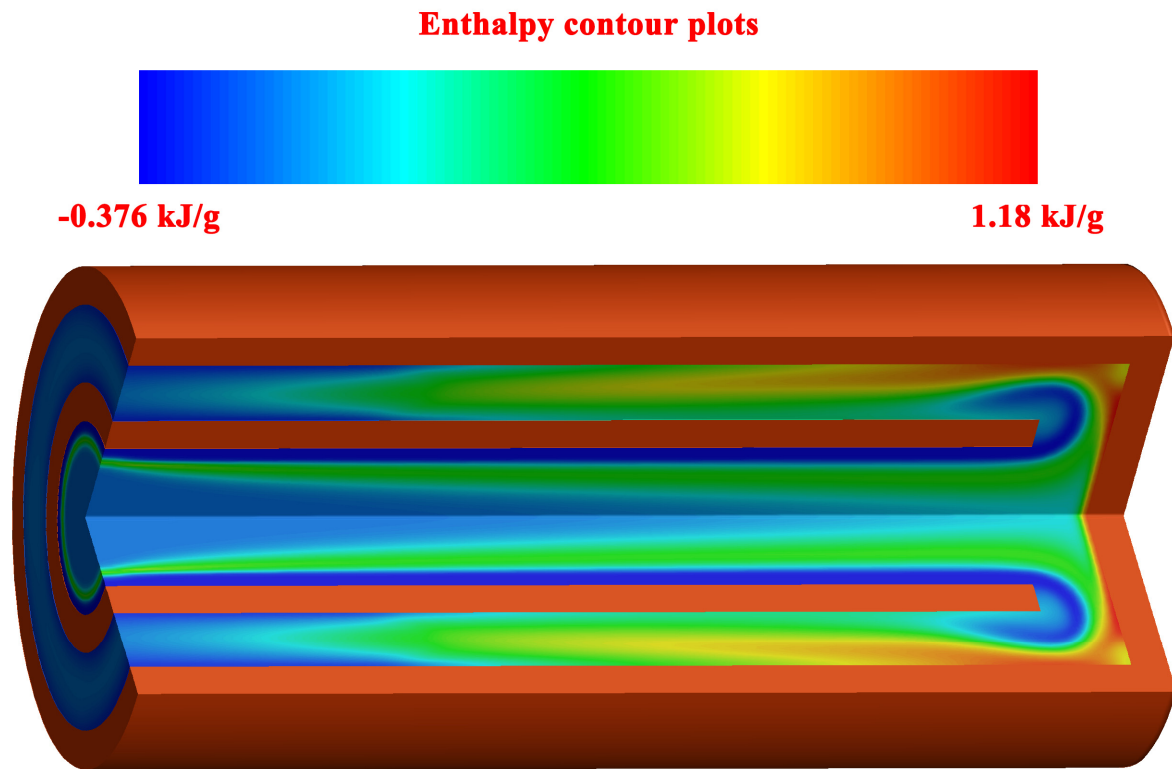


Figure 1. Enthalpy contour plots in the pre-mixed homogeneous-heterogeneous hybrid system with combustion of small alkanes on noble metal surfaces.

The temperature contour plots in the pre-mixed homogeneous-heterogeneous hybrid system are illustrated in Figure 2 with combustion of small alkanes on noble metal surfaces. The products of combustion of fossil fuels include carbon dioxide, carbon monoxide, unburnt hydrocarbons and nitrogen oxides [53, 54]. Various control schemes and hardware configurations have been used to control the concentration of such emissions while at the same time providing fuel-efficient and stable engine operation [55, 56]. Regulatory changes continue to reduce the allowable level of emissions from electric power generating plants utilizing gas turbine engines. To achieve low levels of emissions, it is necessary to establish and to maintain very lean combustion conditions. Lean combustion is known to be less stable than rich combustion, and lean-burn combustors are more prone to damaging pressure pulsations generated within the combustor. Precise tuning of the combustion process is needed to establish a balance between stable combustion and low emissions. A precisely tuned engine may be susceptible to drift over time, with a resulting increase in emissions or an increase in the level of combustion instability. One known approach to controlling the emissions from a gas turbine power plant is to run the combustor at a relatively rich setting, thereby ensuring stable combustion while generating excessive amounts of undesirable emissions. The exhaust gas is then cleaned to regulatory limits by passing it through a combustion catalyst installed downstream of the combustor in the turbine exhaust system. Alternatively, a catalyst may be used to achieve a majority of the fuel combustion, with only a final portion of the combustion being accomplished in a flame combustor located downstream of the primary catalyst. Catalyst systems are very expensive and are often used as a last resort in especially rigorous regulatory situations. The generation of nitrogen oxides emissions is directly related to the peak flame temperature in the combustor. The peak flame temperature in a gas turbine combustor can be controlled by injecting water into the combustor. The cost of the demineralized water used for water injection can be significant, particularly in areas where the supply of fresh water is limited. Accordingly, it is beneficial to limit the use of injected water to the extent possible. A radial flow catalyst element can be integrated into an aerodynamically stabilized burner to provide a catalytically

reacted fuel-air mixture for enhanced flame stabilization with catalyst temperature maintained by recirculation of hot combustion gases at a temperature high enough even for combustion of methane at ambient combustor inlet air temperatures yet at a temperature well below the adiabatic combustion temperature thus allowing burner outlet temperatures high enough for modern gas turbines. An aerodynamically stabilized combustor or burner is one wherein gas phase combustion is stabilized by aerodynamic recirculation of hot combustion products such as induced by a swirler, a bluff body, opposed flow jets, or a flow dump. Preferred are swirlers. In operation of a burner, a fuel-air mixture is passed into contact with a catalytic element for reaction thereon. The resulting reacted admixture is then admixed with the fresh fuel and air passing into the combustor thus enhancing reactivity and enabling stable combustion even with very lean fuel-air admixtures. Light-off of burners may be achieved using any conventional ignition means such as spark plugs, glow plugs, laser beams, or microwave energy. Advantageously, for ignition the catalytic element is heated electrically to a temperature high enough for fuel ignition followed by introduction of fuel and air. This not only achieves ignition but assures that the catalyst is at an effective temperature to stabilize lean combustion in the burner from the start of combustion.

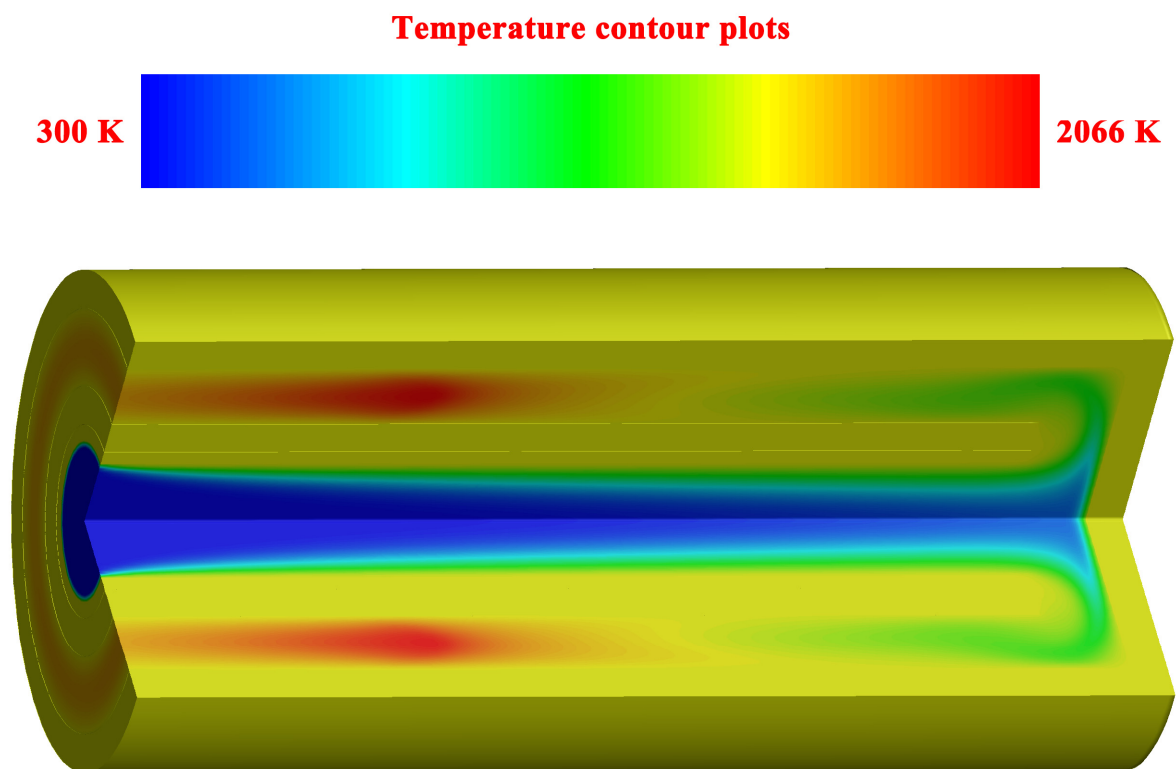


Figure 2. Temperature contour plots in the pre-mixed homogeneous-heterogeneous hybrid system with combustion of small alkanes on noble metal surfaces.

The front wall edge temperature profiles in the transverse direction are presented in Figure 3 for the pre-mixed homogeneous-heterogeneous hybrid system. Intake air in the pre-mixed homogeneous-heterogeneous hybrid system is compressed by a compressor turbine, and the compressed air then may be apportioned into at least two parts, one part of which is intimately admixed with a carbonaceous fuel and introduced into a combustion zone to be thermally combusted, preferably by homogeneous thermal combustion and a second part of which is combined with the effluent from such combustion. The relative amount of air in each part or portion is adjustable and proportionately interdependent. Attempts have been made to control the fuel-to-air ratio in conventional combustors [57, 58]. Such attempts, however, have not satisfactorily dealt with the problem of sustained low emission combustion which is responsive to variations in load on the engine and other operating

conditions [59, 60]. In fixed geometry conventional combustors which burn fuel in air at approximately the stoichiometric ratio, the hole pattern of the combustor liner is ordinarily designed for best operation of the primary or combustion zone, at nearly full load. With such apparatus, the overall fuel-air ratio decreases at light load or at idle resulting in a leaner mixture in the combustion zone, which can lead to reduced combustion efficiency and increased exhaust emissions. This problem can be overcome by using variable combustor geometry to operate the primary or combustion zone at a constant fuel-air ratio, namely close to stoichiometric at all turbine operating conditions. Although this does solve the hydrocarbon and carbon monoxide problem, it does not even address the nitrogen oxides problem. Formation of nitrogen oxides occurs at relatively high temperatures, which inevitably are reached in adiabatic combustion systems with near-stoichiometric fuel-air ratios. Consequently, simply changing the combustor geometry to maintain near-stoichiometric ratios will not avoid nitrogen oxides formation. Further, at a fixed fuel-air ratio the combustion temperature will vary accordingly to variations in the temperature of the air at the inlet to the combustor so that combustion temperature is not fixed. Flammable mixtures of most fuels, for complete combustion, normally burn at relatively high temperatures, namely above about 1800 °C, which inherently results in the formation of substantial amounts of nitrogen oxides. In the case of conventional gas turbine thermal combustors, formation of nitrogen oxides can be reduced by limiting the residence time of the combustion products in the combustion zone. However, due to the large quantities of gases being handled, undesirable amounts of nitrogen oxides are produced. Many conventional combustors, by injecting the fuel into the combustor in droplet form and separately from the air used for combustion present serious drawbacks to low pollution operation. Such a system substantially precludes very lean sustained combustion. Consequently, the combustion temperature of the droplet boundaries in the pre-mixed homogeneous-heterogeneous hybrid system will frequently be approximately the theoretical adiabatic flame temperature of a stoichiometric mixture of the fuel and air; this temperature will be substantially over 1800 °C, and typically in excess of 2200 °C. Therefore, even though the overall temperature in the combustor may be quite low and not high enough to form nitrogen oxides, the temperature near the droplet surface is typically in excess of that required to form nitrogen oxides. Consequently, nitrogen oxides forms and is present in the combustor effluent.

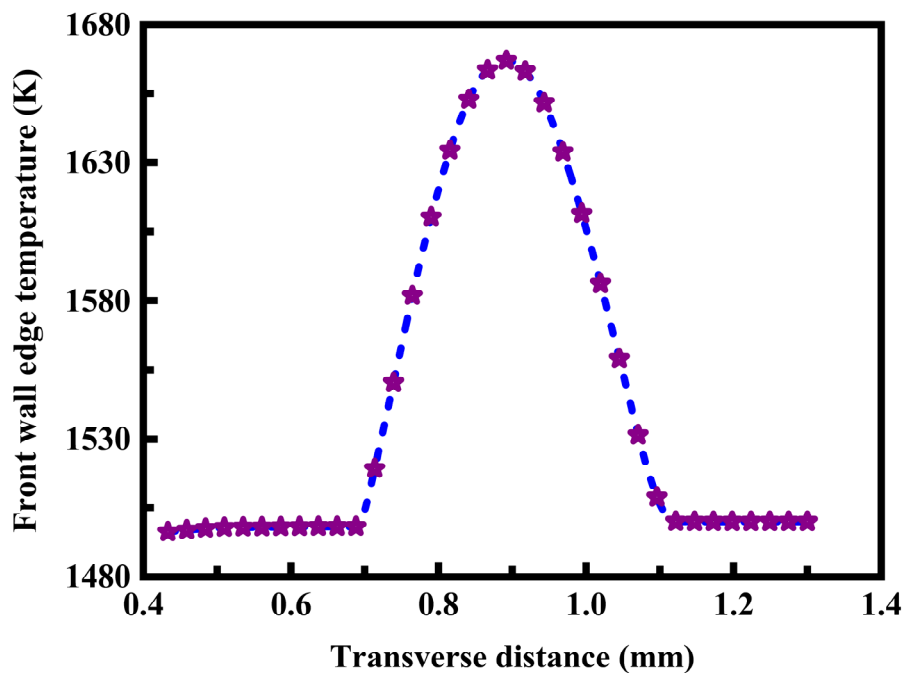


Figure 3. Front wall edge temperature profiles in the transverse direction of the pre-mixed homogeneous-heterogeneous hybrid system.

The fluid centerline temperature profiles in the streamwise direction are presented in Figure 4 for the pre-mixed homogeneous-heterogeneous hybrid system. In a conventional combustion system typical of industrial and commercial burners, the combustion reaction is relatively uncontrolled [61, 62]. That is, a flame can vary in conformation such that its shape and location at any particular point in time is unpredictable [63, 64]. This unpredictability, combined with high peak temperatures encountered especially at the stoichiometric interface in a diffusion flame can cause operational problems such as coking of reaction tubes and uneven heating of steam tubes. Moreover, the length of a conventional flame causes a relatively long residence time during which combustion air is subject to high temperature. What is needed is a technology for reducing pollutants released by combustion systems such as industrial and commercial burners. What is also needed is a technology that can improve flame control in such systems. Fuel and combustion air are mixed to form a fuel-air mixture. The amount of combustion air mixed with the fuel is sufficient to substantially fully oxidize the fuel. Energy is transferred to the fuel-air mixture to increase a temperature of the mixture prior to ingestion and oxidation by the catalytic reactor so that the fuel-air mixture is above a minimum operating temperature of the catalytic reactor when it is ingested. The catalytic reactor oxidizes substantially all of the ingested fuel and produces thermal energy. Exhaust gasses from the catalytic reactor expand across a turbine. This causes the turbine to rotate and thereby convert thermal energy to mechanical energy. Fuel may be injected into the low-pressure inlet of a compressor, rather than downstream of the compressor. This eliminates the need for complex or high-pressure fuel delivery systems having fuel gas compression. A fuel mixer mixes the fuel with combustion air to form the fuel-air mixture. The concentration of any unburned fuel in the bleed air is reduced prior to being exhausted to the environment. This is achieved by oxidizing any unburned fuel with a catalyst. Gas-turbine engines and systems are capable of sustained catalytic combustion over a wide range of operating power levels. For sustained catalytic combustion, the operating temperature of a gas-turbine engine should preferably remain within a limited band of operating temperatures over a wide range of operating power levels. A typical band of catalytic reactor operating temperatures is approximately between 400 °C and 600 °C. However, for conventional gas-turbine engines, operating temperature is a function of power level. Thus, when conventional gas-turbine engines operate at part load, they typically reduce their operating temperature while maintaining a constant engine speed. This reduction of operating temperature causes the operating temperature of the conventional gas-turbine engines to fall outside the limited band of catalytic reactor operating temperatures. Unlike known constant-speed gas-turbine engines, gas-turbine engines adjust their engine speed with power level to maintain a nearly constant operating temperature over a wide range of operating power levels. In addition to adjusting engine speed with power level to maintain a nearly constant operating temperature, gas-turbine engines and systems have recuperators and pre-heaters that help maintain the minimum operating temperature needed for sustained catalytic combustion, even during periods of fuel interruption. There is no need for complex or high-pressure fuel delivery systems having fuel gas compression. In fact, in some cases, no fuel-metering valve is needed, as controlling the speed of the gas-turbine engine can control the fuel flow to the engine. During operation, fuel and air are mixed together to form a fuel-air mixture having a desired fuel-air ratio. The pressure of the fuel-air mixture is increased to a desired pressure by the compressor. As an example, with conventional high-temperature materials in the recuperator, the maximum safe operating temperature of the recuperator may be about 600 °C, and hence an air-fuel mixture temperature of about 500 to 550 °C is about the highest that can be achieved. This temperature range is higher than the minimum catalyst operating temperature for some types of catalysts and therefore the catalytic combustor may operate properly at one particular operating condition such as 100 percent load and standard-day ambient conditions. At other operating conditions, however, such as part-load and cold ambient conditions, the combustor inlet temperature may fall below the minimum temperature. In order

to be compatible with practical turbine systems, it is desirable that the residence time of the combustion gases in the catalytic and thermal oxidation zones is sufficient to give essentially complete combustion of the fuel without the production of objectional amounts of nitrogen oxides. Specific operations will generally define the maximum flame velocity which is controlled by various conditions of operations, such as amount of air and fuel present, the type of fuel employed, temperature, and pressure. Suitable gas velocities are above the actual maximum linear velocity for flame propagation.

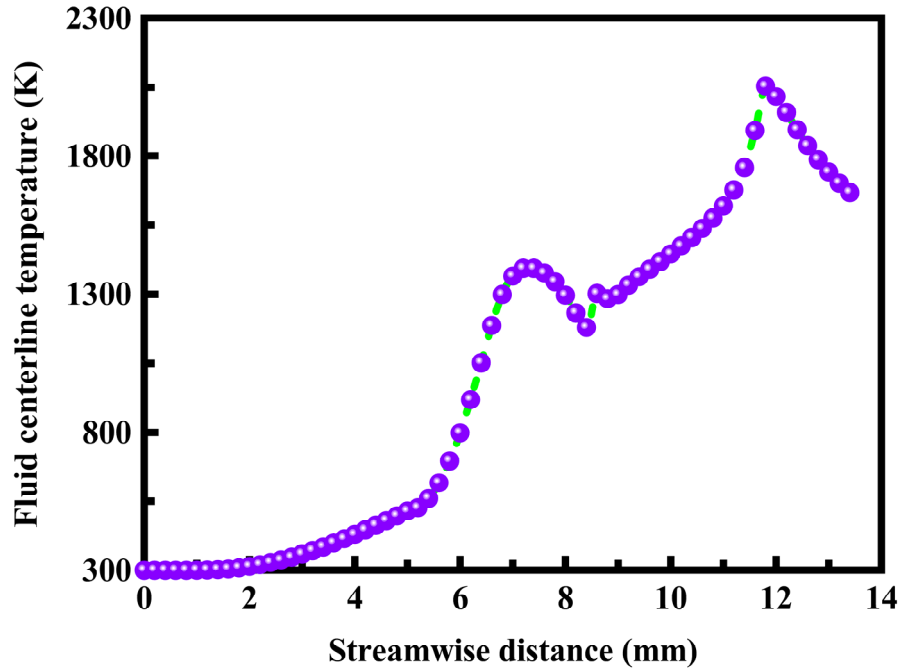


Figure 4. Fluid centerline temperature profiles in the streamwise direction of the pre-mixed homogeneous-heterogeneous hybrid system.

The velocity contour plots in the pre-mixed homogeneous-heterogeneous hybrid system are illustrated in Figure 5 with combustion of small alkanes on noble metal surfaces. The fuel-air admixture is maintained at about a constant theoretical adiabatic flame temperature by measurement of various parameters and delivery of interdependent amounts of fuel and air which amounts depend on these parameters by employing any convenient means. For instance, air flow metering and temperature sensing means, coupled with a valve or separating means to regulate the air flow to the combustion zone in relation to the fuel flow to the combustion zone, for example, a venturi meter or like device in combination with a thermocouple and an air flow control valve can be used to determine the amount of air to be admixed with the fuel for a given inlet air temperature. A compressor speed indicator together with a valve position indicator on the air flow valve can alternatively be used in place of the venturi meter. The fuel flow control valve is regulated by a fuel flow controller, based on power requirements of the turbine. Adiabatic combustion systems, from a practical standpoint, have relatively low heat losses, thus substantially all of the heat released from the combustion zone of such systems appears in the effluent gases as thermal energy for producing power. In general, conventional adiabatic thermal combustion systems operate by contacting fuel and air in inflammable proportions with an ignition source to ignite the mixture which then will continue to burn. Frequently the fuel and air are present in stoichiometric proportions. These conventional systems usually operate at such high temperatures in the combustion zone as to form nitrogen oxides [65, 66]. Many thermal combustors employed in turbine systems utilize separate injection of air and fuel into the combustion zone without premixing [67, 68]. Such combustors frequently have a fixed combustor air inlet geometry, so that a predetermined fraction of the inlet air enters the primary or combustion zone and the balance enters the secondary or dilution zone. This allows for variation of the turbine power by adjusting the fuel rate to

the combustor and thus varying the temperature of the effluent to the turbine inlet and consequently the turbine power. Conventional combustors frequently produce high amounts of pollutants because of inefficient combustion. In the type of combustor previously described, the fuel delivery system can normally be designed for optimum fuel delivery over only a small portion of the operating range of the combustor. Such narrow limits of most efficient operation tend to produce high levels of carbon monoxide, unburned hydrocarbons, soot and the like in certain operating modes. For example, at idle conditions the fuel flow may be so low as to result in improper atomization because of low fuel pressure at the fuel nozzle. Further, the global air to fuel ratio tends to be relatively high in the combustion zone whenever a decrease in power level occurs because only the fuel flow is decreased while the air flow remains constant for at least a short period of time thereafter. This excess air results in premature quenching which produces carbon monoxide, unburned hydrocarbons, and the like. For operation above the optimum design limits, the combustion zone tends to operate excessively fuel rich at least in certain random regions, with the result that unburned fuel droplets are coked to make soot and quenched in the dilution zone with high emissions of carbon monoxide, soot, and unburned hydrocarbons, for example, many commercial aircraft on takeoff operate at such conditions.

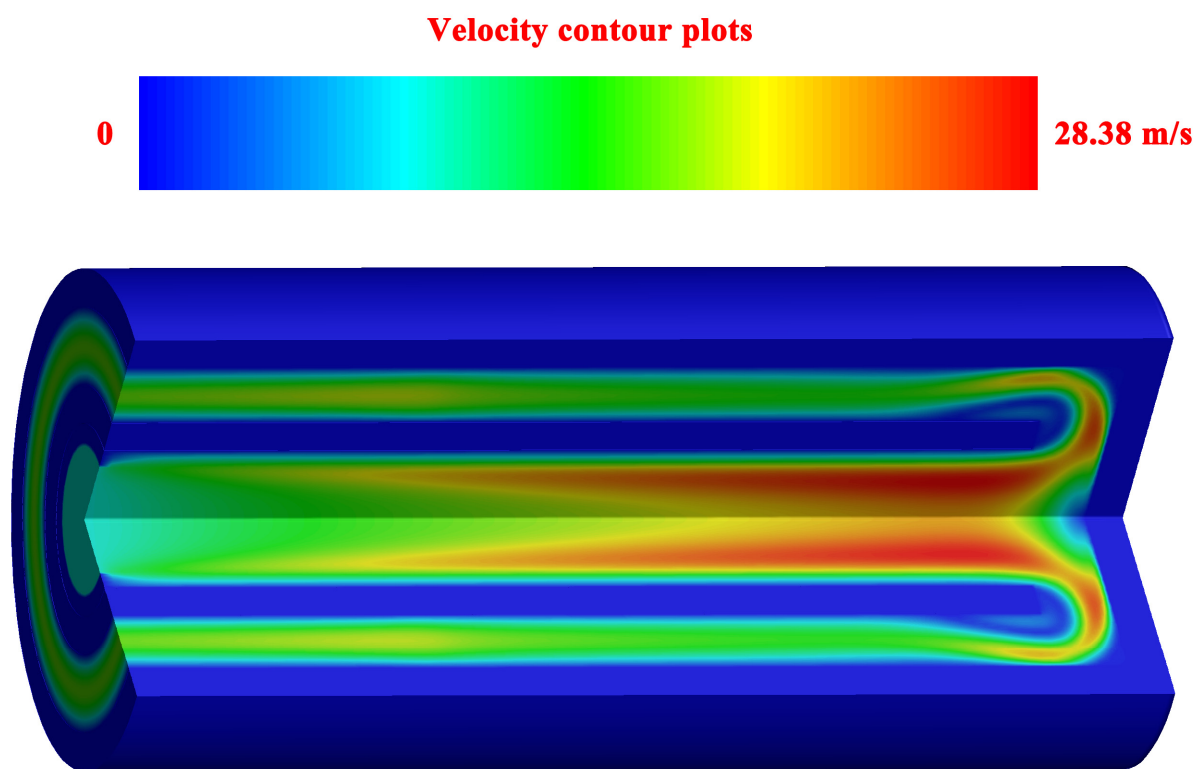


Figure 5. Velocity contour plots in the pre-mixed homogeneous-heterogeneous hybrid system with combustion of small alkanes on noble metal surfaces.

The reactant mole fraction contour plots in the pre-mixed homogeneous-heterogeneous hybrid system are illustrated in Figure 6 with combustion of small alkanes on noble metal surfaces. The use of catalytic processes for combustion or oxidation is a well-known method for potentially reducing levels of nitrogen oxides emissions from gas turbine engine systems [69, 70]. There are various processes for converting the chemical energy in a fuel to heat energy in the products of the conversion [71, 72]. The primary processes are gas phase combustion, catalytic combustion, and catalytic oxidation. There are also combinations of these processes, such as processes having a first stage of catalytic oxidation followed by a gas phase combustion process. In catalytic oxidation, an air-fuel mixture is oxidized in the presence of a catalyst. In all catalytic processes the catalyst allows the temperature at which oxidation takes place to be reduced relative to non-catalytic combustion temperatures. Lower oxidation

temperature leads to reduced nitrogen oxides production. In catalytic oxidation, all reactions take place on the catalytic surface. There are no local high temperatures and therefore the lowest possible potential for nitrogen oxides to be formed. In either catalytic combustion or catalytically stabilized combustion, some part of the reaction takes place in the gas phase, which increases local temperatures and leads to higher potential for nitrogen oxides being formed. Such low levels in general cannot be achieved with conventional non-catalytic combustors, catalytic combustion, or catalytically stabilized combustion. The term catalytic combustor is used to refer to any combustor utilizing catalysis, preferably one utilizing catalytic oxidation. The catalyst employed in a catalytic combustor tends to operate best under certain temperature conditions. In particular, there is typically a minimum temperature below which a given catalyst will not function. For instance, palladium catalyst requires a combustor inlet temperature for the air-fuel mixture higher than 500 °C when natural gas is the fuel. In addition, catalytic oxidation has the disadvantage that the physical reaction surface which must be supplied for complete oxidation of the hydrocarbon fuel increases exponentially with decreasing combustor inlet temperatures, which greatly increases the cost of the combustor and complicates the overall design. The need for a relatively high combustor inlet temperature is one of the chief reasons why catalytic combustion in general, and catalytic oxidation in particular, has not achieved widespread use in gas turbine engine systems. More specifically, such high combustor inlet temperatures generally cannot be achieved in gas turbines operating with compressor pressure ratios less than about 40 unless a recuperated cycle is employed. In a recuperated cycle, the air-fuel mixture is pre-heated, prior to combustion, by heat exchange with the turbine exhaust gases. Recuperation thus can help achieve the needed combustor inlet temperature for proper catalyst operation, at least under some conditions. However, there are often other operating conditions that will be encountered at which the minimum required combustor inlet temperature still cannot be achieved even with recuperation. For instance, when recuperation is applied in small gas turbines, material temperature limitations in the recuperator can limit the maximum air or air-fuel mixture temperature.

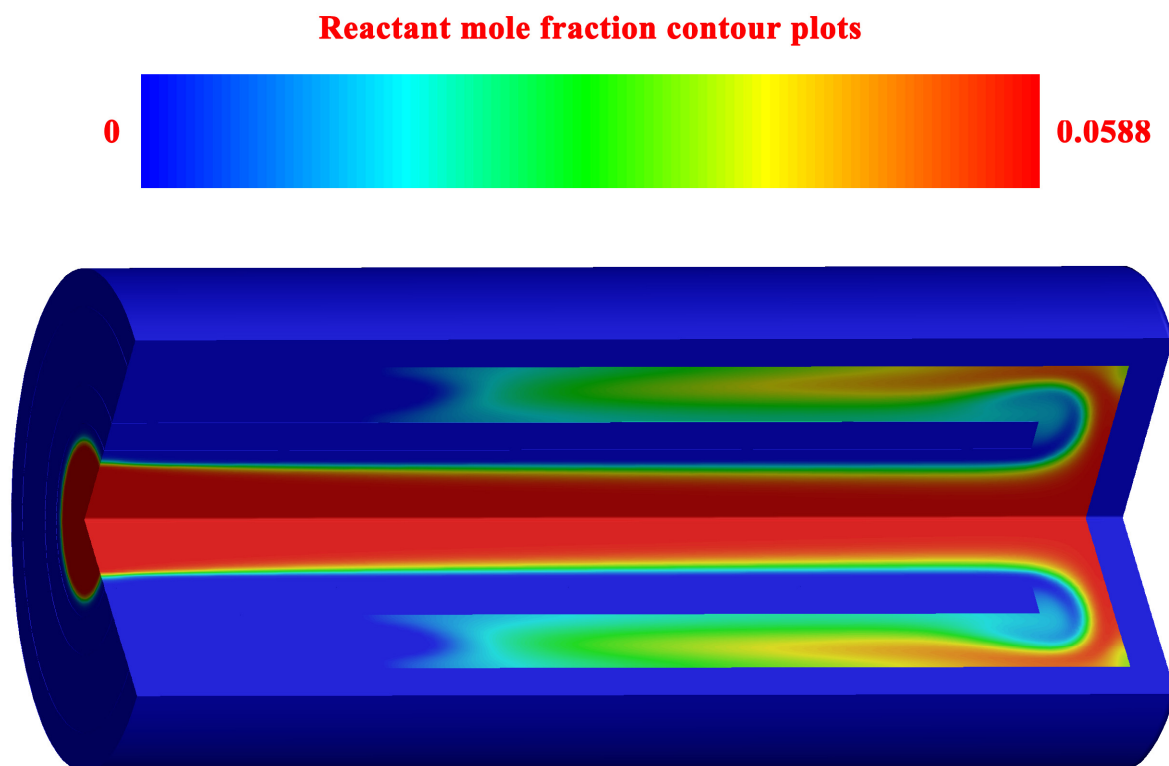


Figure 6. Reactant mole fraction contour plots in the pre-mixed homogeneous-heterogeneous hybrid system with combustion of small alkanes on noble metal surfaces.

The reactant mole fraction profiles in the streamwise direction are presented in Figure 7 for the pre-mixed homogeneous-heterogeneous hybrid system. The ratio of fuel to air in the admixture introduced into the combustion zone is ultimately determined by the desired operating temperature of the combustion zone. The operating temperature is determined by the theoretical adiabatic flame temperature of the fuel-air admixture passed to the combustor and thus is dependent on the initial temperature of the air as well as the amount of fuel contained therein. In the operation of any engine various changes in load occur. For example, increases or decreases in output speed of a turbine may be required thus changing the amount of fuel needed. Further, even at constant speed, load changes are encountered. In certain turbine applications, for example, automobiles, increases or decreases in turbine power often result in an increase or decrease in compressor speed and respectively an increase or decrease in the compression and temperature of the air supplied to the system by the compressor [73, 74]. The theoretical adiabatic flame temperature of an admixture having a given fuel-to-air volume ratio will vary directly with the temperature of the air in the admixture [75, 76]. Thus, for example, as power requirements of the turbine are increased, a number of interrelated control changes must take place. The air charged to the system will be at a higher temperature which, unless compensated for, would increase the adiabatic flame temperature of a given fuel-air mixture. Further, a power increase implies a fuel flow increase; therefore, the portion of the total compressed air which is directed to the combustor must increase to maintain the theoretical adiabatic flame temperature approximately constant. The portion of the total compressed air directed to the bypass will be decreased to allow the temperature of the combined effluent gas-additional air admixture to increase. The relative amounts of each air stream, that is, the air introduced to the combustor and the air directed to the bypass are varied in an inverse manner. These interdependent changes maintain the combustor at an approximately constant temperature by controlling the fuel-air admixture introduced into the combustor to have an approximately constant theoretical adiabatic flame temperature. The combustion effluent is preferably combined with additional, cooler air to quench the effluent and provide a motive fluid for the gas turbine at a desired temperature. The additional air can be at any convenient temperature, for instance, at about the temperature at which the air leaves the compressor, or it can be at a somewhat lower or higher temperature achieved by, for example, indirect heat exchange with the combustion zone or with the exhaust gases from the turbine. Conveniently, the additional air is at a temperature between about 40 and 1100 °C, and preferably about 260 to 800 °C. Thus, the greater the amount of cooler additional air combined with the combustion effluent, the lower the temperature of the combined gases and, hence, the less the power obtainable from the combined gases when used as a motive fluid in a turbine system. Similarly, if the amount of additional air employed is reduced, the power output from the turbine is increased. The temperature of the combined gases passed to the turbine inlet is generally about 400 °C to 1500 °C, and preferably for increased turbine efficiency, about 600 °C to 1500 °C. Another means for increasing the energy of the combined combustor effluent-bypass air in response to increased amounts of fuel is to increase proportionately both the amount of air to the combustion zone and the amount of additional air to be combined with the combustion effluent. The solid catalyst can have various forms and compositions and can be the types used to oxidize fuels in the presence of molecular oxygen. The catalyst can be in the form of relatively small, solid particles of various sizes and shapes, often in sizes below about one inch in the largest dimension, with a plurality of such particles being arranged together to form one or more catalyst masses or beds in the combustion zone. The catalyst is preferably of larger form and has a skeletal structure with gas flow paths therethrough. The catalyst generally has one or more metal containing components which are catalytically active towards promoting the desired oxidation reactions, and in view of the rather high temperatures at which the catalyst operates, materials normally considered to be relatively inactive or insufficiently active, to promote adequately the oxidation of the fuel, may be suitable.

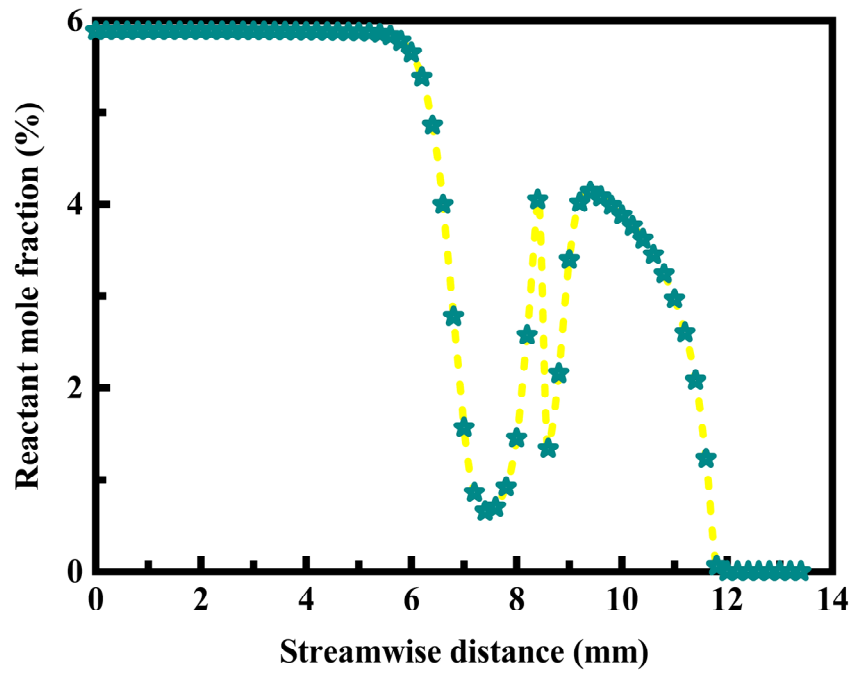


Figure 7. Reactant mole fraction profiles in the streamwise direction of the pre-mixed homogeneous-heterogeneous hybrid system.

The inner wall temperature profiles in the streamwise direction are presented in Figure 8 for the pre-mixed homogeneous-heterogeneous hybrid system. The higher the temperature of the combustion gas entering the turbine, the higher the efficiency of the turbine. However, absent perfect mixing of fuel and air, there will be islands of high fuel concentration where the temperature is high enough to form nitrogen oxides [77, 78]. Catalytic combustion offers the possibility of reducing the nitrogen oxides concentration [79, 80]. Temperature control in a catalytic combustor is a serious problem [81, 82]. The conventional gas turbine combustor, as used in a gas turbine power generating system, requires a mixture of fuel and air which is ignited and combusted uniformly [83, 84]. Generally, the fuel injected from a fuel nozzle into the inner tube of the combustor is mixed with air for combustion, fed under pressure from the air duct, ignited by a spark plug and combusted [85, 86]. The gas that results is lowered to a predetermined turbine inlet temperature by the addition of cooling air and diluent air, then injected through a turbine nozzle into a gas turbine [87, 88]. The catalyst in the catalytically supported thermal combustion generally operates at a temperature approximating the theoretical adiabatic flame temperature of the fuel-air admixture charged to the combustion zone. The entire catalyst may not be at these temperatures, but preferably a major portion, or essentially all, of the catalyst surface is at such operating temperatures. The temperature of the catalyst zone is controlled by adjusting the composition and initial temperature of the fuel-air admixture as well as the uniformity of the mixture. Relatively higher energy fuels can be admixed with larger amounts of air in order to maintain the desired temperature in a combustion zone. At the higher end of the temperature range, shorter residence times of the gas in the combustion zone appear to be desirable in order to lessen the chance of forming nitrogen oxides. The residence time is governed largely by temperature, pressure and space throughput, and generally is measured in milliseconds. Part of the catalytically supported thermal combustion of the fuel-air mixture is conducted upstream of the turbine by combustion of the mixture while passing through an insufficient amount of catalyst to effect complete combustion of the fuel prior to passing through the turbine wheel or expansion zone. The partially combusted effluent from the catalyst, with or without substantial intermediate but incomplete further combustion, is introduced into a gas expansion zone of the turbine so that the partially combusted effluent is further thermally combusted while undergoing expansion. The further thermal combustion converts remaining combustible fuel

components to carbon dioxide and water. The addition of heat to the system provided by combustion in the turbine gas expansion area counteracts the cooling in the system concomitant with the gas expansion. The turbine is thus operated under conditions which may be referred to as continuous reheating. The operating efficiency and work output of the turbine are thereby enhanced according to known reheating principles. Also, the reheating effect can be obtained without the necessity of employing plural turbine stages and separate reheating equipment. The present design thus provides benefits even in turbines with a single impeller wheel or single stage; however, the present design can also be used where the combustion is accomplished in the gas expansion zones of a plurality of turbine wheels or stages. In the latter type systems, advantageous efficiencies can be obtained. Partial combustion is conducted upstream of the turbine by catalytically supported thermal combustion. A lesser amount of catalyst is required for complete combustion of the fuel is used in the catalyst zone. Accordingly, and since at least a portion of the combustion is conducted in a downstream turbine gas expansion area, the system responds quickly to desired changes in operation, and yet the combustion can still produce an effluent from the work-performing zone having a relatively small amount of nitrogen oxides. As a consequence, the operation can be highly advantageous in turbines used for propelling automotive vehicles. A temperature lowering effect from expansion of the gases within the turbine expansion zone normally occurs in turbines, and this is counteracted by providing at least some thermal combustion of fuel within the turbine gas expansion zone. Thus, for a turbine which operates at a given temperature, more fuel can be burned in the method as compared with conventional operations, without producing excessive temperatures in the turbine. The catalytic metal may be in a combined form, such as an oxide, rather than being solely in the elemental state, and preferably the catalytic metal compound is carried by a less catalytically-active, or even an essentially inert, support which may be, for instance, ceramic in nature. In these catalysts, the more catalytically-active metal component is often a minor amount of the catalyst, while the support is the major portion.

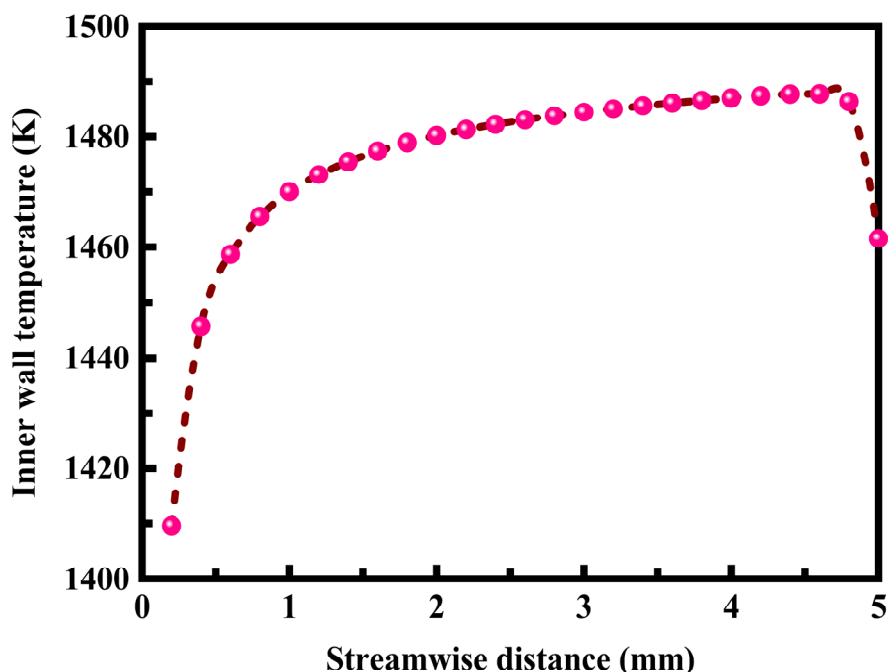


Figure 8. Inner wall temperature profiles in the streamwise direction of the pre-mixed homogeneous-heterogeneous hybrid system.

4. Conclusions

The present study is focused primarily upon the combustion characteristics of small alkanes on noble metal surfaces in pre-mixed homogeneous-heterogeneous hybrid systems. The

homogeneous-heterogeneous combustion characteristics small alkanes on noble metal surfaces are investigated to gain a greater understanding of the mechanisms of flame stabilization and to gain new insights into how to design pre-mixed combustors with improved stability and robustness. The essential factors for design considerations are determined with improved combustion characteristics and flame stability. The primary mechanisms responsible for the loss of flame stability are discussed. The major conclusions are summarized as follows:

- The combustion effluent is characterized by high thermal energy and typically by low nitrogen oxides content.
- Precise tuning of the combustion process is needed to establish a balance between stable combustion and low emissions.
- Simply changing the combustor geometry to maintain near-stoichiometric ratios will not avoid nitrogen oxides formation.
- The catalytic reactor oxidizes substantially all of the ingested fuel and produces thermal energy.
- Adiabatic combustion systems, from a practical standpoint, have relatively low heat losses, thus substantially all of the heat released from the combustion zone of such systems appears in the effluent gases as thermal energy for producing power.
- Catalytic oxidation has the disadvantage that the physical reaction surface which must be supplied for complete oxidation of the fuel increases exponentially with decreasing combustor inlet temperatures, which greatly increases the cost of the combustor and complicates the overall design.
- The operating temperature is determined by the theoretical adiabatic flame temperature of the fuel-air admixture passed to the combustor and thus is dependent on the initial temperature of the air as well as the amount of fuel contained therein.
- The temperature of the catalyst zone is controlled by adjusting the composition and initial temperature of the fuel-air admixture as well as the uniformity of the mixture.

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