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Effect of natural gas components on its flame temperature, equilibrium combustion products and thermodynamic properties

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ABSTRACT

It is a known fact that the composition of natural gas varies widely from source to source and from time to time even in the same source. Such variations in gas composition cause variations in flame temperature, its combustion products and thermodynamic properties which can affect gas-fueled engine performance and its emissions. The purpose of this study is to investigate effects of varying amounts of natural gas diluent components such as ethane (C_2H_6), isobutane (C_4H_{10}), propane (C_3H_8), carbon dioxide (CO_2) and nitrogen (N_2) on methane–air combustion under different pressures, unburned mixture temperatures and equivalence ratios. Results show that adiabatic flame temperature is mostly increased by isobutane followed by propane and ethane however it is mostly influenced by CO_2 content in the gas which decreases flame temperature 80 K in %70 CH_4 - %30 CO_2 mixture at stoichiometric conditions. As for specific heat, the highest increase is again for isobutane followed by propane and ethane content but it is decreased mostly by N_2. Effect of increasing secondary fuel content on product species is greatest at equivalence ratio near unity except for CO and H_2. Analysis results including equilibrium compositions are validated and expected to be a reference guide for scientists, engineers and NG consumers to evaluate and compare natural gas samples of different compositions.

1. Introduction

Rapid progress has been made worldwide in recent years in the discovery of new natural gas (NG) deposits and its transportation over the globe, both as a gas and in its cryogenic liquid state, liquefied natural gas (LNG). Its increased availability, the need to meet increasingly lower emission controls, and its relatively low cost have tended to increase its usage as a fuel in a wide variety of applications. The gas has been increasingly viewed as a premium fuel that is in much demand, and may well be for quite some time in the future a prime source of usable fuel energy (Karim, 2015). Additionally it is more cost-competitive than gasoline and diesel fuels because it does not need to be refined from petroleum (Zumerchik, 2001). By virtue of its simple chemical structure, is not rapidly reactive in comparison to other common fuels. This feature helps to render methane a very attractive engine fuel with exceptionally high knock-resistant properties (Karim, 2015). Apart from its direct usage as an engine fuel, natural gas can also be used as a diluent or pilot fuel in diesel or spark-ignition engines (Liu et al., 2013; Azimov et al., 2013; Papagiannakis et al., 2010a; Papagiannakis and Hountalas, 2004; Kusaka et al., 2000; Papagiannakis et al., 2010b; Papagiannakis and Hountalas, 2003). Above all, it is increasingly being used to produce the hydrogen needed for the upgrading of common fossil fuels, especially those that are of low quality, to make them more acceptable operationally and ecologically.

This source of energy, consisting mainly of methane, originates from multiple gas fields worldwide and global reserves are still rich (Johansson, 2011). The composition of natural gas varies widely from source to source and also from time to time in the same source (Ali, 2012). These gases exist in natural gas in different fractions depending on the source of the gas supply, nature and level of treatment it may have undergone. For this reason, gas properties in countries of different regions of the world differ substantially (McAllister et al., 2011).

With its high calorific value, the major constituent of natural gas is methane (CH_4). Other constituents which directly affect its quality are ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), nitrogen (N_2) water (H_2O) and carbon dioxide (CO_2). The amounts of other gases are usually trace.

The variations in gas composition can bring about significant changes to the flame temperature and thermodynamic properties

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of burned gases and accordingly affect gas-fueled engine performance and its emissions (Karim, 2015). Gas composition directly affects the flame temperature. In internal combustion engines, the higher the mean temperature of heat addition process is, the higher the upper limit of its thermal efficiency which is usually defined as $\eta_{th} = 1 - (T_L/T_H)$ where T_L and T_H are the maximum and minimum temperatures that the cycle is working in-between. Higher thermal efficiency allows for less fuel consumption. Apart from its economical benefits, consuming less fuel, decreases CO_2 emission, a significant contributor of global warming (Lefebvre and Ballal, 2010; Sturgess et al., 1992). Additionally, when the flame temperature exceeds 1800 K, a decrease of 30–70 K in peak flame temperature can decrease NO formation by half (McAllister et al., 2011) which is adversely proportional to CO emissions (Keating, 2007; Petchers, 2003; Khartchenko and Khartchenko, 2014). So, apart from being an important identifier of cycle thermal efficiency and CO_2 emissions, flame temperature is also an important identifier of CO and NO_x.

Following studies present the effects of NG composition and secondary fuels/diluents on methane burning engine performance and emissions as methane is conventionally regarded as a good representative of NG:

Kakaee et al. (2014). have reviewed the research works on effect of natural gas composition in CNG engines and discussed the effects of fuel composition comparing various samples which consist of different components.

Li et al. (2014). investigated the effects of carbon dioxide, nitrogen and argon diluted natural gas on combustion and NO_x emissions of a turbocharged SI engine.

Karim et al (Shrestha and Karim, 2001). worked on the effects of presence of the diluents carbon dioxide and nitrogen with methane, and its effect on the performance of a gas fueled SI engine over a range of operating conditions.

In another study, Karim et al (Shrestha et al., 2009). explored the maximum diluent concentration in a gaseous fuel–diluent mixture that just permits flame propagation following ignition. The fuels investigated were methane, ethylene, ethane, propane, butane, carbon monoxide and hydrogen and the diluents nitrogen, carbon dioxide, helium and argon.

NG composition is also an issue for gas turbine engines which have significantly advanced their application to a broad range of commercial and new naval configurations and utility power generation as well.

Samaras (2010) investigated effects of NG composition in gas turbine engines and stated that even in the same pipeline the composition of natural gas is not constant. Both NO_x and CO emissions vary daily due to the fuel composition change. According to his pipeline measurements, the hydrocarbon content of fuel was 98.66% at 2 January whereas it was 100% at 31st. He reported that this small change in gas composition resulted in a 4.24% and 5.69% rise in NO_x and CO emissions respectively.

Additionally gas composition may be critical for natural gas fired lean-premixed combustors used in ultra-low-NO_x gas turbine engines which have to sustain a stable combustion below stoichiometric AFRs. These combustors have low turndown capability which means that flame stabilization is more problematic. So, NG composition may undermine its effective utilization in ultra-low-NO_x gas turbine engines depending on the operating conditions.

As stated by Kakaee et al. (2014), studying the effect of natural gas composition on performance and emission characteristics of natural gas fueled internal combustion engines become one of the utmost important research directions for engine researchers and presence of diluent components can bring about significant changes to the combustion characteristics of the fuel mixture. As no complete investigation on the effects of NG components on thermodynamic properties, flame temperature and equilibrium species could be found in the available literature, effects of NG components such as ethane (C_2H_6), butane (C_4H_{10}), propane (C_3H_8), carbon dioxide (CO_2) and nitrogen (N_2) on methane-air combustion are investigated to be a reference guide for engineers and scientists working on design and optimization of NG fired engines as well as for NG consumers to evaluate and compare quality of NG from different pipelines. Methane is selected as the primary gas as it is often regarded as the representative of NG (Karim, 2015). As the minimum methane content of NG is given as 70% (Lyons and Plisga, 2016), change of thermodynamic properties of combustion products such as enthalpy, entropy and specific heat as well as adiabatic flame temperature and equilibrium combustion products for varying secondary gas mole fraction from 0% to 30% are explored under varying pressures, equivalence ratios and unburned mixture temperatures. Results have been verified with famous computer software CEA (Gordon and McBride, 1994) and GASEQ (Morley, 2005). Additionally, relations between the rates of formation of non-equilibrium pollutant emissions and equilibrium combustion products are given in the Appendix.

2. The equilibrium combustion products and thermodynamic properties

As presence of various hydrocarbon gases in NG change flame temperature and burned gas composition, presence of diluent components such as carbon dioxide, water vapor, and, to a much lesser extent, nitrogen will also tend to increasingly undergo endothermic dissociation reactions that increase rapidly in intensity as high combustion temperatures are approached. The net effect will be substantial reductions in the flame temperature and associated reaction rates due to the presence of the diluents (Karim, 2015). According to Heywood (1988), Rashidi (1998), Rakopoulos et al. (1994), Bozza et al. (1994). and a 2002 NATO report (NATO, 2002), for performance prediction of thermodynamic cycle models of internal combustion engines, it is a good approximation to consider combustion products as in chemical equilibrium and taking dissociations of product species is critical for exact calculation of gas composition inside the combustion chamber. Mole fractions of each product species are also key data for estimating pollutants such as nitric oxide (NO) and carbon monoxide (CO) with the principles of chemical kinetics (Rakopoulos et al., 1994; Olikara and Borman, 1975) as explained in Appendix.

A multi-featured combustion model is established taking the equilibrium constants into account. Products of combustion are calculated as a function of temperature, pressure and equivalence ratio. Principle assumption is that all gas phase species are ideal gases so their thermodynamic properties except from entropy change only with temperature. 10 main products are considered for this model as it meets sufficient precision for internal combustion engines where equivalence ratios are always less than 3 according to (Ferguson, 1986). Chemical equation for the combustion model is given below:

$$\begin{aligned}&\varepsilon\phi\left[C_{\alpha1}H_{\beta1}O_{\gamma1}N_{\delta1} + p\left(C_{\alpha2}H_{\beta2}O_{\gamma2}N_{\delta2}\right)\right] + 0.21O_2 + 0.79N_2 \rightarrow \\ &\upsilon_1 CO_2 + \upsilon_2 H_2O + \upsilon_3 N_2 + \upsilon_4 O_2 + \upsilon_5 CO + \upsilon_6 H_2 + \upsilon_7 H + \upsilon_8 O + \upsilon_9 OH + \upsilon_{10} NO\end{aligned} \quad (1)$$