# Plasma-Assisted Fuel Reforming of Methane Using Non-Equilibrium Excitation

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## Introduction

Gas flaring is the practice of burning excess natural gas released while drilling for oil. As this gas is a by-product of the drilling process, it is oftentimes safer to burn the gas rather than allow it to vent to the atmosphere or overpressure drilling facilities ill-equipped to handle the excess [1]. However, such flaring still represents a significant amount of wasted energy and greenhouse gas emissions. The World Bank reported that in 2016, 149 billion cubic meters of natural gas were flared worldwide [2]. In terms of yearly natural gas production, that represents 15.7% and 4% of the United States' and the world's natural gas production, respectively [3]. In terms of CO2 emissions, gas flaring is estimated to contribute up to 1% of annual global CO2 emissions [4][5]. Indeed, this is a huge waste of limited fossil fuel resources with a large impact on the environment and climate change. Thus, there is a large incentive to develop methods to transform this natural gas into an easily stored and transported product.

Methanol stands out as a promising target product as it is a liquid at ambient conditions and easier to store than a compressed gas. Methanol also can be used as an intermediate to other chemicals such as formaldehyde and can be part of a fuel cell system as a mobile source of $H_2$/CO (syngas).

Traditional methanol synthesis involves mixing methane with high temperature steam to create syngas and flowing the syngas over a catalyst bed to form methanol. This process is known as "steam methane reforming." The disadvantages to this approach include requiring large facilities to perform this reforming and the need to supply thermal energy to the reaction. This thermal energy typically comes from combusting methane, which is not ideal.

Plasma-assisted fuel reforming has been shown to generate methanol in one step and can potentially eliminate both the need for a combustor and a large facility [6]. This could have important ramifications for remote oil drilling operations that cannot accommodate traditional fuel reforming due to space constraints. However, the main challenges facing plasma-assisted fuel reforming are energy efficiency and selectivity toward desired products. Pairing plasma with a catalyst has been shown to improve the energy efficiency of the process due to the enhanced dissociation of vibrationally excited methane on the catalyst surface [7]. This suggests that generating large amounts of vibrationally excited species will translate to increased energy efficiency of the reforming process.

Vibrational excitation of molecules via impact from free electrons in the plasma is maximized at electron energies of 1-3 eV [8]. However, in nanosecond-pulsed dielectric barrier discharge plasmas, the electrons cool between pulses [9]. Modeling results from our lab have shown that applying an excitation to heat electrons in between plasma pulses can alter the populations of vibrationally excited molecules such as methane. To confirm these findings, *in situ* diagnostics need to be developed to measure the time evolution of the electron temperature, electron density, and the population of vibrationally excited species in a nanosecond-pulsed plasma.

## Experimental Methods

Thomson Scattering is the elastic scattering of light off electrons. The electron temperature can be inferred from the Doppler broadening of the scattered light. Since the electrons move with respect to the laser, the electrons see that light at a shifted frequency due to the Doppler effect. The electrons reradiate this light at this shifted frequency and the retrieved Doppler-broadened signal can be used to calculate the plasma's electron temperature. If the energy distribution of the electrons is Maxwellian, then the scattered signal is a Gaussian with the width corresponding to the electron temperature and the area corresponding to the electron number density [10]. A major challenge to implementing Thomson Scattering is its weak signal and the much larger Rayleigh Scattering signal at the laser wavelength. One method to deal with the Rayleigh Scattering is to use a spatial filter at the spectrometer exit to block the Rayleigh scattered light. This was implemented for a Raman Scattering experiment in a CO2 plasma [11].

With this data, a plasma-chemical model can be validated for prediction of the fuel reforming products. Currently, we have a 0-D kinetic model for a nanosecond-pulsed discharge plasma coupled with chemical reactions [12]. The above diagnostics will be used to compare with and improve the model such that we can gain insight into the important mechanisms in plasma-assisted fuel reforming.

## Current Work

The design and setup of the laser scattering system has completed. The setup uses a pulsed Nd:YAG laser that is focused by a 1.35 m focal length lens. Brewster windows at the entrance and exit reduce stray light generated from the windows. A quartz cell is located at the center where the plasma will be generated. The scattered light will be collected by an achromatic lens and focused onto a spectrometer by another achromatic lens. At the spectrometer exit focal plane, a thin metal sheet will be used as a filter and this filtered image will be focused onto the ICCD.

A plasma in the quartz cell has been successfully tested and created using a nanosecond pulse generator. Laser scattering measurements will soon follow.

## Future Work

Future work includes studying plasma-assisted methane reforming with carbon dioxide ("dry reforming") or water ("steam reforming") with laser diagnostics. This data can then be used to validate the predictions of our current 0-D kinetic model and give insight into the mechanisms of plasma-assisted fuel reforming. Such insights may open new avenues of inquiry to better improve the efficiency of the fuel reforming process and the selectivity toward oxygenated products like methanol.