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Evaluation of Light-Off Limits for a Novel Oxy-Combustion Process for Advanced EOR

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A pressurized oxy-fuel burner is being developed for the down-hole generation of heat, steam, and CO_2 for direct injection into an oil reservoir, to improve the energy efficiency of extraction of heavy oils. A simple chemical ignition system for this process is desired, rather than attempting to use an electrical ignition system that would need to be retractable from the combustion chamber. Several approaches to low-temperature chemical ignition have been explored in this work. First, the auto-ignition of different short-length alkanes in oxygen was investigated under the relevant pressure conditions (approx. 10 bar). Comparisons of the results with computed auto-ignition times, using the best-available chemical kinetic mechanisms, showed good agreement. Then, to reduce the pre-heating requirements, two cetane enhancers were used to lower the auto-ignition temperature of pentane and hexane from 350 deg C to 240 deg C. Seeking to further reduce the required temperature for chemical ignition, silane was investigated as an ignition source for a methane/oxygen flame. Ignition of this system is shown to be possible below room temperature.

1. Introduction

As oil reservoirs mature, recovery of the remaining oil becomes increasingly difficult and techniques for enhanced oil recovery (EOR) must be employed. Extraction requires at a minimum a method of pressurizing the reservoir with a liquid (typically water) or gas to displace the oil. In addition to pressurization, further recovery requires a thermal, chemical, or biological means of reducing the viscosity of the remaining oil [1,2]. Current thermal EOR methods include steam assisted gravity drainage and cyclic steam stimulation, where steam is generated at the surface (usually from the combustion of natural gas) and injected into the reservoir. Resource Innovations Incorporated North America (RII-NA) was founded in 2008 to implement an advanced thermal EOR method known as the Solvent Thermal Resource Innovation Process (STRIP). STRIP technology involves the down-hole generation of heat, steam, and CO_2 using a novel natural gas oxy-combustion burner. Producing the combustion products in the reservoir efficiently delivers these useful chemicals and heat to the oil reservoir without the extensive thermal losses associated with the current approach in which steam is piped from the surface to the reservoir. Furthermore, with the STRIP approach emissions of the greenhouse gas CO_2 are reduced by the higher efficiency of the process and by sequestering much of the combustion-generated CO_2 in the reservoir.

The work reported here focuses on the ignition process of a pressurized down-hole natural gas oxy-combustion burner as used in the STRIP process. In a pressurized system operating at the depth of an oil reservoir, a retractable electrical igniter is impractical and materials for an igniter that could withstand the extreme temperature of oxy-fuel burner operation are non-existent. For the chemical ignition envisioned, a gas with a low auto-ignition temperature is added to or replaces the burner's natural gas stream, and when this ignition gas makes contact with the oxygen flowing to the burner in the reservoir at the proper temperature, ignition will occur. The flame should remain stable as fuel is switched back to natural gas. The most efficient and simple chemical igniter does not require any preheating of the fuel and will ignite at the reservoir temperature.

For safety reasons, auto-ignition has been widely studied (see, for example Ref. [3]). The auto-ignition temperature is often listed on the MSDS of flammable chemicals and there is an ASTM standard test method for determining the auto-ignition temperature of liquids [4]. In addition to auto-ignition research focused on safely handling fuels, there are a multitude of studies on auto-ignition as applied to internal combustion compression ignition engines (e.g. diesel and HCCI) and jet engines. With these applications as a basis for traditional studies, there is much less work on the auto-ignition of fuels in oxygen-enriched environments, and at the pressures of interest for lighting off the STRIP process (~ 10 bar).

We began this project investigating the auto-ignition of methane. Preheating the down-hole burner to the auto-ignition temperature of methane is infeasible in practice, but these investigations gave us a good starting point to evaluate our experimental method and to compare the data to predictions based on well-developed chemical kinetic models before proceeding to study more exotic methods of ignition. After evaluating the auto-ignition of methane, we investigated the auto-ignition of larger alkanes. In general, as the chain length increases, the auto-ignition temperature of alkanes decreases, but at the same time the boiling point increases, as shown in Fig. 1. As the proposed burner will be fueled by gas, we wanted to use fuels that could be delivered as gas at the relevant operating pressure. We chose to investigate pentane and hexane because they were fuels we could handle in the lab by pouring them as liquids (at 1 atm) and vaporizing them at fairly low temperatures. These fuels have lower auto-ignition temperatures than methane and we were able to mix in liquid additives to further lower the ignition temperature. In diesel combustion the cetane number is inversely related to the ignition delay at a given temperature. To lower the ignition delay (or increase the cetane number), many

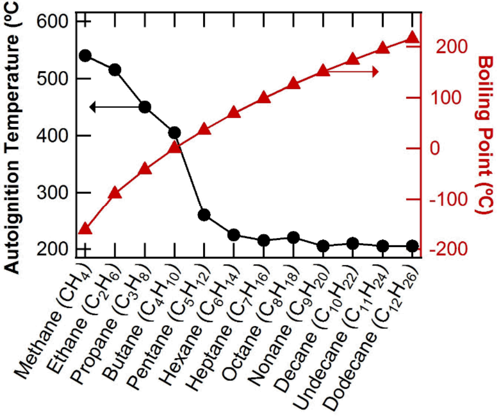

Figure 1. Auto-ignition temperature [3] and boiling point [5] at 1 atm for the normal alkanes.

cetane enhancers can be added to diesel fuel. Generally, these additives are either nitrates or peroxides, and they are added to diesel fuels in low concentrations (<1%) [6,7]. In this study, we evaluated the ability of a typical nitrate cetane enhancer, 2-ethyl-hexyl-nitrate (2-EHN) and a typical peroxide cetane enhancer, di-tert-butyl-peroxide (DTBP) to lower the ignition temperature (at a given delay) of our liquid fuels.

The final method for achieving low-temperature auto-ignition that was investigated in this study was to use silane. Silane has been reported to auto ignite in air at temperatures as low as -165 °C, although the ignition characteristics can be unpredictable [8,9]. Silane has been used for scramjet ignition and has been considered for a scramjet fuel on its own [10]. In a similar application to this paper, Hill et al. [11] describe a silane/propane igniter/burner for underground coal gasification.

2. Experimental Description

A system capable of reacting high pressure gaseous and vaporized liquid fuels with an oxidizer stream was designed and built. A schematic of the flow system is shown in Fig. 2. As shown in the schematic, gases are supplied from high pressure cylinders and high pressure mass flow controllers (Fathom Technologies) are used to control the flow into the reactor. When using liquid fuels, an HPLC pump (LDC Analytical ConstaMetric 3200) pressurizes and controls a steady flow of liquid fuel into a bank of custom-built fuel heaters. These heaters are controlled to a temperature above the vaporization temperature (at the operating pressure) for the fuel, and the vaporized fuel flows through heated lines into a temperature-controlled reactor. A backpressure regulator (Tescom) is used to control the pressure in the reactor (and simultaneously in a bypass

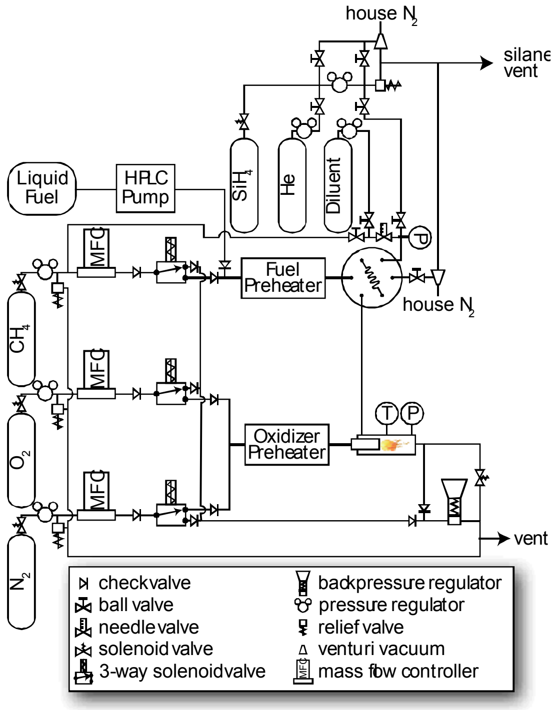

Figure 2. Schematic of the flow system used to react gaseous and vaporized liquid fuels with an oxidizer stream (from pure oxygen to simulated air).

line), and a pressure transducer and thermocouples are used to monitor the reactor pressure and the temperature at several locations. Solenoid valves are used to switch the flow of gases from a bypass line to the reactor.

A high pressure inconel reactor rated to 12,000 psi at 650 ºC with 3 quartz optical ports was used for the alkane auto-ignition experiments. Light emission can be seen through the optical ports if a flame is present. The reactor has an inside diameter of 0.188 inch. For these experiments the oxidizing gas was introduced along the reactor centerline using either 1/8" or 1/16" OD inconel tubing. A so-called "inverse" diffusion flame is generated if ignition occurs.

A typical alkane auto-ignition experiment consists of first establishing a flow of fuel and nitrogen to the reactor, and oxygen in the bypass line. When the temperatures and flow rates are steady, the nitrogen flow and oxygen flow are swapped so that oxygen flows to the reactor and nitrogen to the bypass lines. As oxygen reaches the reactor, light emission can usually be observed and the temperature will increase if ignition occurs. The flow of nitrogen and oxygen are swapped again, and as the oxygen concentration decreases the flame will extinguish.

As the project progressed and silane was used as the ignition source, the components shown in the upper right of Fig. 2 were added to the system. These flow components were set up to allow complete purging and backfilling of the silane delivery system to avoid reactions of silane and oxygen (from air) in these lines. A continuous flow of silane to the experiment was considered unnecessary and had safety implications, so a method of dosing a charge of silane into the fuel line was devised. A 6-port two-position GC valve was used for this purpose. In one position, a mixture of silane and a diluent (inert or fuel) gas is fed into a known volume ignition charge loop. In the second position, the gas flowing in the fuel line sweeps through the ignition charge loop, flushing the pyrophoric gas mixture into the reactor.

A typical silane ignition experiment consists of charging the sample loop, establishing a flow of fuel and oxidizer and then swapping the 6-port two-position GC valve. As the pyrophoric mixture is convected in the fuel line and comes in contact with the oxidizing gas in the reactor, ignition can occur, leading to a temperature increase and light emission (if using the optical reactor). After the pyrophoric volume in the ignition charge loop has been convected through the reactor, the flame can continue burning until fuel gas (typically CH_4) is convected into the reactor subsequent to delivery of the pyrophoric mixture. The oxygen flow can then be diverted to the bypass line and the flame will extinguish as the mixture drops below a flammable stoichiometry.

3. Results and Discussion

3.1 Methane Ignition

The auto-ignition temperature of methane at 150 psig was determined over a range of residence times. In Fig. 3, the black circles represent the observed experimental occurrence of ignition at a given temperature and residence time. The residence time was varied by changing the flow rate of gases in the reactor. This residence time is calculated by dividing the reactor volume by the volumetric flow rate of fuel and oxidizer. A range of global stoichiometries were evaluated experimentally, although local stoichiometry is determined by the diffusional and convective mixing of the coflowing gas streams and the mixture will ignite (if given sufficient residence time) at whatever stoichiometry is most favorable for ignition.

Also shown in Fig. 3 are the CHEMKIN-PRO model results for ignition delay as a function of initial gas temperature, using the low-temperature chemical kinetic mechanism of Bourque et al. [12], which was developed to describe ignition of natural gas at elevated pressures. The transient, closed, adiabatic homogeneous reactor model was used in CHEMKIN, which simulates the temporal evolution of an isolated gas mixture. In these simulations, ignition delay was defined as the time from the start of the simulation to the beginning of a rapid temperature increase. It can be seen that richer mixtures ignite more readily (i.e., have a lower ignition delay time) for a given preheat temperature. In comparing the simulated ignition delay to the experiments, it is clear that all observed ignitions occurred at or above the theoretically calculated ignition delay, as expected.

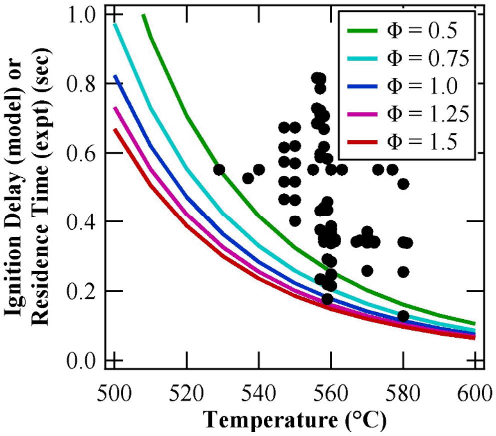

Figure 3. Auto-ignition properties of a methane/oxygen system at 150 psig. Solid lines indicate the computed ignition delay. The different lines represent different stoichiometries (Φ = ($[O_2]/[CH_4]$)stoic/($[O_2]/[CH_4]$)). The circles indicate characteristic reactor residence times for which ignition was observed experimentally.

3.2 Higher Alkane Ignition

The observed and computed ignition delays of pentane and hexane at several reactor pressures are shown in the top frame of Fig. **Error! Reference source not found.**4. The low temperature auto-ignition mechanism of Buda et al. [13] was used for these simulations. There is fairly good agreement between the model results and the experimental results, although the experimentally measured delay times are slightly lower than the modeled delay times. Experimentally, there is some uncertainty in the residence time measurement, as flow instabilities and other gas dynamic issues can occur in the test reactor. Furthermore, while the rich stoichiometry of Φ = 1.5 was modeled, an even richer mixture may have been igniting experimentally, leading to a shorter ignition delay. The trend of higher pressures reducing the ignition delay is certainly captured by both the model and the experiment. Experimentally, hexane ignition was observed at a temperature as low as 285 ºC and pentane ignition as low as 304 ºC, without additives.

Fig. **Error! Reference source not found.**4 also shows the effects of adding varying concentrations of 2-EHN and DTBP to pentane and hexane. Both cetane enhancers significantly lower the ignition delay of the liquid fuels. Increasing the concentration of these additives further lowered the ignition delays. The experiments were run at 40 psi for hexane and 75 psi for pentane so that the fuel vaporization temperature was lower than the auto-ignition temperatures of these mixed fuels. This allowed vaporization and transport of the fuels to the reactor while still being able to evaluate the auto-ignition temperature. Good agreement between the model predictions and the experimental results is shown. In some of the experimental cases, there is limited data at the lower temperatures and higher flow rates, causing these data points to be reported at higher temperatures than they should be. DTBP is more effective at lowering the auto-ignition temperature (at a set residence time) than the 2-EHN. In the highest concentration used in this study (20% DTBP), the lowest temperature the hexane ignited was 243 ºC, and the pentane mixture autoignited as low as 238 ºC.

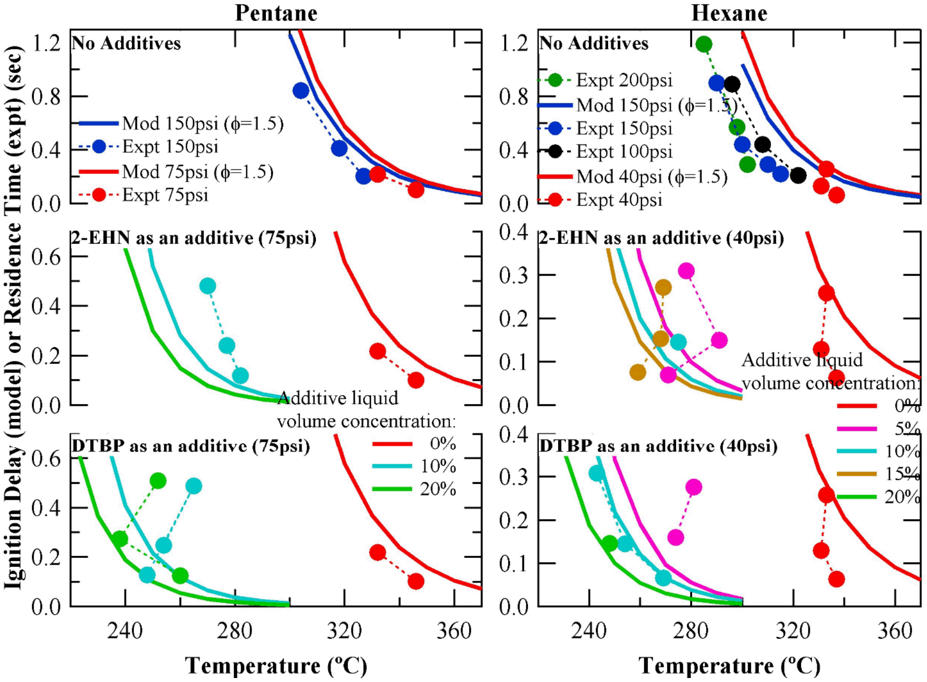

Figure 4. **Auto-ignition properties of a pentane/oxygen system and a hexane/oxygen system. Solid lines show the calculated ignition delay using chemical kinetic mechanisms provided by Westbrook [13]. Different lines represent different pressures in the top frame and different additive amounts in the lower panels. The circles indicate the minimum gas residence times for which ignition was experimentally observed.**

3.3 Silane Ignition

With the end goal of achieving ignition at as low a temperature as possible, silane was explored as a possible ignition source. There were several variables whose impact on silane ignition could be explored. In addition to flow rates (residence time) and temperature, we could control the diluent, the concentration of silane, and the volume of silane-containing gas delivered to the reactor. Inconsistencies in the experiments with silane were observed, which we attributed to solid silica depositing on the walls of the reactor and changing the gas dynamics from experiment to experiment. Depressurizing the experiment, cleaning the system and repressurizing was possible, but quite a tedious exercise. To reduce the deposit buildup and allow more experiments before cleaning, the reactor was reoriented vertically so that gravity would pull the solids away from the burner tip. The reactor was also redesigned to mimic a STRIP burner situation, where the walls were far from the burner tip. In this configuration, ignition of a methane/oxygen mixture was possible down to the lowest temperature tested of 11 °C. It is also expected that the solids deposition will not present a problem in the full scale STRIP burner. The following observations were also made when using silane as an ignition source:

1. Increasing the temperature of the reactor increases the likelihood of ignition.
2. A longer residence (mixing) time increases the likelihood of ignition.
3. Increasing the partial pressure of silane beyond a minimum value does not improve the propensity for ignition.
4. Mixtures of silane diluted with helium and argon are more likely to ignite than mixtures with methane or hydrogen.

Observations 1 and 2 are fairly intuitive and consistent with the auto-ignition of all fuels. Observation 3 implies that a minimum ignition energy is required, and this requirement is easily saturated by silane. Observation 4 is likely a function of the molar heat capacity differences among the different diluents. Differences in diffusivity do not explain this observation because silane diluted by hydrogen is less likely to ignite than silane diluted by helium, or even argon. However, the lower molar heat capacity of the monatomic gases helium and argon allows a given exothermic reaction to provide a greater local temperature rise, favoring thermal runaway to ignition [15].

Several groups have developed kinetic mechanisms describing reactions in the Si-H-O (and sometimes N) systems with various ranges of applicability [16-20]. In this study, we chose to make ignition predictions utilizing a mechanism developed for low-temperature silane ignition [19] in combination with the methane ignition mechanism that we had previously used [12]. This mechanism grossly overpredicted the temperature required for ignition under our experimental conditions, showing a one second ignition delay for a temperature of 210 °C for dry silane and methane and an ignition temperature of 110 °C for silane and methane with 2% moisture. Further model development work is clearly needed at near-ambient temperatures for silane ignition.

4. Conclusions

Ignition delay times were measured at 150 psig for the methane-oxygen system in a heated, high-pressure inconel reactor. Comparisons with chemical kinetic simulations show very good agreement, validating the experimental approach as an appropriate one for measuring short-time ignition delays of relevance to operating an oxy-fuel burner for down-hole thermal EOR applications. At 150 psig and 530 °C, methane auto-ignites in oxygen in approximately 0.6 sec. The higher alkanes, pentane and hexane auto-ignite at lower temperatures than methane. For a 0.8 second ignition delay, the auto-ignition temperature of hexane is around 285 ºC and pentane is around 305 ºC. 2-EHN and DTBP, both typical diesel fuel cetane enhancers, were added to these liquid fuels and were found to significantly lower the auto-ignition temperature. DTBP lowered the auto-ignition temperature to about 240 ºC for both of these alkanes, whereas 2-EHN lowered it to ~ 260 ºC. Simulations of the auto-ignition of these alkanes and their mixtures with the cetane enhancers showed good agreement with the experimental observations. The simulations showed that richer stoichiometries ignite at lower temperatures. Silane was observed to be an effective ignition source for a gaseous burner at room temperature or below (down to at least 11 °C), although solid silica deposits from the oxidation of silane can disrupt the gas dynamics within the experimental rig. Mixtures of silane with helium and argon ignite more readily than mixtures of silane with hydrogen and methane, due to the lower molar heat capacity of the monatomic noble gases.

Acknowledgments

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