Investigation of *n*-pentane pyrolysis at elevated temperatures and pressures in a variable pressure flow reactor

Mario H. Saldana, Gregory E. Bogin Jr.*

Colorado School of Mines, 1610 Illinois Street, Golden, Colorado 80401, United States

*E-mail:gbogin@mines.edu

Abstract

Thermally cracking fuel in a fuel processing facility or undergoing pyrolysis in the anode channel of a fuel cell can lead to coke deposition. The formation of coke occurs via chemical kinetic pathways that are largely dependent on poly aromatic hydrocarbons (PAHs). The formation of PAH's largely depends on species which include ethylene, acetylene, butadiene, benzene and toluene. Pentane is a relatively simple structure for modeling purposes, yet large enough that it produces some of the relevant chemistry of real fuels. Experiments were conducted in a newly designed variable pressure flow reactor (VPFR) built to process both liquid and gaseous reactants at pressures to 4.0 MPa and temperatures to 1373 K. The VPFR was initially validated via ethane pyrolysis experiments and comparing the results with existing literature data. Pentane experiments were done over a range of temperatures (923 K – 1073 K), pressures (1 – 2.0 MPa) and residence times (30 ms – 40 s). The product selectivity appeared to be greatest influenced by pressure and level of fuel conversion. Pressure increases ethylene production but has an inverse effect on ethane production. Soot precursors appeared at higher levels of conversion. The results of the experiments were compared to an existing chemical kinetic mechanism with good agreement.

Keywords: *n*-Pentane; Pyrolysis; High Pressure; Flow Reactor; Product Distribution; Kinetics

1 Introduction

Pyrolysis of fuels plays a vital role in virtually every fuel process, from the production of chemicals for the petrochemical industry to the application in new technologies. Take olefins for an example, they are rare in nature but are vital for several commodities such as plastics, rubber and fuel. Almost all commercial light olefins are produced from higher alkanes using some form of accelerated thermal breakdown¹⁻³. Olefin production is a multi-billion dollar industry. Pyrolysis also plays a large role in all combustion devices. Before fuel is oxidized it is usually preheated in some fashion, either the oxidation reaction provides this heat or there is some other method of providing this preheat. This preheating assists in the break down the fuel and understanding this chemistry is essential in being able to predict ignition timing⁴⁻⁶. At the other end of the combustion process during rich conditions fuel pyrolysis leads to molecular

weight growth and this molecular weight growth leads to particulate emissions which are hazardous to human health⁷⁻⁹. The use of combustion technologies is so widespread that it is essential that pathways to molecular weight growth be understood in order to inhibit their production. Solid oxide fuel cells are able to directly use hydrocarbons and convert them to electricity. These devices typically operate at elevated temperatures ranging around 1073 K. Due to these elevated temperatures the inlet composition may vary, this composition needs to be quantified in order to properly characterize the reactants being delivered to the anode channel¹⁰⁻¹².

Many hydrocarbon processes take place at elevated pressures and temperatures, for example diesel combustion within internal combustion engines and combustion inside the ramjet of a supersonic aircraft. In addition to the combustion within a hypersonic aircraft pyrolysis could also play a role in providing endothermic cooling¹⁴⁻¹⁷. One of the largest issues that affects olefin production, rich combustion, endothermic cooling in hypersonic vehicles, solid oxide fuel cells and human health comes from alkanes' propensity to lead to molecular weight growth products when thermally decomposed.

Studying alkanes is important in understanding real fuel behavior because alkanes are often used as surrogates for real fuels¹⁸⁻²⁰. For example *n*-heptane blended with isooctane can be used to match the vapor pressure and laminar flame speeds of gasoline. For the sets of experiments in this study *n*-pentane was chosen as the fuel because it is small enough to model yet large enough that it still produces some of the relevant chemistry seen in real fuels. Data on *n*-pentane pyrolysis is relatively sparse. There has been some work done on *n*-pentane pyrolysis, Liu et al.²¹ studied pyrolytic coke deposits from *n*-pentane pyrolysis catalyzed with Fe(CO)₅ to understand the carbonaceous products formed. Liu found that by varying the temperature profile, residence time and the Fe(CO)₅ content different carbonaceous deposits could be formed including graphite film, carbon nanotubes and carbon nanoballs.

Several groups have investigated larger chain alkanes. For instance Randolph et al. studied²² hexane pyrolysis, with experiments conducted at residence times of 5 seconds, a temperature range from 823-948 K and at atmospheric pressure. For these experiments the species that appeared in highest concentrations was ethylene followed by methane, propylene, ethane and then hydrogen. The model developed for the analysis did a fair job predicting the experimental trends. Groups have also studied the pyrolysis of heptane, Pant and Kunzru²³ investigated heptane pyrolysis in a stainless steel tubular reactor, experiments were conducted over a temperature range from 953-1023 K at atmospheric pressure, with steam as a diluent. The major products were methane, ethylene, propylene, and 1-butene and the minor products for these experiments were 1,3-butadiene, ethane, propane, *n*-butane, 3-methylbutene, 1-pentene, 1-hexene and benzene at higher levels over conversion. For all conditions the main species produced was ethylene, this group observed ethylene taper off at higher levels of

conversion and propylene, 1,3 butadiene, 1-butene, 1-pentene and 1-hexene also displayed this behavior. Chakraborty and Kunzru¹³ investigated heptane pyrolysis in a tubular reactor at elevated pressures (0.1 – 2.93 MPa) over a temperature range of 793 – 953 K with residence times of 0.2 – 14.8s. The main products produced for the experiments were methane, ethylene, ethane, propylene, 1-butene, 1-pentene and 1-hexene. As pressure is increased the selectivity of hydrogen, methane, ethylene and propylene decreased, and those of propane, n-butane and 1-butene increased. The temperature of the reactor in this system was determined by using thermocouples placed on the outer wall of the reactor and the inside temperature was computed using these temperature readings.

There is a need for additional high pressure experimental data to build a more robust understanding of pressure effects on alkane pyrolysis kinetics; this was the primary motivation behind the design of the variable pressure flow reactor presented in the next section.

2 Experimental

2.1 Experiment Description

A variable pressure flow reactor was designed to have a wide range of capabilities. The reactor was primarily designed to experimentally study fuel oxidation and pyrolysis behavior. The reactor can run at pressure up to 40 bar at 1073 K. A wide range of residence time (30 ms – 40 s) is achieved by utilizing mass controllers with various flow ranges and by having the capability to change the diameter of the flow reactor. A process flow schematic is included in Figure 1. Gaseous products (inert and gaseous fuels) are contained in high pressure gas cylinders. The high pressure in these cylinders is regulated with high pressure regulators (Matheson, Model 3030 Series) for ethane and (McMasterCarr, 6677A12) for nitrogen. From the pressure regulators the flow is diverted to a bank of mass flow controllers (Bronkhorst, F-201-AV-50K) that were calibrated for nitrogen and ethane at low and high pressure. For these mass flow controllers the flow range varied from 0-50 SLPM for nitrogen and 0-25 SLPM for ethane. To cover the lower range of flow, a separate bank of mass flow controllers is utilized (Alicat Scientific, MC-5SLPM-D/5M); these mass flow controllers operate over a flow range from 0-5 SLPM for both ethane and nitrogen. All mass flow controllers have an uncertainty of $\pm 1\%$ of the full scale. To prevent back flow check valves are installed downstream of the mass flow controllers. The mass flow controllers are interfaced through the data acquisition system, with the hardware portion consisting of national instruments hardware (National Instruments, myRIO-1900 and thermocouple module NI 9211). The hardware is interfaced through LabVIEW. In addition to controlling the mass flow controllers the temperatures and pressures are also recorded at various positions throughout the reactor as to ensure proper system operation. Temperatures are acquired via K-type thermocouples with an uncertainty of $\pm 1.1\text{K}$ and the pressures are read from pressure transducers (Omega, PXM309-070G10V) with an uncertainty

Figure 1: Variable pressure flow reactor process flow schematic configured for gaseous and liquid pyrolysis

of ± 0.07 MPa. Liquid fuel is metered and delivered to the system via a HPLC pump (Lab Alliance, Series II), with a range 0-15 ml/min with an uncertainty of ± 0.1 ml/min for *n*-pentane. Over the range of *n*-pentane experiments the flow rate varied from 1 – 8 ml/min. A misting nozzle is installed downstream of the fuel pump it is designed to atomize the fuel and induce turbulence in the mixer. To help ensure fuel is atomized a coaxial flow consisting of nitrogen is introduced around the nozzle that entrains the fuel. The fuel/nitrogen mixture is introduced into the inlet of the preheater. The heat for the preheater is provided from a 675 W band heater (Watson, 125CH93A1X-1154) helically wrapped around a 2.54 cm diameter x 30.48 cm in length tube. The heater is controlled using a K-type thermocouple on the surface of the band heater and utilizing a PID controller (Athena, C-Series 16C). The preheater ensures that all reactants being introduced into the reactor are in the gas-phase; the temperature at this point is maintained above 520 K, at this temperature *n*-pentane is well into the gas phase at both low

and high pressure. From the preheater the mixture enters the main reactor section. The reactor is made from 321 stainless steel which has been treated with an inert silicon coating (SilcoTek, SilcoKlean), this coating is stable at temperatures above 1373 K²⁴. 321 stainless steel is stable at temperatures up to 1090 K. The coating is chemical vapor-deposited amorphous silicon layer. Inert silicon coatings deposited on stainless steels have been shown to have superb surface inertness comparable to glass lined steel²⁵⁻²⁷. The overall length of the reactor is 142 cm long with an inside diameter of 3.86 mm for experiments where the residence time was less than 1 second and an inside diameter 10.92 mm for the residence times greater than 1 second. Heat is delivered circumferentially to the reactor via an array of 4 custom fiber insulated heaters (Zircar Ceramics, Type FIH). This array of heaters consists of 3 1.2 kW heaters that are 30.48 cm in length and 1 600 W heater that is 15.24 cm in length.

Figure 1: Main reactor heat provided by 4 independently controlled heaters separated by 3.18 cm vestibules.

The control for the heaters is provided by PID controllers (Omega, CNI-CB240-K-EI and CNI-CB120SB-K-EI) with feedback from K-type thermocouples (Omega, Nextel Series). Pressure in the reactor is maintained by utilizing a back pressure regulator (Swagelok, KPB1L0A412P-1-4). From the outlet of the flow reactor the effluent is diverted to the exhaust and sampling section. In order to prevent condensation experiments are conducted with high levels of nitrogen dilution > 80%. Additionally all exposed lines are heated utilizing tape heaters (Omega, HTWC101-012) the exposed lines are kept above 480 K from the reactor outlet to the back pressure regulator. Downstream of the back pressure regulator and to the sampling section pressure is close to atmospheric, these lines are maintained above 380 K. The effluent is analyzed using gas chromatography that utilizes a flame ionization detector (FID) for hydrocarbon speciation and a thermal conductivity detector (TCD) for methane, hydrogen and nitrogen.

2.2 Gas Chromatography

Hydrocarbon speciation was performed using an Agilent 6890 GC equipped with a split/splitless injector and FID. An eight-port heated VICI Valco gas-sampling valve was plumbed into the GC between the injection port outlet and FID detector. The purpose of the valve was to ensure reproducible volumetric gas injections via a fixed volume sample loop, and to back-flush the GC

Figure 3: GC FID signal for for 10000ppm for various species

column in-between runs. The valve was heated slightly to ensure analyte condensation would not occur. Gas sample loops allow for precise gas injections, as long as the pressure is repeatable. For this analysis, the sample was pre-diluted before being loaded into the sample loop, and always allowed to come to ambient pressure before injection into the GC. Back-flushing this chromatography column for this analysis is necessary as high molecular weight hydrocarbons, if present, would collect at the front of the column and perhaps never elute. These compounds could build up over time and reduce the separation efficiency of the column. The column used for separation was a Restek RT-AluminaBond/ Na_2SO_4 (30m x

Figure 4: Signal strength vs number of carbons at 10000 PPM

0.32mm x 5um Cat #19757-6850), chosen because of its ability to separate methane at room temperature.

A similar process is used for speciation of hydrogen, nitrogen and methane using a separate Agilent 6890 GC equipped with a split/splitless injector and TCD. The column used for the TCD was a Restek Molecular Sieve 5A Porous Layer Open Tubular Capillary Column.

Calibration of the GC systems was performed using Refinery Gas Standard #2 (DCG Partnership I, LTD)²⁸. Additional species such as cyclopentane, cyclopentene, cyclopentadiene, 1,3 cyclohexadiene, 1,4 cyclohexadiene, benzene and toluene were obtained from Sigma Aldrich and identified individually. The calibration for these species was accomplished by grouping the signals of the calibrated species as seen in Figure 3. Figure 4 highlights that the signal strength increases linearly for alkanes, as does the signal for alkenes with a single bond. Based on the observed trends the calibration factors for each unquantified species were estimated.

2.3 Validation of flow reactor operation

The data for *n*-pentane pyrolysis is sparse, for this reason ethane was chosen as the fuel to validate the operation of the reactor. Xu et al.²⁹ carried out ethane experiments at 0.08 MPa, a dilution of 50% nitrogen and a residence time of approximately 5 seconds. For the current study several temperatures were chosen at a residence time of approximately 5 seconds in order to compare data generated from the reactor to existing literature. Unlike the Xu et al.²⁹ experiments, the current study involved no dilution, for comparisons the data obtained from Xu et al.²⁹ was normalized using Equation 1.

$$\overline{Ethane}_{Converted} = 1 - \frac{x_{ethane}}{(\sum_i^n x_i) - x_{N_2}} \quad \text{Eq.1}$$

Where x_{ethane} is the mol fraction of ethane in the system, x_i is a product in the effluent, and x_{N_2} is the mol fraction of nitrogen. The results are in good agreement with the Xu et al.²⁹ data, as is highlighted in Figure 5 and Figure 6.

For the ethane pyrolysis experiments the largest species by far were ethylene and hydrogen. Similarly to the normalization of the Xu et al.²⁹ ethane data, the ethylene and hydrogen are normalized using Eq.2,

$$\bar{X}_i = \frac{x}{(\sum_i x_i - x_{N_2})} \quad \text{Eq.2}$$

Figure 5: Ethane conversion as a function of temperature at a residence time of approximately 5 seconds for comparison between data and Xu et al.²⁹

where x is the mol fraction of the species in the system. Over the set of experiments the majority of ethane is converted to ethylene and hydrogen. The agreement for the distribution of these species over the range of ethane conversion is good between the current study and Xu et al.²⁹. Other dominant species produced during ethane conversion were methane, 1, 3 butadiene, acetylene and benzene; with the exception of acetylene the comparison with these data is also good.

The Xu et al.²⁹ paper modeled the experiment utilizing the plug flow assumption. At a residence time of 5 seconds the computed Reynolds numbers are in the laminar regime. For the reactor used in the Xu et al.²⁹ experimental validation was accomplished by comparing the plug flow model to the parabolic flow model CRESLAF in CHEMKIN³⁰, the results of the two models were very similar indicating that the plug flow assumption was reasonable for this system.

The reactor in the Xu et al.²⁹ has been utilized for many published studies involving gas-phase kinetics^{10,22,32-34}. The agreement between the two reactors helps validate the operation of this new system.

Figure 6: Comparison of experimental data to existing literature for the major products of ethane pyrolysis

3 Results and discussion

3.1 Modeling Description

A plug flow model was utilized with a detailed chemical kinetic mechanism and associated thermodynamics within CHEMKIN-PRO release 15131³¹. The plug flow model assumes that axial diffusion is negligible and that there exists no gradients of any kind in the radial direction.

At residence times greater than about 600 ms the calculated Reynolds numbers extend into the laminar regime which presents opportunities for wall shear and a non-uniform velocity profile. To analyze the effect of the parabolic profile on the product distribution, the cylindrical shear model was compared to the plug flow model. For the cylindrical shear model the species concentrations were averaged in the radial direction and the results were very similar to the results produced by the plug flow model. For the ethane and *n*-pentane experiments an analysis found that mass flow in the system due to bulk transport was several orders of magnitude larger than mass flow due to axial diffusion.

The mechanism used for analysis in this study was the *n*-heptane detailed mechanism 3.1 from Lawrence Livermore National Laboratory (LLNL)²⁰. The *n*-heptane mechanism is primarily used for analyzing combustion chemistry in IC engines. It was generated and validated by rapid compression machines and shock tubes over a pressure range 0.3 – 5 MPa and 650 – 1200K. In addition to the thermodynamic and kinetics file several other inputs are needed for the modeling software.

Inputs for plug flow model:

- Chemical kinetic file
- Thermodynamic file
- Reactor dimensions (length and diameter)
- Absolute pressure
- Mass flow rate
- Inlet composition
- Temperature profile

Figure 7: Temperature as a function position at various mass flow rates (pressure did not have effect on profile).

The temperature profiles were characterized over a range of conditions.

By analyzing various mass flow rates at pressures of 0.1 and 2 MPa and a fixed temperature of 1073 K it was observed that the temperature profile was strongly a function of the mass flow rate. Temperature sweeps were conducted at 0.1 and 2 MPa to determine the effect of pressure. The temperature sweeps at pressure were accomplished by using K-type thermocouple of varying lengths to generate the temperature profile at various conditions. For modeling, the temperature profile input is the one that was generated for the corresponding flow condition.

3.2 *n*-Pentane pyrolysis

Pentane pyrolysis was carried out at pressures of 0.1 and 2 MPa. Pentane (Sigma Aldrich, 99%) was diluted in 80% nitrogen (Airgas, 99.999%). Conversion of the fuel was accomplished in two ways, one by adjusting residence time at a fixed temperature and pressure. Secondly, conversion was achieved by adjusting temperature and maintaining a fixed residence time and pressure. For these experiments pentane was diluted with approximately 85% nitrogen.

The data in the pentane analysis has been normalized in the same manner as presented earlier in the ethane section with equations Eq.1 and Eq.2.

Figure 8 presents *n*-pentane conversion as function of residence time at 0.1 and 2 MPa and at a temperature of 1073 K and at 923 K; with comparisons with the LLNL *n*-heptane mechanism²².

There are some general trends that can be observed, with the exception of the 2 MPa 1073 K experiments the LLNL model under predicts the observed results. Additionally all modeling data predicts an initial rapid decomposition rate followed by a slower rate. Figure 9 presents temperature sweep data at a fixed residence time and pressure. The model again under predicts the results at 0.1 MPa. For the 2 MPa temperature sweep experiments the model initially under predicts the experimental data but as temperature increases the model switches to over prediction.

Figure 8: Pentane conversion as a function residence time at 923 K and 1073 K at pressures of 0.1 and 2 MPa.

Figures 10-13 show how product selectivity is affected by temperature, pressure and residence

Figure 9: Pentane conversion as a function of temperature at a fixed residence time

time. In analyzing this data it should also be possible to gain some insight into the conditions that promote molecular weight growth. Figure 10 presents concentrations of hydrogen, ethylene and ethane, which show moderate to strong pressure dependence. At 0.1 MPa two sets of experiments were conducted. At 2 MPa three sets of experiments were conducted. For a fixed temperature, pressure appears to inhibit the production of hydrogen. The least amount of hydrogen was produced at 923 K and 2 MPa. The highest amount of hydrogen was produced at 0.1 MPa and 1073 K. The LLNL model captures the pressure dependence of hydrogen but fails to capture the trends and the magnitude of the pressure effects accurately. Ethylene displays the same trends as hydrogen and again the model captures this behavior. The model does a decent job at capturing the experimental trends.

In Figure 10, ethane displays inverse progression of ethylene and hydrogen in that increasing pressure increases the observed concentration and lowering the temperature also increases the yield. Again the model captures the pressure effects but not the magnitude. These three species display the highest pressure dependence of any other species.

The next species presented in Figure 11 are some of the other major products of pentane pyrolysis, which are methane, propylene and 1-butene. Methane selectivity is not affected as much by temperature as it is by pressure, the 923 K 2 MPa, 1073 K 2 MPa and 2 MPa temperature sweep experiments all produce similar methane results. The data also groups together for the 0.1 MPa experiments.

Figure 10: Comparison of hydrogen, ethane and ethylene as a function parent fuel conversion with included modeling. 0.1 MPa 1073 K – (τ : 50-200ms), 0.1 MPa TS (τ : 150ms), 2 MPa TS (τ : 200-600ms), 2 MPa 923 K (τ : 3-45s)

Figure 11: Comparison of methane, propylene, and 1-butene as a function of pentane conversion with included modeling. 0.1 MPa 1073 K – (τ : 50-200ms), 0.1 MPa TS (τ : 150ms), 2 MPa TS (τ : 200-600ms), 2 MPa 923 K (τ : 3-45s)

The model fails to capture the temperature independence for the experiments done at 2 MPa at both 923 K and 1073 K. Propylene is the next higher olefin following ethylene. For ethylene pressure decreased the observed concentration but this is not the case for propylene.

Figure 12: Comparison of methane, propylene, and 1-butene as a function of pentane conversion with included modeling. 0.1 MPa 1073 K – (τ : 50-200ms), 0.1 MPa TS (τ : 150ms), 2 MPa TS (τ : 200-600ms), 2 MPa 923 K (τ : 3-45s)

Figure 13: Comparison of acetylene, propadiene and 1,3 butadiene as a function of pentane conversion with included modeling. 0.1 MPa 1073 K – (τ : 50-200ms), 0.1 MPa TS (τ : 150ms), 2 MPa TS (τ : 200-600ms), 2 MPa 923 K (τ : 3-45s)

Propylene concentration increases with pressure, additionally lowering the temperature from 1073 K to 923 K at 2 MPa also increased its net production. Similarly to all the other data the temperature sweep data at a fixed pressure, grouped together with the residence time sweep data at the same pressure. Like propylene, 1-butene increased in concentration with an

increase in pressure. Additionally both propylene and 1-butene reach a maximum in concentration and then begin to decrease. For propylene this decrease occurs at approximately 80% fuel conversion, while for 1-butene the decrease occurs at approximately 60% fuel conversion.

Figure14: Comparison of benzene and toluene as a function of pentane conversion with included modeling. 0.1 MPa 1073 K – (τ : 50-200ms), 0.1 MPa TS (τ : 150ms), 2 MPa TS (τ : 200-600ms), 2 MPa 923 K (τ : 3-45s)

Figure 12 shows species profiles for 2-butene, 1-pentene and 2-pentene. For 2-butene the model does a fairly decent job at predicting the pressure dependence however it does not capture the magnitude of the pressure effect. Some of the same trends seen in propylene and 1-butene are observed in 2-butene, for example when decreasing the temperature from 1073 K to 923 K at 2 MPa there is an increase in the concentration. For 1 and 2-pentene the results are similar in that the data tends to group together with pressure. These olefins all reach a maximum and then begin to decrease at levels above 60% fuel conversion.

Figure 13 highlights the behavior of some of the major molecular weight precursor's acetylene, propadiene and butadiene. For the 923 K experiments there was no noticeable acetylene produced, at these temperatures there was some propadiene produced but only small amounts compared to the levels produced at 1073 K. Increasing the pressure reduces the concentration for all three species. The LLNL Model does a good job at predicting trends in acetylene and propadiene, but fails to capture the pressure effects at higher levels of conversion.

The LLNL model does not include pathways for poly aromatic hydrocarbons. Figure 14 shows species profiles for benzene and toluene as a function of pentane conversion. Benzene and toluene display the inverse behavior of acetylene; propadiene and butadiene in that at 923 K 20 bar where the previous species were at the lowest levels; benzene and toluene in contrast, are at the highest levels. The majority of the benzene and toluene were produced at levels above 60% fuel conversion. It is important to note that at these higher levels of conversion it is also where the majority of the olefins are decreasing in concentration.

3.3 Sensitivity Analysis

In order to gain insight into the reactions dominating the chemical kinetics a sensitivity analysis was conducted. The sensitivity analysis was performed using CHEMKIN-PRO²² and is carried out by analyzing the sensitivity coefficients. The sensitivity coefficients are the ratios of the relative change in mole fractions at a specified time to the relative change in the rate constants.

Figure 15: Sensitivity analysis for pentane at 1073 K at 0.1 and 2 MPa

The sensitivity coefficients were only analyzed if the absolute value of the coefficient was greater than 0.1, this was done in order to maintain only the most dominant reactions. Beginning with analyzing the sensitivity coefficients for *n*-pentane presented in Figure 15, the sensitivity analysis on *n*-pentane revealed that the most important reaction in the decomposition was the thermal decomposition of pentane into propyl and ethyl radicals, reaction R.1

The β -scission of ethyl into ethylene and hydrogen radicals, reaction R.2 is the next important reaction.

From the major reactions highlighted in the sensitivity analysis in Figure 15, only reaction R.2 is pressure dependent.

At both high and low pressure the model highlighted reactions R.1 and R.2 are important, they are important because they generate radicals that in turn carry out hydrogen abstractions, this is why reactions R.3 and R.4 were also identified in the sensitivity analysis as being important.

The hydrogen abstractions that lead to pentyl radicals, lead to olefins through β -scissions in addition to providing additional radicals that are able to carry out more hydrogen abstractions.

Figure 16: Sensitivity coefficients for hydrogen and ethylene as a function of pentane conversion at 1073 K and 0.1 MPa

These β -scission reactions R.5, R.6, and R.7 are primary pathways to higher olefins like propylene, 1-butene and 1-pentene. As the concentrations of the higher olefins build up, so do the concentrations of the resonantly stabilized allylic radicals. Recently Wang et al.³⁵ have shown that these allylic radicals have important pathways leading to molecular weight growth. Additionally the stability of the allylic radicals allows for the buildup of their concentrations, this leads to a decrease in the decomposition rate of pentane. This inhibition to decomposition is highlighted in Figure 15, reactions generating allyl radicals are inhibiting the conversion of pentane.

The next species to receive a sensitivity analysis are hydrogen and ethylene at 0.1 MPa and 1073 K. Ethylene and hydrogen are some of the major species produced from pentane pyrolysis. Figure 16 shows that the reaction that most strongly inhibits the production of hydrogen is the recombination reaction involving 2 ethyl radicals and leading to butane, the reverse of reaction R.8.

It appears that reactions terminating ethyl inhibit the production of hydrogen and ethylene. Unlike the ethane experiments where hydrogen and ethylene were approximately the same in terms of production, the pentane experiments make almost twice as much ethylene for every case.

Figure 17: Ethane sensitivity coefficient as a function of pentane conversion at 0.1 and 2 MPa for LLNL

The next species presented is ethane in Figure 17. It is important to note that the β scission reaction involving ethyl reaction R.2, was the dominant reaction in the production of both hydrogen and ethylene. Reaction R.2 plays an opposite role in ethane, in that it inhibits its production, the model captures this behavior. The model also predicts that hydrogen abstractions by ethyl are the dominant reactions in the formation of ethane. The abstraction reactions by ethyl are not pressure dependent. Similarly to hydrogen and ethane the thermal decomposition of pentane into ethyl and propyl radicals reaction R.1 is also a dominant reaction. Out of all of the species ethane showed the greatest sensitivity to pressure. A sensitivity analysis at the higher pressures gives some clues as to where the increase in ethane production comes from at higher pressures. The pressure dependence on ethane may be because the β scission reaction involving ethyl reaction R.2, is reduced at higher pressures, being a unimolecular reaction increases in pressure result in proportional increases in the rate. While bimolecular reactions increase proportional to the pressure squared, this is one of the reasons why more ethane is produced at higher pressure and less hydrogen is produced.

The final sensitivity analysis is for methane at 1073 K and 0.1 MPa and is presented in Figure 18. At low levels of conversion the model highlights the β -scission of ethyl as the dominant reaction R.2 but this effect fades as conversion progresses past 20%. The model predicts the thermal decomposition reaction R.1 as being important, followed by hydrogen abstractions by methyl on pentane in R.4.

Figure 18: Methane sensitivity coefficient as a function of pentane conversion at 0.1 MPa 1073 K

4 Conclusion

A design for a variable pressure flow reactor capable of achieving high pressures was presented. Reactor operation was validated against existing literature data for ethane pyrolysis with good agreement. Next a presentation of experimental data on *n*-pentane pyrolysis over a range of conditions was presented and compared with an existing chemical kinetic model to predict experimental trends. Through experiments it was observed that as olefin (C3+) production reached a maximum and began to taper off, benzene and toluene ramped up in production around the same point. It was observed that an increase in pressure reduced the production of ethylene, acetylene, hydrogen, propadiene and 1, 3 butadiene. These species have been identified as being important in the development of molecular weight growth. At higher pressures molecular weight growth was increased with pressure as observed with the concentration profiles of toluene and benzene. The (C3+) alkenes also had a higher observed concentration at higher pressures.

A sensitivity analysis revealed that pentane pyrolysis was extremely sensitive to only a few reactions. The most sensitive reaction by far was the thermal decomposition reaction R.3 of pentane into propyl and ethyl radicals. The analysis highlighted that most alkenes were generated through β -scission reactions which led to the formation of more hydrogen and alkyl radicals. In the experiments it was observed that the alkenes reached a maximum, this happens when the parent fuel was more than 60% converted. The methyl, ethyl and hydrogen radicals at this point appeared to continue carrying out hydrogen abstractions from the alkenes as more favorable path compared to the parent fuel. This would explain the rate decrease observed in pentane at higher levels of conversion as well as the decrease in the concentration of alkenes.

The experiments carried out in this study hint at the possibility that allylic radicals are key intermediates in the formation of molecular weight growth products. The experiments also highlight the need for future work on alkane pyrolysis at high conversion and elevated pressures.

Acknowledgements

The authors would like to acknowledge financial support from the Air Force Office of Scientific Research, Award number FA9550-12-1-0495, Dr. Michael Berman, Technical Monitor. The authors wish to thank Prof. Anthony Dean and Dr. Kun Wang for helpful discussions. The authors would also like to thank Jon Luecke for the assistance with the setup and calibration for the product speciation via the gas chromatography systems.

References

1. Powers, Donald H. "Olefin production utilizing whole crude oil." U.S. Patent No. 6,743,961. 1 Jun. 2004.
2. Gayubo, Ana G., et al. "Olefin production by catalytic transformation of crude bio-oil in a two-step process." *Industrial & Engineering Chemistry Research* 49.1 (2009): 123-131.
3. Vora, Bipin V., Terry L. Marker, and Paul T. Barger. "Enhanced light olefin production." U.S. Patent No. 6,049,017. 11 Apr. 2000.
4. Assanis, Dennis N., et al. "A predictive ignition delay correlation under steady-state and transient operation of a direct injection diesel engine." *Journal of Engineering for Gas Turbines and Power* 125.2 (2003): 450-457.
5. He, X., et al. "An experimental and modeling study of iso-octane ignition delay times under homogeneous charge compression ignition conditions." *Combustion and Flame* 142.3 (2005): 266-275.
6. Spadaccini, L. J., and M. B. Colket. "Ignition delay characteristics of methane fuels." *Progress in Energy and Combustion Science* 20.5 (1994): 431-460.
7. Maricq, M. Matti, Stephen J. Harris, and Joseph J. Szenté. "Soot size distributions in rich premixed ethylene flames." *Combustion and Flame* 132.3 (2003): 328-342.
8. Weilmünster, P., A. Keller, and K-H. Homann. "Large molecules, radicals, ions, and small soot particles in fuel-rich hydrocarbon flames: Part I: positive ions of polycyclic aromatic hydrocarbons (PAH) in low-pressure premixed flames of acetylene and oxygen." *Combustion and flame* 116.1 (1999): 62-83.
9. Skjøth-Rasmussen, Martin Skov, et al. "Formation of polycyclic aromatic hydrocarbons and soot in fuel-rich oxidation of methane in a laminar flow reactor." *Combustion and Flame* 136.1 (2004): 91-128.
10. Gupta, Gaurav K., et al. "Comparison of conversion and deposit formation of ethanol and butane under SOFC conditions." *Journal of power sources* 158.1 (2006): 497-503.
11. Cimenti, Massimiliano, and Josephine M. Hill. "Direct utilization of liquid fuels in SOFC for portable applications: challenges for the selection of alternative anodes." *Energies* 2.2 (2009): 377-410.
12. Pomfret, Michael B., et al. "Hydrocarbon fuels in solid oxide fuel cells: In situ Raman studies of graphite formation and oxidation." *The Journal of Physical Chemistry C* 112.13 (2008): 5232-5240.
13. Chakraborty, Jyoti Prasad, and Deepak Kunzru. "High pressure pyrolysis of n-heptane." *Journal of Analytical and Applied Pyrolysis* 86.1 (2009): 44-52.
14. Fau, Guillaume, et al. "Fuel pyrolysis through porous media: Coke formation and coupled effect on permeability." *Journal of Analytical and Applied Pyrolysis* 95 (2012): 180-188.
15. Lander, H., and A. C. Nixon. "Endothermic fuels for hypersonic vehicles." *Journal of Aircraft* 8.4 (1971): 200-207.
16. Huang, He, David R. Sobel, and Louis J. Spadaccini. "Endothermic heat-sink of hydrocarbon fuels for scramjet cooling." *AIAA paper* 3871 (2002): 2002.
17. Nixon, A. C., et al. *VAPORIZING AND ENDOTHERMIC FUELS FOR ADVANCED ENGINE APPLICATION*. No. S-13992. SHELL DEVELOPMENT CO EMERYVILLE CA, 1966.
18. Vasu, Subith S., David F. Davidson, and Ronald K. Hanson. "Jet fuel ignition delay times: Shock tube experiments over wide conditions and surrogate model predictions." *Combustion and Flame* 152.1 (2008): 125-143.
19. Fikri, M., et al. "Autoignition of gasoline surrogates mixtures at intermediate temperatures and high pressures." *Combustion and flame* 152.1 (2008): 276-281.

20. Mehl, Marco, et al. "Kinetic modeling of gasoline surrogate components and mixtures under engine conditions." *Proceedings of the Combustion Institute* 33.1 (2011): 193-200.
21. Liu, Xin-Ying, Bi-Chun Huang, and Neil J. Coville. "The Fe (CO) 5 catalyzed pyrolysis of pentane: carbon nanotube and carbon nanoball formation." *Carbon* 40.15 (2002): 2791-2799.
22. Randolph, Katie L., and Anthony M. Dean. "Hydrocarbon fuel effects in solid-oxide fuel cell operation: an experimental and modeling study of n-hexane pyrolysis." *Physical Chemistry Chemical Physics* 9.31 (2007): 4245-4258.
23. Pant, Kamal K., and Deepak Kunzru. "Pyrolysis of n-heptane: kinetics and modeling." *Journal of analytical and applied pyrolysis* 36.2 (1996): 103-120.
24. "Anti-coking Coating, Automotive, Aerospace." Anti-coking Coating. SilcoTek, n.d. Web. 30 Aug. 2015. <http://www.silcotek.com/SilcoKlean-anti-coking-coating>
25. Jones, E. Grant, Lori M. Balster, and Walter J. Balster. "Autoxidation of aviation fuels in heated tubes: Surface effects." *Energy & fuels* 10.3 (1996): 831-836.
26. Ervin, Jamie S., et al. "Surface deposition within treated and untreated stainless steel tubes resulting from thermal-oxidative and pyrolytic degradation of jet fuel." *Energy & fuels* 17.3 (2003): 577-586.
27. Edwards, T., Gord, J., and Bunker, C, "Advanced Supercritical Fuels," abstract from Army Research Office and Air Force Office of Scientific Research 2001 Contractors' Meeting in Chemical Propulsion, Los Angeles, California, June, 2001, pp. 78-81.
28. Refinery Gas Standard #2 / Sample Handling / Chromatography Products at Restek.com/<http://www.restek.com/catalog/view/3556/34442>
29. Xu, Chen, et al. "Kinetic modeling of ethane pyrolysis at high conversion." *The Journal of Physical Chemistry A* 115.38 (2011): 10470-10490.
30. Kee, Robert J., Fran M. Rupley, and James A. Miller. *Chemkin-II: A Fortran chemical kinetics package for the analysis of gas-phase chemical kinetics*. No. SAND-89-8009. Sandia National Labs., Livermore, CA (USA), 1989.
31. Design, Reaction. "CHEMKIN-PRO 15131, San Diego (2013)."
32. Villano, Stephanie M., et al. "Selective removal of ethylene, a deposit precursor, from a "dirty" synthesis gas stream via gas-phase partial oxidation." *The journal of physical chemistry A* 114.23 (2010): 6502-6514.
33. Al-Shoaibi, A. S. Ph.D. Thesis, Colorado School of Mines, 2008
34. Wang, Kun, Stephanie M. Villano, and Anthony M. Dean. "Fundamentally-based kinetic model for propene pyrolysis." *Combustion and Flame* 162.12 (2015): 4456-4470.
35. Wang, Kun, Stephanie M. Villano, and Anthony M. Dean. "Reactions of allylic radicals that impact molecular weight growth kinetics." *Physical Chemistry Chemical Physics* 17.9 (2015): 6255-6273.