First-order Kinetic Study of the Reformation of Jet Fuel in Supercritical Water

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Abstract

A global first-order kinetic study was conducted for the supercritical water reformation of jet fuel. Experiments were performed non-catalytically in a continuous mode of operation using supercritical water in a specially designed 926 mL Inconel 625 Grade-1 tubular reactor at temperatures varying from 803 to 972 K and at a pressure of 24.15 ± 0.06 MPa. The process was modeled as three reactions in series: pyrolysis of the jet fuel, reformation of the smaller pyrolysis fractions, and the subsequent water gas shift of the resulting carbon monoxide. Global first order kinetics was assumed throughout. Using a first-order Arrhenius plot, the activation energy and frequency factor was calculated for each of the three reactions. In this paper, the chemical kinetics of this novel process are elucidated based on the experimental data.

Introduction

The non-catalytic supercritical water reformation of jet fuel was studied in a 926 ml Inconel 625 Grade-1 tubular reactor, at temperatures varying from 803 to 972 K at a pressure of 24.15 ± 0.06 MPa. Supercritical water reformation is a novel technology that is compact and requires no catalysts, hence avoiding the subsequent problems of catalytic reforming including poisoning due to feedstock impurities, such as sulfur, coking and fouling. In calculating the kinetics of each reaction, it is assumed that all hydrocarbons in the effluent gas are the product of pyrolysis, all carbon monoxide is the result of reformation, and all carbon dioxide is from the forward water gas shift reaction. It is assumed that all carbon monoxide is the result of reformation due to the lack of oxygenated hydrocarbons in jet fuel. First order kinetics were assumed for all reactions. With these assumptions, the activation energy and frequency factor can be calculated for each reaction. The goal is to better understand and model the reactions that occur during the non-catalytic supercritical water reformation of jet fuel to produce hydrogen. Hydrogen gas is a superb energy source due to its cleanliness and combustion efficiency, but since hydrogen gas does not occur naturally on earth in any reasonable quantity; it must be produced from compounds that contain it. [1] While future technologies may incorporate renewable resources to produce hydrogen, for a seamless integration into the hydrogen economy it is imperative that all avenues of production be explored.

Apparatus & Chemicals

The water used was deionized water, and the jet fuel was both civilian jet fuel (Jet-A) and military aviation logistic fuel (JP-8), both of which are an assortment of hydrocarbons including straight chain, branched and cyclic. An ASTM D2887 boiling range distribution analysis determined that the length of the carbon bonds varied from five to twenty carbons, with the average being twelve for both fuels.[2] Therefore, the fuel was modeled as a single representative molecular species, n-dodecane, which has the chemical formula $C_{12}H_{26}$. Both jet fuels were sent to Texas Oil Tech Laboratories, which tested them for sulfur content and found that the Jet-A contained 990 parts per million and the JP-8 contained 810 parts per million.

The supercritical water system consists of a liquid feed system, integrated heat exchanger, preheat, reactor, reactor heaters, sample collection system, and data acquisition and control system, of which a schematic process flow diagram is illustrated in Figure 1. The reactor is a 926 mL Inconel 625 Grade-1 tubular reactor, which has a safe operational range up to 975 K at 25.86 MPa.[3] The gaseous products were analyzed using a HP 5890 Series A gas chromatograph with a thermal conductivity detector. The gas chromatograph is calibrated to detect hydrogen, nitrogen, carbon monoxide, methane, carbon dioxide, acetylene, ethylene and ethane.

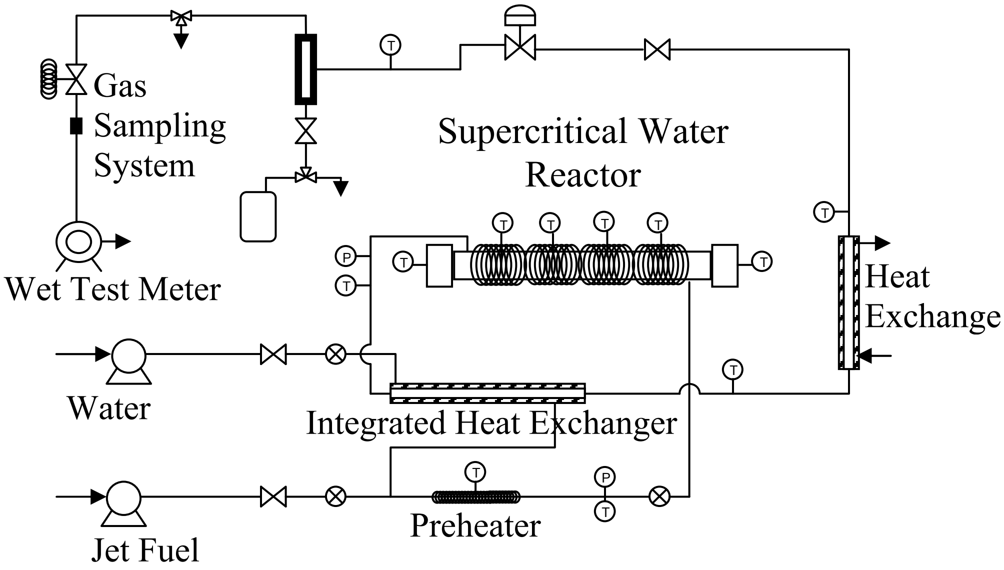

Figure 1. A schematic of the supercritical water reaction system at Missouri University of Science and Technology.

Chemical Reactions

There are various chemical reactions that could take place during the supercritical water reformation of jet fuel, but the primary reactions are reformation, pyrolysis and the water gas shift reaction. These three reactions can account for all of the species present in the effluent gas. The pyrolysis reaction is given by

$$C_mH_n \rightarrow C_aH_b + C_xH_y \quad (m = a + x \text{ and } n = b + y) \tag{1}$$

The pyrolysis reaction is endothermic, but much less so than the reformation reaction, requiring about 70 kJ/mol depending on the carbon number of the hydrocarbon.[4] The pyrolysis reaction is thought to be responsible for any gaseous hydrocarbons contained in the effluent gas, such as methane or ethane. Repeated pyrolysis leaves hydrogen deficient fractions, which eventually become solid coke or function as coking precursors.[5] The reformation reaction is given by

$$C_mH_n + m\ H_2O \rightleftarrows (n/2 + m)\,H_2 + m\ CO \tag{2}$$

Reformation is the most critical reaction, because water participates in the reaction and liberates hydrogen, the desired product. Reformation is also an endothermic reaction, the amount of energy necessary depending on the carbon number of the hydrocarbon being reformed. Methane reformation requires 206 kJ/mol, while the direct reformation of jet fuel (modeled as n-dodecane, $C_{12}H_{26}$) would require 1866 kJ/mol.[4,6] In addition to these reactions, the forward water gas shift (WGS) reaction can also occur. This would be a highly desirable reaction, since additional hydrogen is produced. The forward reaction is equilibrium limited and thermodynamically favored at temperatures of 1090 K or below:[7]

$$\mathrm{CO} + \mathrm{H_2O} \rightleftarrows \mathrm{CO_2} + \mathrm{H_2} \qquad \Delta H^\circ_{298} = \text{-41.2 kJ/mol} \tag{3}$$

Any carbon dioxide present in the effluent gas is assumed to be the result of the water gas shift reaction. Various other reactions, like methanation or the Boudouard reaction, could also be possible, but unlikely given their behavior in other medium.[8,9] This discussion was limited to the aforementioned reactions for simplicity and because they effectively and accurately describe all of the products observed.[4]

Experimental

The above chemical reactions can proceed by different pathways, one of which will be elucidated. This pathway is the simplest model of the reformation of jet fuel, and can serve as a starting point for later, more complicated analysis. As stated above, the assumption that all gaseous hydrocarbons are the result of pyrolysis, all carbon monoxide the result of reformation, and all carbon dioxide the result of the water gas shift reaction will be used for the purposes of kinetic modeling throughout. Using the symbol "*A*" for the carbon atoms in jet fuel, "*B*" for the carbon atoms in the gaseous hydrocarbons, "*C*" for carbon monoxide and "*D*" for carbon dioxide, the reaction pathway is as follows.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D \tag{4}$$

This pathway assumes that all the jet fuel first undergoes pyrolysis, then reformation and then the water gas shift. This pathway increases the importance of pyrolysis and neglects any direct reformation of large liquid hydrocarbons, such as jet fuel itself.[10] Integral analysis of the reaction mechanism of Equation 4 gives:

$$C_a = C_{ao} e^{-k_1 t} \tag{5}$$

$$C_b = C_{ao} k_1 \left[\frac{1}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right) \right] \tag{6}$$

$$C_c = C_{ao} k_1 k_2 \frac{\left(k_1 e^{-k_3 t} - k_1 e^{-k_2 t} + k_2 e^{-k_1 t} - k_2 e^{-k_3 t} + k_3 e^{-k_2 t} - k_3 e^{-k_1 t} \right)}{\left(k_1 - k_2 \right)\left(k_1 - k_3 \right)\left(k_2 - k_3 \right)} \tag{7}$$

$$C_d = C_{ao} \frac{\left(-k_2^2 k_3 (e^{-k_1 t} - 1) + k_3^2 k_2 (e^{-k_1 t} - 1) - k_3^2 k_1 (e^{-k_2 t} - 1) + k_1^2 k_3 (e^{-k_2 t} - 1) - k_1^2 k_2 (e^{-k_3 t} - 1) + k_2^2 k_1 (e^{-k_3 t} - 1) \right)}{(k_1 - k_2)(k_1 - k_3)(k_2 - k_3)} \tag{8}$$

Where C_{ao} is the molar flow rate of carbon in the entering jet fuel, and C_a is the remaining, unreacted jet fuel carbon. C_b is the molar carbon flow rate of the effluent hydrocarbon gasses, methane, ethane and ethene; C_c represents the molar flow rate of carbon monoxide gas and C_d the carbon dioxide molar flow rate. The space time, *t*, and concentrations are known, so the rate constants k_1, k_2, and k_3 can be solved for numerically. The space time was calculated, as a function of inlet fluid density, using the Peng-Robinson equation of state with Van der Waals' mixing rules. With these equations, the rate constants can be determined, and when rate constants at different temperatures are analyzed, the activation energy, E_a, and Arrhenius frequency factor, A, can be regressed using the Arrhenius equation:

$$k = Ae^{-E_a/RT} \tag{9}$$

Table 1 outlines the pressure, temperature, space time, molar carbon flow rate and the water and fuel flow rates for each experimental run. The experiments were conducted in the order given by the Run ID, from one to ten. The temperature was increased from 803 to 972 K at a constant pressure of 24.15 ± 0.06 MPa. A constant water flow rate of 19.4 ± 0.3 grams per minute was maintained, while the reactant jet fuel flow rate was varied, with run numbers 3, 4, 5 and 10 having a fuel flow rate of 0.51 ± 0.01 and the rest having a flow rate of 0.96 ± 0.03 grams per minute. Since the water flow rate is held constant, the space time decreases for increasing temperature because as temperature increases the molar volume increases.

Table 1. Experimental results of jet fuel reformation in supercritical water.

Run ID	**T**	**P**	**Water flow**	**Space time**	**C_{ao}**	**C_b**	**C_c**	**C_d**
	K	MPa	g/min	sec	mol C/min	mol C/min	mol CO/min	mol CO_2/min
8	803	24.28	19.2	231	$7.25\text{x}10^{-2}$	$1.40\text{x}10^{-2}$	$2.75\text{x}10^{-5}$	
7	831	24.27	19.1	218	$7.04\text{x}10^{-2}$	$2.13\text{x}10^{-2}$	$2.29\text{x}10^{-4}$	
6	860	24.30	19.2	204	$6.93\text{x}10^{-2}$	$2.44\text{x}10^{-2}$	$4.25\text{x}10^{-4}$	
5	888	24.21	19.1	193	$7.04\text{x}10^{-2}$	$2.87\text{x}10^{-2}$	$1.16\text{x}10^{-3}$	
4	899	24.21	19.2	189	$3.76\text{x}10^{-2}$	$1.57\text{x}10^{-2}$	$1.21\text{x}10^{-3}$	$1.93\text{x}10^{-4}$
3	914	24.16	19.3	182	$3.52\text{x}10^{-2}$	$1.69\text{x}10^{-2}$	$1.84\text{x}10^{-3}$	$3.73\text{x}10^{-4}$
2	932	24.14	18.8	182	$3.52\text{x}10^{-2}$	$1.68\text{x}10^{-2}$	$2.55\text{x}10^{-3}$	$7.85\text{x}10^{-4}$
9	957	23.71	21.5	150	$3.52\text{x}10^{-2}$	$1.21\text{x}10^{-2}$	$2.64\text{x}10^{-3}$	$1.05\text{x}10^{-3}$
1	972	24.04	19.5	164	$5.64\text{x}10^{-2}$	$2.39\text{x}10^{-2}$	$4.48\text{x}10^{-3}$	$1.78\text{x}10^{-3}$

The values for C_b, C_c and C_d where calculated from the flow rate of the effluent gas and the gas analysis. There are no values for the molar flow rate of carbon dioxide, labeled as C_d, for temperatures between 803 and 888 K because the amount of carbon dioxide in the effluent gas was below the detection limits of the gas chromatograph, which is one mole-percent. The value of C_a, the carbon remaining as jet fuel in the effluent, was not calculated or used in any calculations because liquid analysis determined that less than one percent of the carbon that was fed into the system left via the liquid effluent in any form. It is assumed that any liquid hydrocarbons are negligible.

While the liquid hydrocarbons may be assumed to be negligible, the solid coke formed from the pyrolysis reaction is not. Figure 2 illustrates the carbon that is converted to the gas phase for both fuel flow amounts, 0.5 and 1 gram per minute. Since the amount of hydrocarbons in the liquid are small, all carbon not in the gas phase remains in the reactor as coke. This discrepancy between the amount of carbon in and the amount coming out can also be seen in Table 1, were the C_{ao} the molar amount of carbon in the entering fuel, never equals the combined C_b, C_c and C_d values, which are the molar amount of carbon exiting as gas. On occasion this solid carbon was removed from the reactor, but no systematic study of its formation was performed during these experiments. Figure 2 shows that as the temperature increases, more of the fuel is converted to the gas phase.

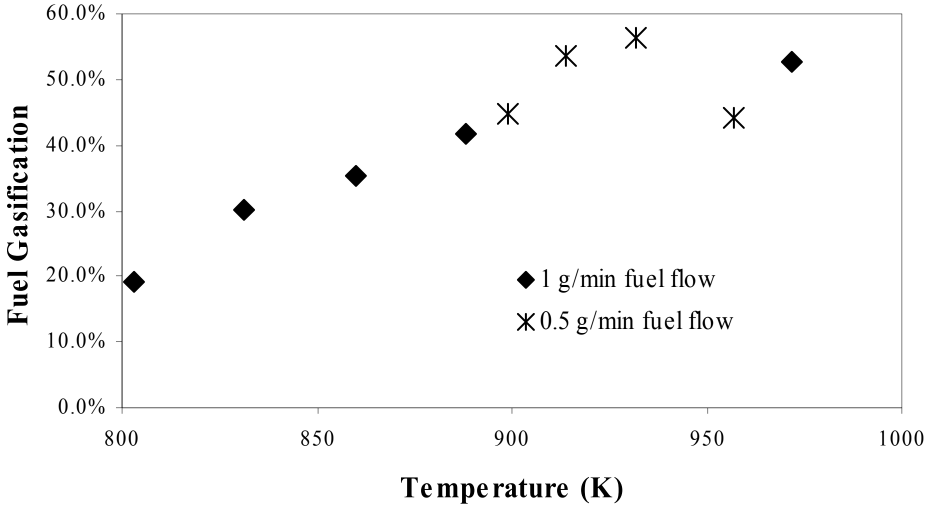

Figure 2. Carbon in the fuel converted to the gas phase as a function of temperature for fuel flow rates of 0.5 and 1 gram per minute.

Results and Discussion

Upon performing the experiments in Tables 1, the effluent gas concentration and flow rate were measured, from which the rate constants for each reaction can be calculated by solving Equations 6-8 simultaneously. The error on this calculation was no more than two percent, on average less than half a percent. The natural log of the rate constants as a function of the inverse temperature is illustrated in Figure 3.

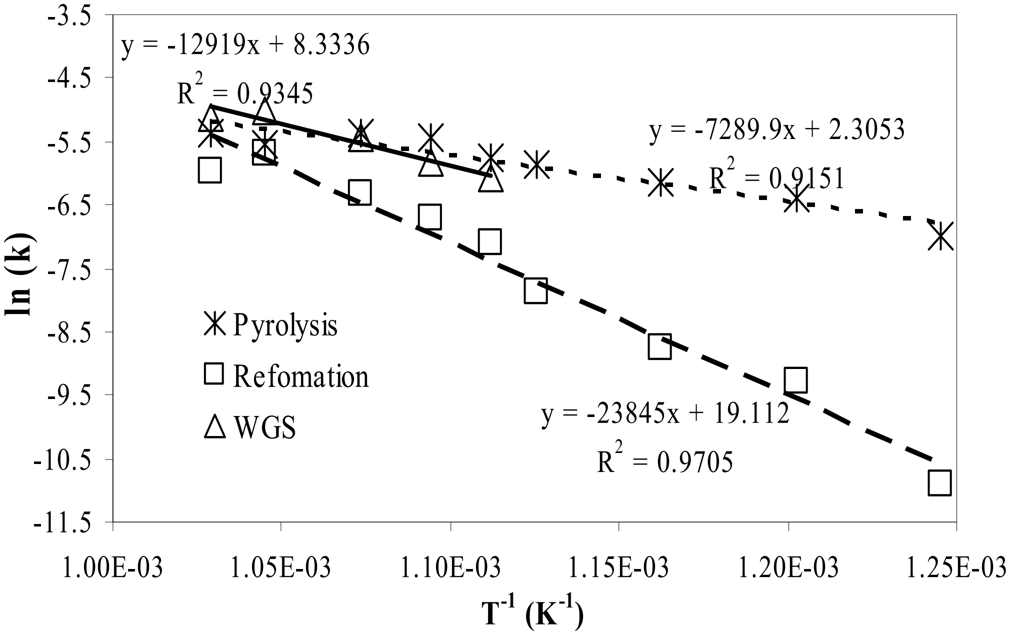

Figure 3. First-order Arrhenius plot for the reactions taking place in the jet fuel-supercritical water mixture.

When the natural log of the rate constant is plotted against the inverse of the temperature for each experiment, the slope is equal to $-E_a/R$ and the intercept is equal to the natural log of A. The activation energy, Arrhenius frequency factor and the autocorrelation coefficient for pyrolysis, reformation and the water gas shift reaction are given in Table 2.

Table 2. Frequency factor and activation energy for pyrolysis, reformation and the water gas shift reaction in supercritical water.

	Pyrolysis	Reformation	WGS
Arrhenius Frequency Factor, s^{-1}	10.03	2.00×10^8	4.16×10^3
Activation Energy, kJ/mol	60.6	198.3	107.4
Autocorrelation Coefficient, R^2	0.915	0.971	0.935

The slope of the Arrhenius plot, and hence the activation energy, describe how dependent the reaction is on temperature. The reformation reaction is the most sensitive to temperature change, followed by the water gas shift and pyrolysis. Other studies of the non-catalyzed water gas shift reaction in supercritical water have determined activation energies between 95 to 145 kJ/mol and between $10^{3.3}$ s^{-1} to $10^{7.2}$ s^{-1} for the frequency factor.[11-14] The reaction pathway was assumed to be a series reaction, in that reformation occurred only after pyrolysis. It could be that pyrolysis and reformation are competing reactions, which would allow direct reformation of the jet fuel along with reformation of the hydrocarbon products of pyrolysis. As a result, this pathway may underestimate the reformation potential of jet fuel, and overestimate the importance of pyrolysis.

Conclusion

A global first-order kinetic study was conducted for the non-catalytic supercritical water reformation of jet fuel in a 926 ml Inconel 625 Grade-1 tubular reactor, at temperatures between 803 and 972 K at a pressure of 24.15 ± 0.06 MPa. Three reactions were used to model the process: pyrolysis of the jet fuel, reformation of the lighter hydrocarbons that result from pyrolysis, and the subsequent forward water gas shift of the resulting carbon monoxide. A set of chemical reactions in series was assumed, for which jet fuel undergoes pyrolysis, then reformation, and the carbon monoxide that is a product of reformation reacts with water to form hydrogen and carbon dioxide. From this reaction mechanism, the rate constants were calculated. The frequency factor and activation energy were regressed using a first order Arrhenius plot of the rate constants. The reformation reaction had the largest frequency factor and activation energy (2.00×10^{8} and 198.3 kJ/mol, respectively), followed by the water gas shift reaction (4.16×10^{3} and 107.4 kJ/mol) and pyrolysis (10.03 and 60.6 kJ/mol). The pyrolysis reaction was the least sensitive to temperature change, followed by the water gas shift and reformation reaction. Increasing temperature facilitates higher percentages of fuel gasification, which decreases the production of solid coke in the reactor and produces higher effluent gas flow rates.

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