Confirmation of Heat Generation during Hydrogenation of Oil

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Abstract The study was devoted to replicating and controlling that excess heat effect during hydrogenation of hydrocarbon. The reactant is phenanthrene, a heavy oil fraction, which is reacted with H2 gas of high pressure and high temperature in the presence of a metal catalyst. This results in the production of excess heat and radiation. After the reaction, an analysis of residual gas reveals a variety of hydrocarbons, but it seems unlikely that these products can explain the excess heat. Most of them form endothermically, and furthermore heat production reached 60 W. Overall heat production exceeded any conceivable chemical reaction by two orders of magnitude.

1. Introduction

This study was stimulated by a liquefying reaction to change the heavy oil to light oil. Abnormal heat generation was observed during the hydrogenation experiments when heated in high-pressure hydrogen gas. The amount of heat generated was abnormally large considering the expected chemical reaction between a few drops of heavy oil and a little hydrogen gas. Based on their estimate, they concluded the heat generated had not come from a conventional chemical reaction.

2. Experimental

2.1 Cell

Figure 1 shows a schematic of the reaction cell and the experimental set up. The reaction chamber is cylindrical. It is constructed from Inconel 625. It has a 16-mm outer diameter, a 10-mm inner diameter, a 300-mm height, and has a 0.01-*l* capacity. It can sustain a pressure of 500 atm, and it can be heated to 850°C. The reactor has a plug for the hydrogen inlet and outlet, and housing for an internal temperature sensor. A platinum catalyst is placed inside the cell. The temperature inside the cell is measured with an R-type thermocouple, 1.6 mm in diameter, 30 cm long, which is enveloped in a 0.3 mm thick SS314 stainless steel shield and grounded to reduce noise. The thermocouple range is from -200 to 1,300°C. Moreover, another thermocouple of the same type is inserted between the outer reactor wall and the inner wall of the electric furnace, to measure the temperature of the outside wall of the reactor cylinder. Thermocouple data is collected by a data logger (Hewlett Packard HP3497A), with a temperature sensitivity of 0.1°C. The error ranges of the temperature measurement system is determined by the resistivity of the thermocouples (4 Ω), the insulation (100 MΩ), and the data logger (100 MΩ). In this case, the error works out to be 0.03% of the instrument reading. At a temperature of 800°C the error is 0.03°C.

2.2 Measurement system

As shown in Fig. 1, the cell is placed in the electric furnace, and hydrogen gas is introduced into the cell through a 6 mm diameters stainless steel pipe. The pipe is fitted with high pressure Swagelok valves which are used to introduce gas into the cell, or to evacuate it. Hydrogen is stored in a tank at 135 atm. It passes through a piezoelectric pressure transducer (Kyowa P-100KA) and amplifier (Shinko Tsushin 603F) and the flow rate is recorded in the data logger. Gas purity is more than 99.999%. The gas line is connected to the vacuum pump and mass spectrometer (ULVAC REGA201) that detects mass numbers up to 400.

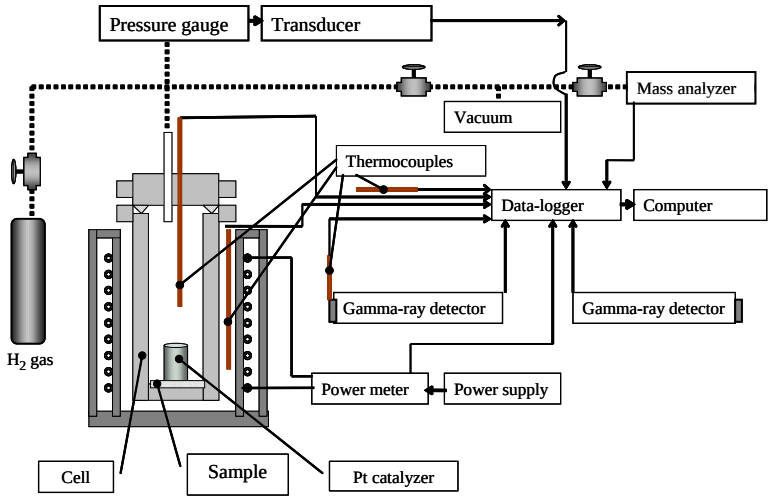


Fig. 1 - Cell and experiment configuration.

The electric furnace is custom made (Tokyo Technical Lab. PH, Mo13763A1). It is 200 mm outside diameter, 65 mm inside diameter and 200 mm high. A direct current regulated power supply is used (Takasago Electric EX-1500H), that produces up to 240 V at 6 A (1.5 kW). The heater power is monitored with high precision meter (Yokogawa PZ4000), which measures amperage and voltage every millisecond, sending averaged data to the data logger at 5-second intervals. The combined error for amperage and voltage is 0.0015%.

Radiation emissions are detected by a γ-ray detector (Aloka ICS-311) that is located 15 cm from the reactor. Its output is recorded continuously by the computer through a digital multimeter (Advantest TR-6845). The ionization chamber has a 14 cm long electrode, a correction plate 1 cm long, a window 0.5 cm thick, and it is pressurized with air at 1 atm. This detector can detect x-rays, γ-rays and β-rays. It can detect x-rays and γ-rays in the range of 30 keV ~ 2 MeV with an efficiency of 0.85 ~ 1.15 calibrated with ^{137}Cs.

This output is sent to the data logger and recorded in the computer. The detection of radiation emission employed a gamma-ray detector, which was calibrated by a 3.7×10^5 Bq ^{226}Ra check source that was positioned at various distances from the gamma-ray detector. Before the experiment, the check source was placed inside the reactor cylinder to obtain a gamma-ray reading. The background radiation level surrounding the system was 0.05 ± 0.008 μSv/h.

The radiation data was further processed with OriginPro software (OriginLab) to analyze multiple peaks. A Gaussian distribution analysis was performed to fit of multiple peaks, with the following equation:

$$y = y_0 + A(w(\pi/2)^{-1/2})\exp(-2(x-x_0)^2/w^2)$$

where, y_0 = Baseline offset, A = Total area from baseline to curve, X_0 = Midpoint of peak, W = 2σ. Full width at half maximum ≒0.849

The midpoint X_0 is the average, where w/2 is the standard deviation. To reduce the difference between the fitted curve and original data, additional peaks were plotted, and the following peak analysis was performed. To analyze multiple peaks, a function with multiple dependent variables and independent variables was defined in the following equations:

$y_1 = f(x_1, x_2, \cdots, a, b, c, \cdots)$

$y_2 = f(x_1, x_2, \cdots, d, e, f, \cdots)$

$\cdots\cdots\cdots$

$y_n = f(x_1, x_2, \cdots, o, p, q, \cdots)$

Here, x_1,x_2 are independent variable and a, b, c,…o, p, q are coefficient for the variables.

The Gaussian peaks derived with these functions are closest to the original data.

2.3 Materials

Fluorescent grade (98.0% pure) phenanthrene ($C_{14}H_{10}$: MW 178.23) was used in this study. It was supplied by the Kanto Chemical Co. LTD. The Pt catalyst was a high purity (99.99%) Pt mesh (Tanaka Noble Metal Co. LTD.) The catalyst is rectangular and is 5-cm high, is 10-cm wide, and weighs 50 g. Before the experiment, the Pt catalyst was activated once in an atmosphere of hydrogen gas for 1 hour at 850°C.

2.4 Experimental procedures

One gram of phenanthrene and the Pt catalyst were put in the reactor; the reactor cell was then sealed with the lid, which was secured in place with bolts. The reactor was connected to the vacuum system and evacuated to 10^{-3} mmHg. The vacuum system exhaust valve was left open for several minutes to remove the residual air from the reactor. The exhaust valve was then closed, and the gas was supplied to the reactor at the set pressure. After gas filled the reactor, the gas supply valve was closed. The temperature of the gas in the reactor then was increased to the starting temperature. Calibration of temperature versus pressure was performed by changing the hydrogen gas pressure from a vacuum to 80 atm.

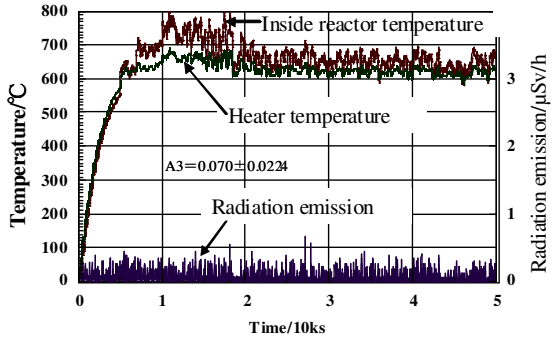
2.5 Temperature calibration

The amount of excess heat is determined by comparing input heater power to a stable temperature in the cell on a calibration curve.

3. Results

3.1 Excess heat generation

Figure 2 shows an example of anomalous excess heat. In this test, 1 g of phenanthrene was exposed to a 70 atm of hydrogen gas. Furnace heater power was set for 60 W. The furnace heater temperature rose faster than the cell temperature. As shown in the calibration curve when there is no anomalous heat, by 10 ks both temperatures stabilize at around 640°C. However, in this test they both soon begin to rise above the stabilization point. After 5 ks, large perturbations begin and the temperatures continue rising. Also, at this point the cell temperature exceeds the furnace heater temperature. This temperature reversal is proof that heat was being produced inside the cell. The cell temperature reaches 800°C, which is 200°C higher than the calibration curve predicts. Since input power is 60 W, we extrapolate that roughly 60 W of anomalous heat is being produced. Because of the extreme fluctuation in heat, total energy is more difficult to estimate than power, but because the excess power persisted for 10 ks it was at least 120 kJ in this test.



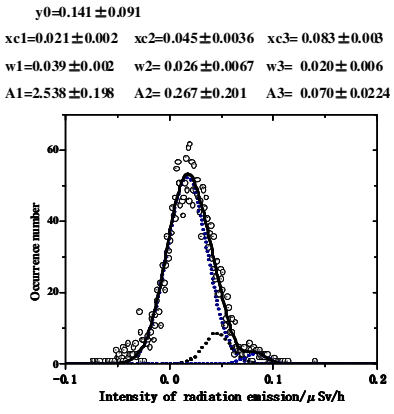


Fig. 2 - An example of anomalous heat. Fig. 3 - Intensity spectrum of radiation emission from Fig. 2.

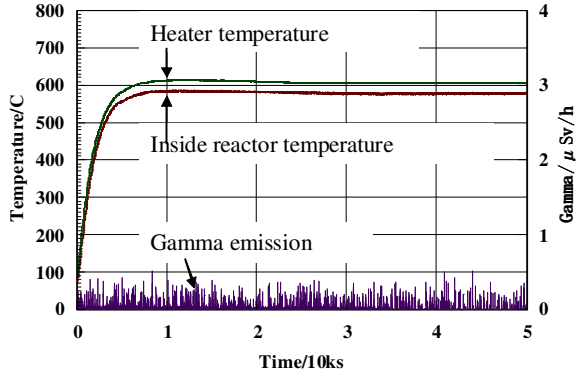


Fig. 4 - An example with no anomalous heat.

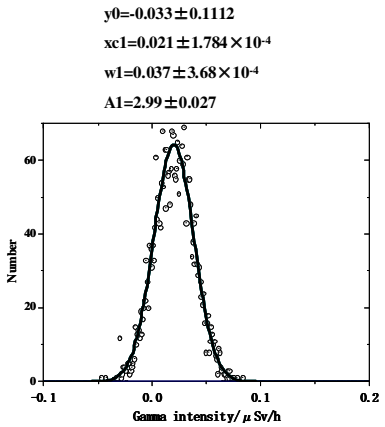


Fig. 5 - Intensity spectrum of radiation emission from Fig. 4.

Total heat production can be estimated from the calibration curve and total duration of excess heat production which started around 18 ks and continued to 50 ks. Over this period, the average temperature was 50°C above the calibration point continuing for 40 ks. Based on the calibration point of 600°C (in Fig 3) the excess was roughly 5 W on average, so total heat production was roughly 160 kJ for the entire run.

Figure 3 shows the intensity distribution of gamma-ray emission from the ionization chamber detector. Two peaks are shown, 0.05 μSv/h and 0.09 μSv/h of the background by calculated peak analysis. These are clearly differentiated from the background of 0.02 μSv/h. Gamma-ray emissions were weak but they were clearly observed when intense excess heat was generated.

Figure 4 shows an example of a test with no excess heat. As in the test shown in Fig. 2, 1 g of phenanthrene was exposed to a 70 atm of hydrogen gas, and furnace heater power was set for 60 W. However, the Pt catalyst was not placed in the cell. By 10 ks, the temperature stabilized at about 600°C. After that the temperature remained stable and settled.

Figure 5 shows the intensity distribution of gamma-ray emission for the test shown in Fig. 4. Only the background peak is observed. Calculated peak analysis reveals no other peaks.

4. Discussion

In these experiments, a 1 g sample of phenanthrene was used, which is 5.6×10^{-3} moles. Oxidation, reduction and other chemical reactions can produce at most a few kilojoules from this much material, whereas this reaction produced on the order of 100 kJ of heat. That is roughly 100 times larger than a chemical reaction. Therefore, a chemical reaction as the source of this heat is conclusively ruled out. Furthermore, during the experiment weak radioactivity was observed, probably γ or x-rays. If these are γ-rays that is proof this is a nuclear reaction; if they are x-rays then they were generated by some other mechanism. The detector used in this study can detect an energy range starting from 20 keV up to high levels. The cell wall is 3 mm thick stainless steel. The x-ray mass absorbent coefficient for 20 keV x-rays is 100 cm^2/g, so most of the radiation would not penetrate the cell wall. However, if these are γ-rays at around 1 MeV, 80% of the radiation would pass through the cell wall. Therefore, although we cannot be certain it is very likely these are γ-rays

The excess heat and radiation were not strongly correlated, but they both indicate that some sort of nuclear reaction occurred. With additional research to understand the mechanism of the reaction, this reaction might possibly become a practical source of energy.

5. Conclusions

The anomalous energy generation cannot be the product of a conventional chemical reaction for the following reasons:

- At these temperatures, hydrogenation reactions are endothermic, not exothermic.
- Based on this massive reaction and the mass of the reactants, the total heat release far exceeded any known chemical reaction.
- There was no chemical fuel in the reactor cells.
- There were no chemical reaction products. Except the platinum screen that was coated with carbon, the components and chemical species in the cell, including phenanthrene and hydrogen gas, remained essentially as they were when the experiment began,
- Gamma-ray emissions were detected. These emissions are characteristic of a nuclear reaction. These emissions might have been x-rays but this is unlikely.

The reaction is reliably triggered by raising temperatures above the threshold temperature of ~ 580°C and hydrogen pressures above 60 atm. The reaction can be quenched by lowering the temperature inside the cell to below ~ 500°C. When the required conditions are satisfied excess heat is generated with high reproducibility, but the rate of heat production is not stable. There is only a small amount of reactant in the cell, and it is likely that the accompanying ordinary chemical reactions that occur in the cell soon consume it all.

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