

Part 1: Comparison of Gasoline Treated with Catalyst vs. Untreated Gasoline

General Considerations: Catalyst was added to gasoline at a concentration equal to 8 g per 50 L of gasoline. A majority of the catalyst was found to dissolve rapidly (see Part 2 for additional details). Resulting solutions were stirred for at least 24 hours prior to analysis. For all analyses, samples of treated gasoline were compared with samples of untreated gasoline.

UV-Vis Spectroscopy: Treated and untreated gasoline samples were analyzed by UV-Vis spectroscopy and found to be nearly identical (see Figure 1). In particular, the vibronic contributions found at the two local maxima between 250 and 290 nm were identical for both samples. The additional absorbance seen in the treated gasoline sample at approximately 230 nm is attributed to presence of naphthalene which has very strong absorbance below 250 nm.

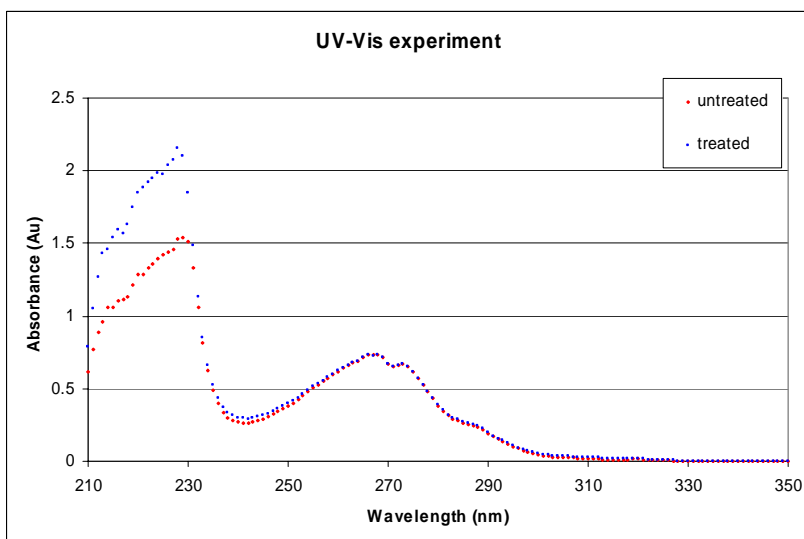


Figure 1. Electronic absorption spectra of (untreated) gasoline and gasoline treated with catalyst.

Gas Chromatography: Treated and untreated gasoline samples were analyzed by gas chromatography (GC). The injector port was set at 250 °C. The column temperature was ramped from 35 °C to 250 °C, at 10 °C/minute. A total of 164 components were identified for the untreated gasoline and 160 components were identified for treated gasoline (see attached data). In general, the compositions of the two samples were nearly identical.

¹H NMR Analysis of Treated and Untreated Gasoline: As shown in Figures 2 and 3, the ¹H NMR spectra of samples of untreated gasoline and treated gasoline were indistinguishable in C₆D₆. Solvents such as CDCl₃ and DMSO-d₆ produced similar results.

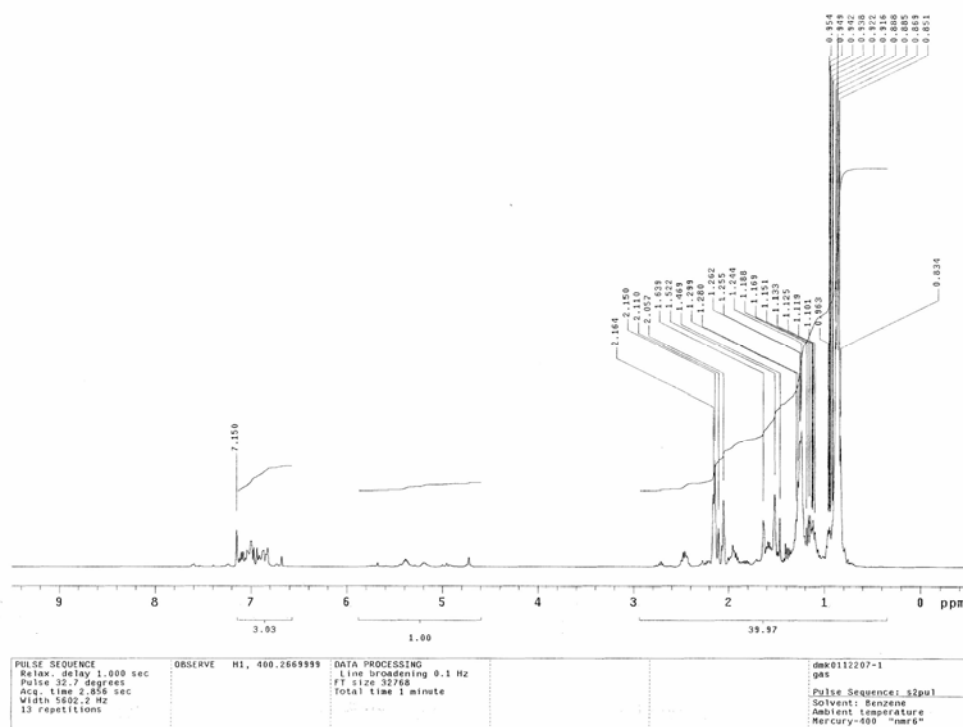


Figure 2. ^1H NMR spectrum of Untreated Gasoline (solvent = C_6D_6).

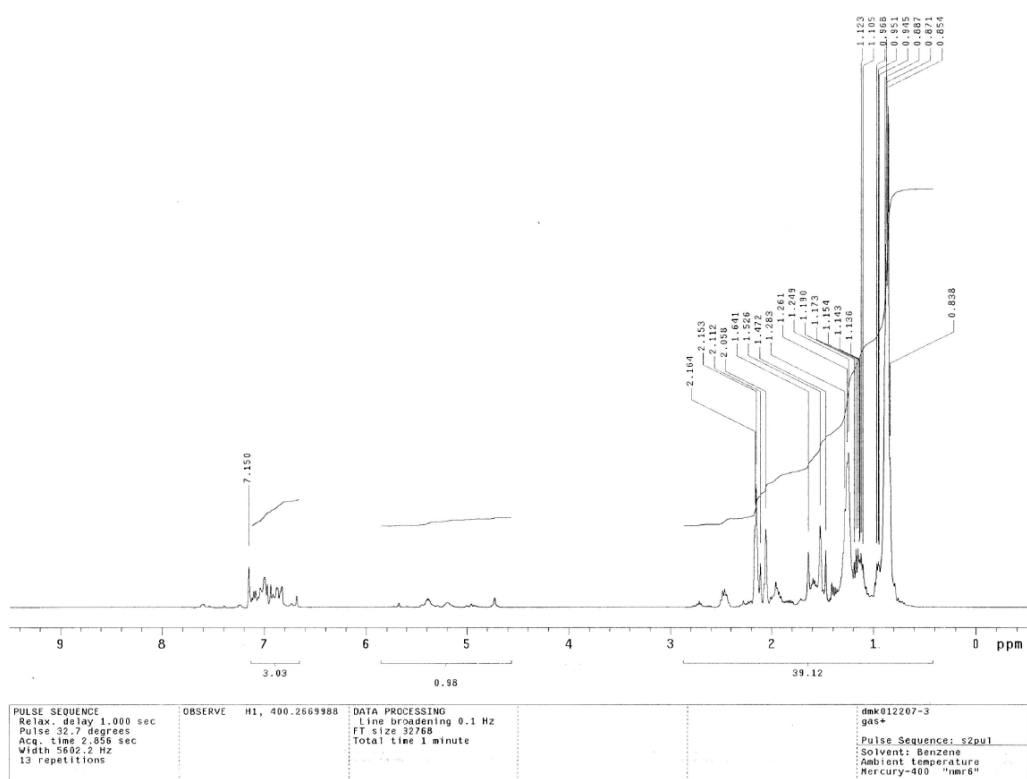


Figure 3. ^1H NMR spectrum of Treated Gasoline (solvent = C_6D_6).

Part 2: Catalyst Analysis

Sublimation: Catalyst (20 g) was placed in a sublimation apparatus (see Figure 4), and the cold-finger (inner vessel) was filled with iced water. Internal vessel pressure was reduced to 2×10^{-3} torr using a vacuum pump, and maintained at this reduced pressure at 30 °C. After 3 hours, a large amount of white material condensed on the inner surface of the cold finger with green residue remaining at the bottom of the vessel. The reactor was re-pressurized with N₂ gas and the white material was collected and weighed (19.5 g, 98% yield). (This material was later identified as pure naphthalene, see below). This sublimation experiment was repeated with a 10 g sample of catalyst to yield 9.8 g of white material (98% yield). The green residue was found to be insoluble in most organic solvents (chloroform, toluene, acetone, methanol, ethanol, dimethylsulfoxide, ethyl ether, and tetrahydrofuran). The green residue was not soluble in gasoline. Solubility was determined by mixing 10 mg of the green residue in 10 mL of solvent followed by filtration, and finally removal of the solvent under reduced pressure. Residual mass remaining after evaporation was found to be negligible for the aforementioned solvents. Limited solubility was achieved with benzene. ¹H NMR analysis (solvent = C₆D₆) of the soluble fraction revealed broad signals, characteristic of aliphatic polymer such as poly(ethylene), poly(propylene), PAO (poly-alpha-olefin), etc.

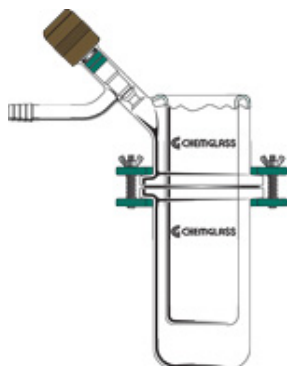


Figure 4. Sublimation apparatus.

Solubility of Catalyst in Gasoline: Catalyst (10 g) was mixed with 20 mL gasoline for 24 hours. The mixture was then centrifuged at 4000 rpm. 40 mg of undissolved material, similar in appearance to the green material obtained by sublimation experiment, was obtained.

GC Analysis of Catalyst: Commercial naphthalene (50 mg, 0.4 mmol) and mesitylene (46 mg, 0.4 mmol, as internal standard) were dissolved in 3 mL of ethyl ether and analyzed by gas chromatography, which indicated a 1:1 composition of the two components, as expected. Next, 46 mg catalyst and 46 mg mesitylene were dissolved in 3 mL of ethyl ether and analyzed by gas chromatography. Again, the data indicated a 1:1 composition of the two components, revealing that 46 mg catalyst is approximately equal to 46 mg of pure naphthalene.

NMR Analysis of Catalyst: A sample of catalyst was added to CDCl_3 , filtered, and then analyzed by ^1H and ^{13}C NMR spectroscopy (see Figure 5 and 6, respectively). Spectra acquired were consistent with commercial naphthalene (see Figure 7).

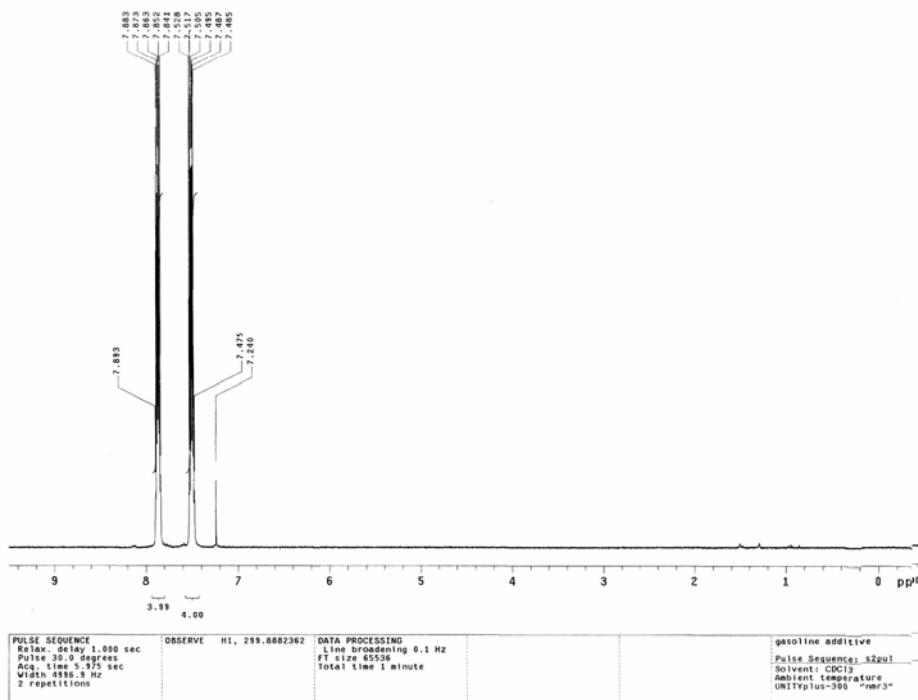


Figure 5. ^1H NMR spectrum of catalyst (solvent = CDCl_3).

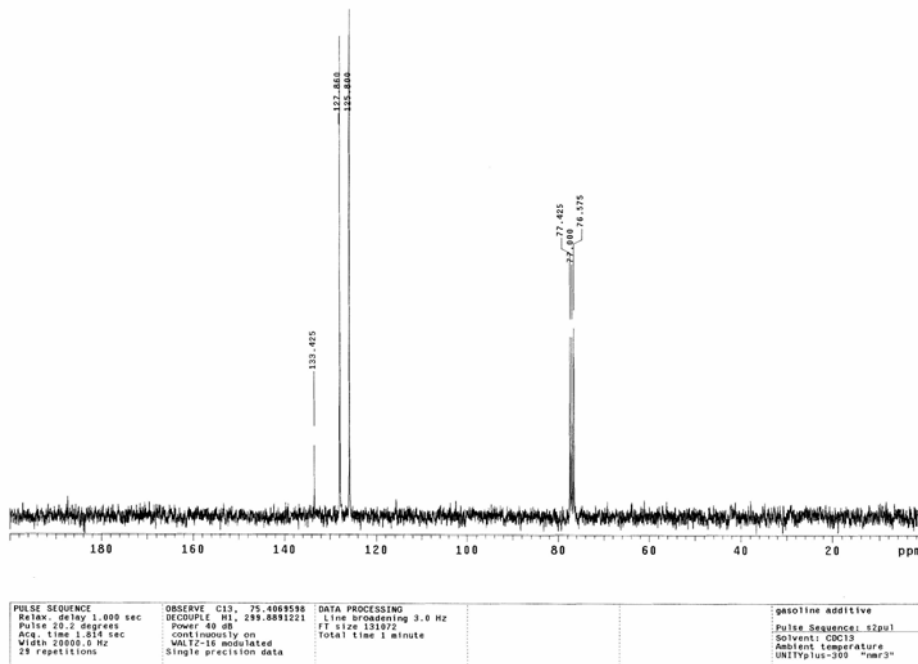


Figure 6. ^{13}C NMR spectrum of catalyst (solvent = CDCl_3).

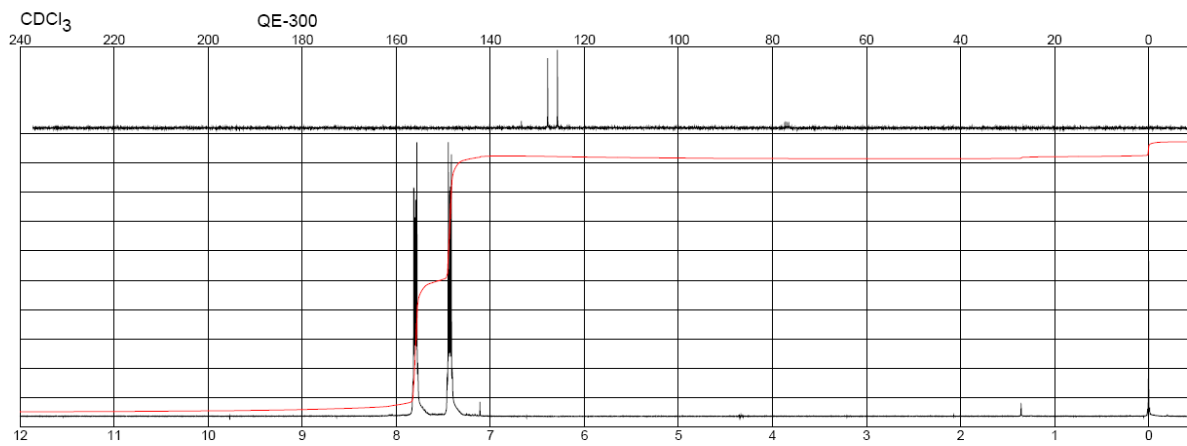


Figure 7. ^1H (bottom) and ^{13}C (top) NMR spectrum for commercial naphthalene, as posted on www.aldrich.com.