1 Month in Green Lab

Keltin Grimes

Project Introduction

- Goal: To create a photocatalyst capable of converting sunlight and CO_2 into hydrocarbon fuels at industrial-level efficiencies
- When exposed to light, semiconductors create an electron-hole pair
- With the right synthesis and addition of co-catalysts, the pairs can split CO_2 and H_2O molecules which recombine into molecules like methane or ethane
- Recent group publications in EES and Materials Today

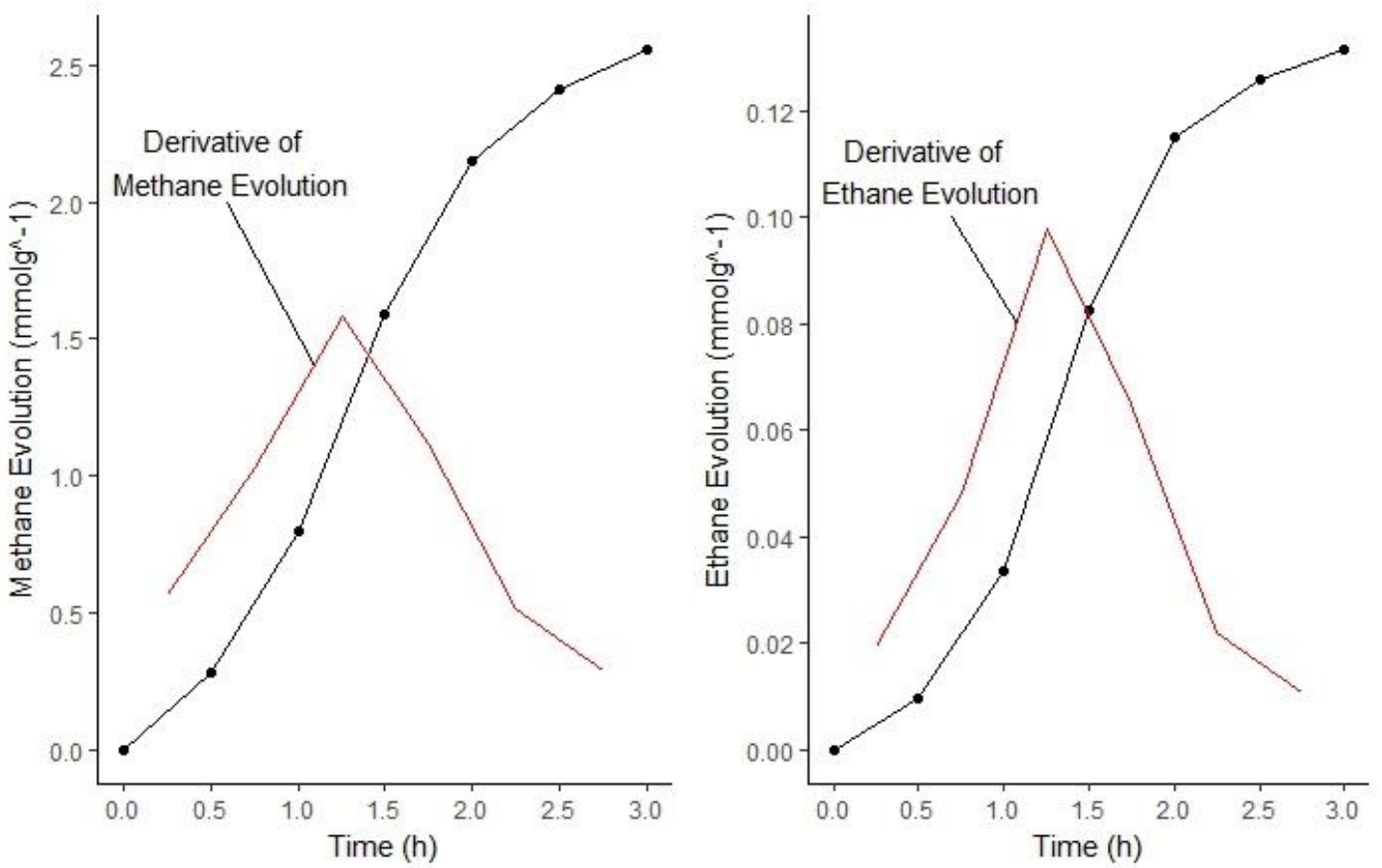
Daily Tasks

- Photocatalytic Tests Using GC
  - Most days
  - Purge the sample
  - Use the software under Saurav’s guidance
- BT Synthesis
  - Last couple of weeks
  - Observe Ali mixing the samples in glove box
  - Do small tasks like nitrogen gun, washing, etc.
  - Helped Ali wash the samples in centrifuge

Research

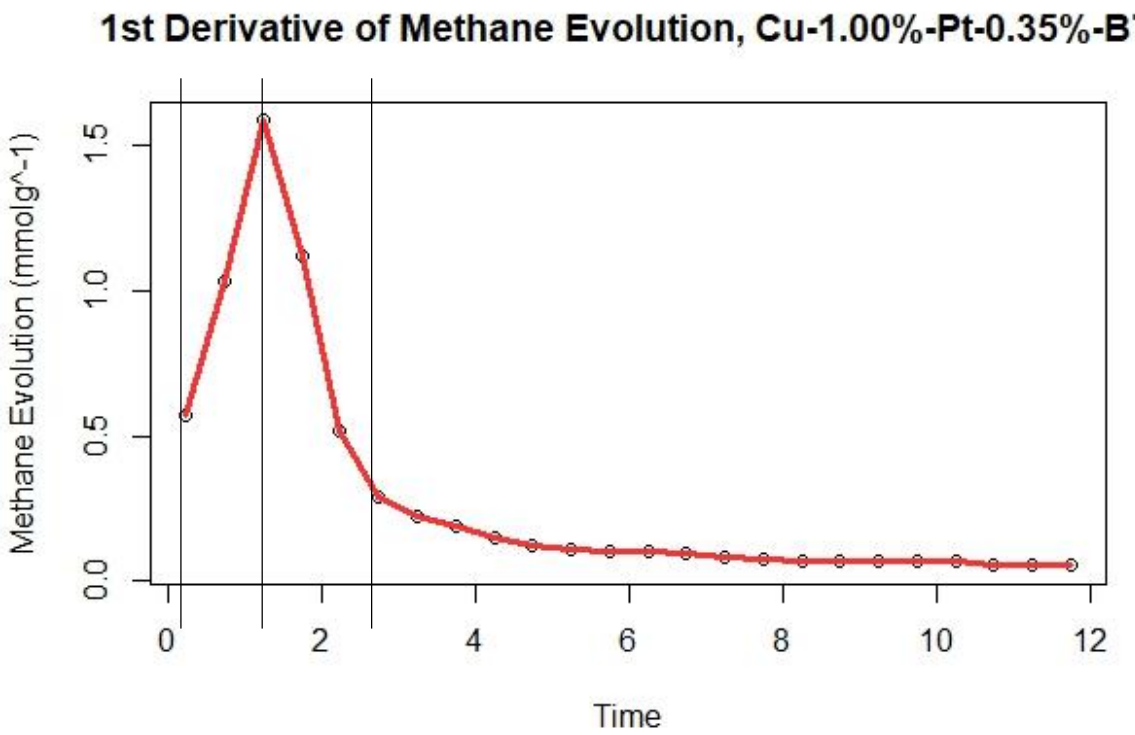
- Dr. Grimes thought to take derivative of product evolution
- Distinct peak and subsequent drop

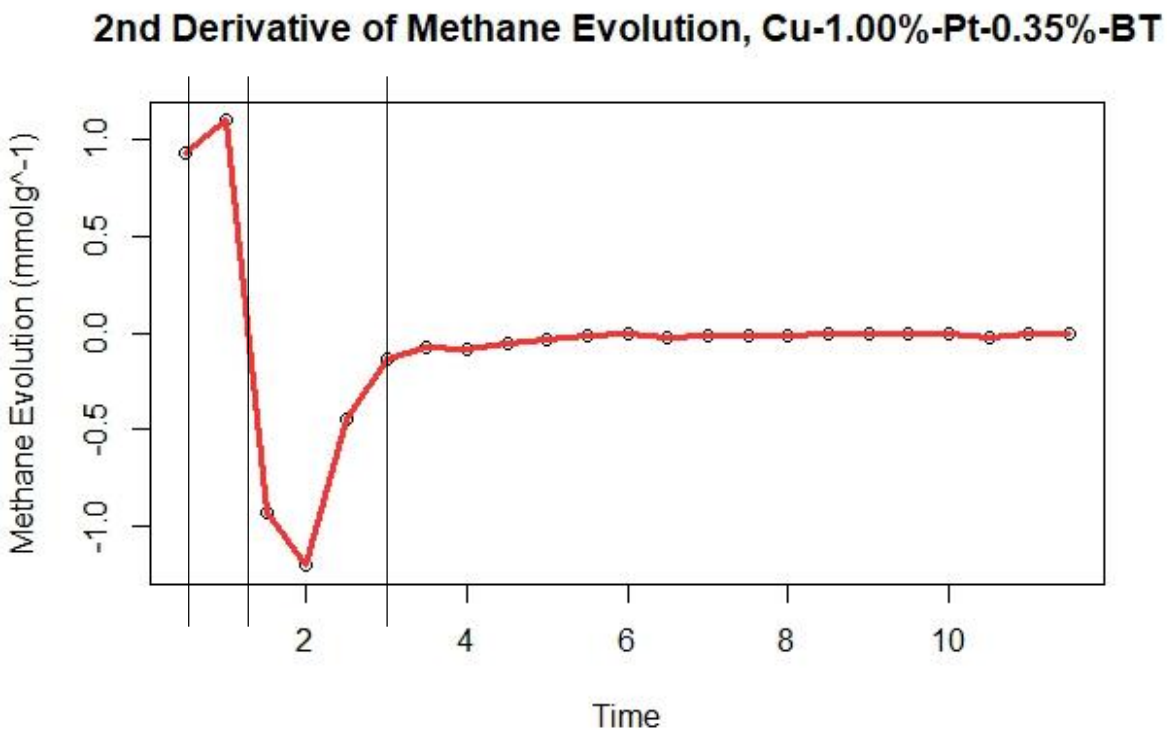
$Cu_{1.00\%}$-$Pt_{0.35\%}$-BT Sample



Research

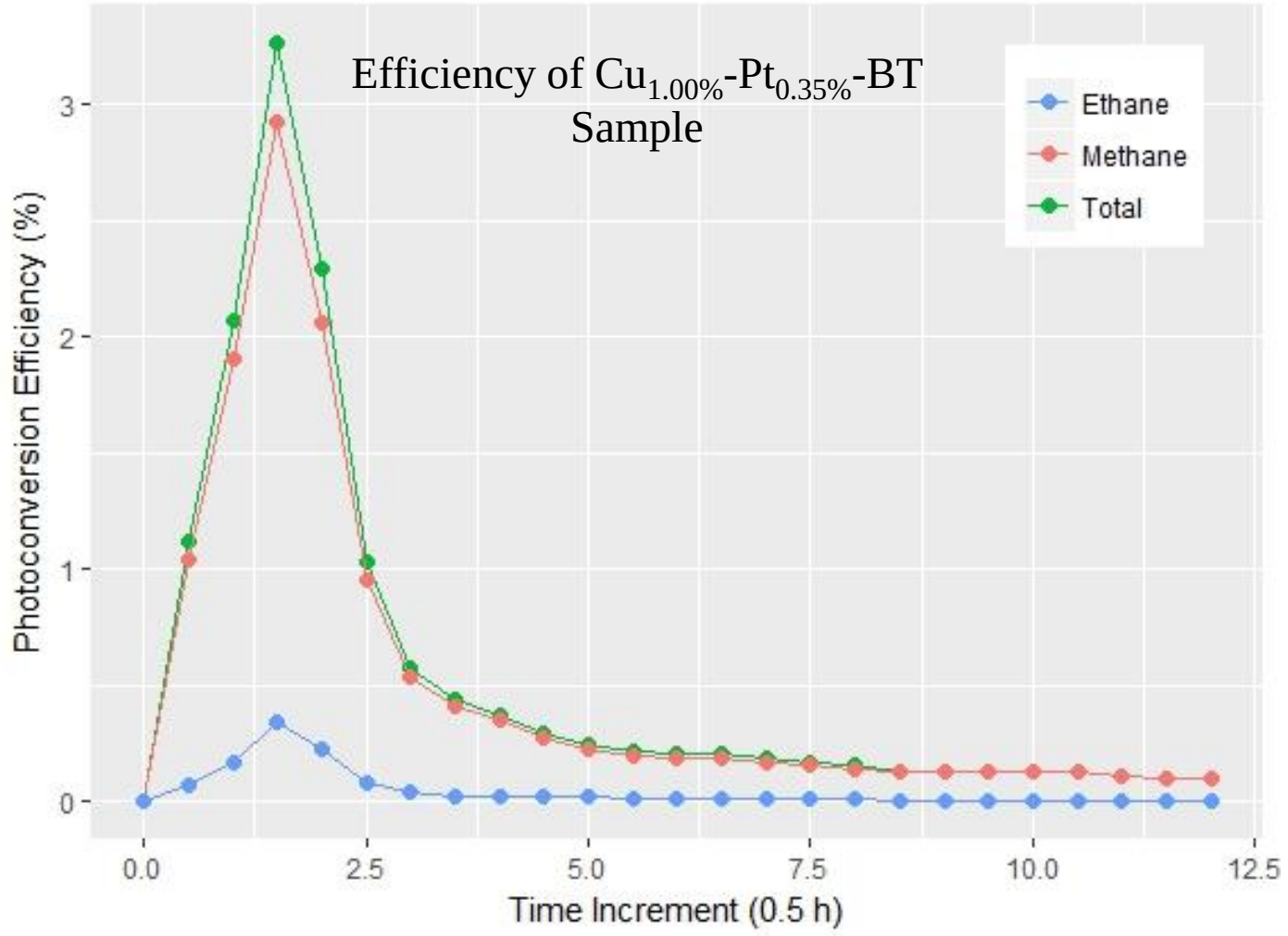
- Now we look at the second derivative
- Clearly, whatever is happening has a huge impact but occurs very quickly
- Three Stages: Activation, rapid deactivation, slow linear deactivation





Research

- Previously had been calculating net efficiency
- Can be done incrementally
- Peak and drop continues



Research

- Automated the plotting and calculation process using R

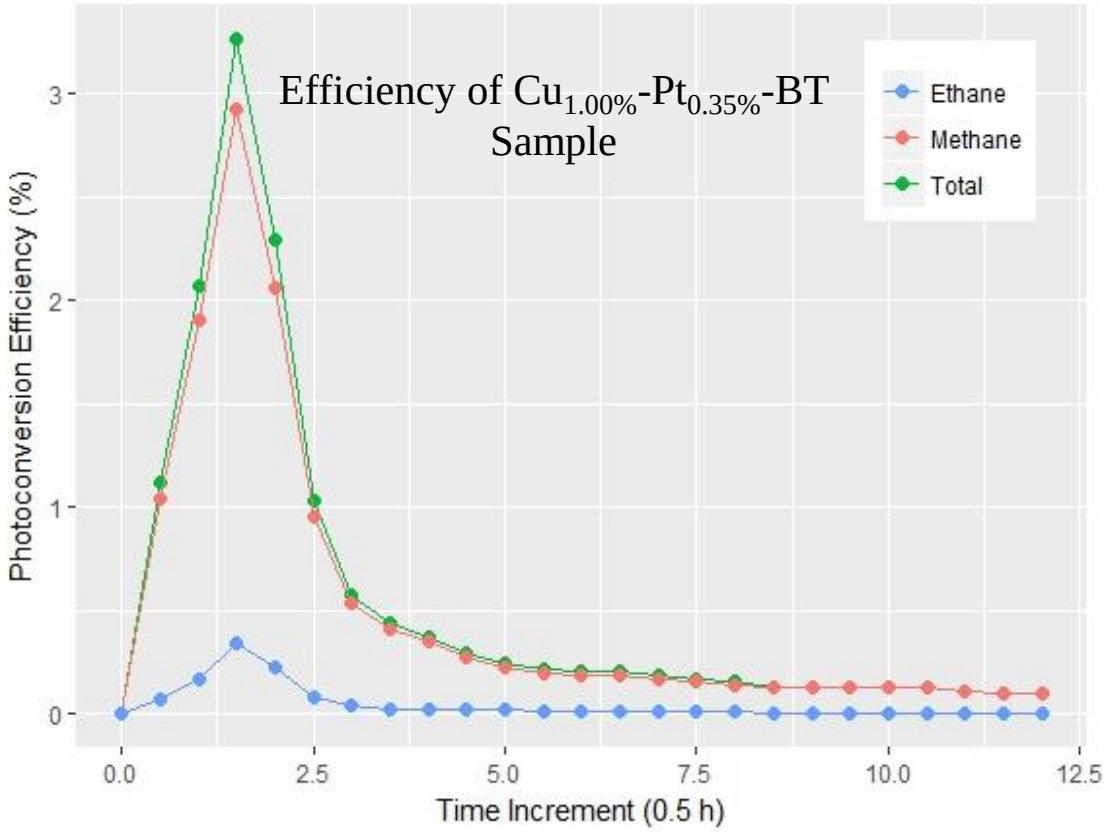
```r
#Efficiency Plot Function
library(ggplot2)

efficiencyData <- read.csv("C:/Users/kelti/Documents/Photoconversion/12 h methane and ethane data.csv")
colnames(efficiencyData) <- c("Time", "Methane", "Ethane")

efficiencyPlot <- function(data, incrementHours) {
  finalData <- data.frame("time" = data[,1], "efficiency" = rep(0, times = nrow(data)),
                          "methane" = rep(0, times = nrow(data)), "ethane" = rep(0, times = nrow(data)))
  inputPerSecond <- 1756.66
  inputPerHour <- inputPerSecond*incrementHours
  sampleWeight <- 40
  methaneEnergy <- 810
  ethaneEnergy <- 1560
  for(i in 2:nrow(data)){
    methaneOut <- (data[i,2] - data[i-1,2])*sampleWeight*methaneEnergy/1000
    ethaneOut <- (data[i,3] - data[i-1,3])*sampleWeight*ethaneEnergy/1000
    energyOut <- methaneOut + ethaneOut
    finalData[i,2] <- (energyOut/inputPerHour)*100
    finalData[i,3] <- (methaneOut/inputPerHour)*100
    finalData[i,4] <- (ethaneOut/inputPerHour)*100
  }
  p <- ggplot() + geom_point(data = finalData, aes(x = time, y = efficiency, color="Total"), size = 2)
  p <- p + geom_line(data = finalData, aes(x = time, y = efficiency, color="Total"))
  p <- p + geom_point(data = finalData, aes(x = time, y = methane, color="Methane"), size = 2)
  p <- p + geom_line(data = finalData, aes(x = time, y = methane, color = "Methane"))
  p <- p + geom_point(data = finalData, aes(x = time, y = ethane, color="Ethane"), size = 2)
  p <- p + geom_line(data = finalData, aes(x = time, y = ethane, color = "Ethane"))
  p <- p + xlab(paste("Time Increment (", incrementHours, " h)", sep = "")) + ylab("Photoconversion Efficiency (%)")
  p <- p + scale_color_manual(values=c('#619CFF','#F8766D','#00BA38')) + scale_fill_discrete(breaks=c("Ethane", "Methane", "Total"))
  p <- p + theme(legend.title=element_blank(), legend.justification=c(1,1), legend.position=c(.95,.95))
  #return(p)
  return(finalData)
}
efficiencyPlot(efficiencyData, 0.5)
```

Research

- Drop is clearly due to deactivation of photocatalyst
- Can we quantify the deactivation process, how does the addition of co-catalysts affect it, and what can we do to prevent it?



Peak – 1hr: 67.39% Loss (Methane Only)

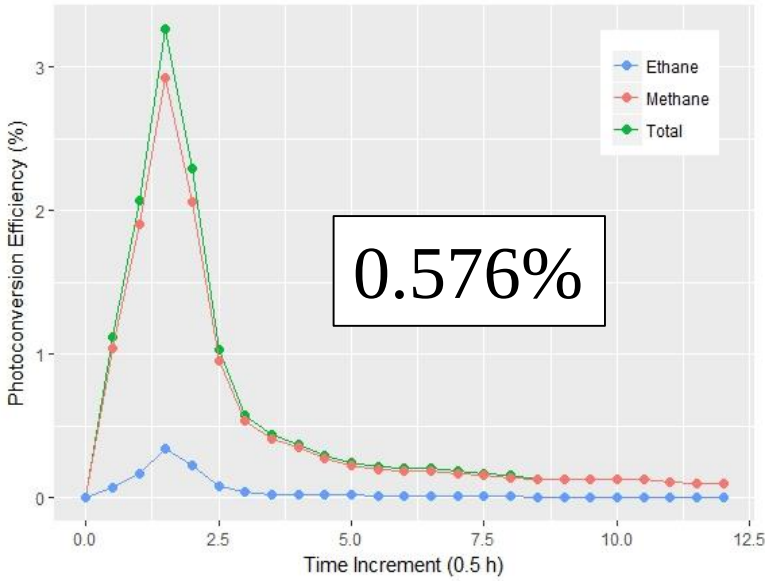
1hr – 2hr: 56.66% Loss (Methane Only)

2hr – 3hr: 33.06% Loss (Methane Only)

Research

- Another problem is the slow activation of the sample
- If we can quickly identify a way to give the sample a ‘hot-start’, that is great, but our efforts should be focused on preventing deactivation

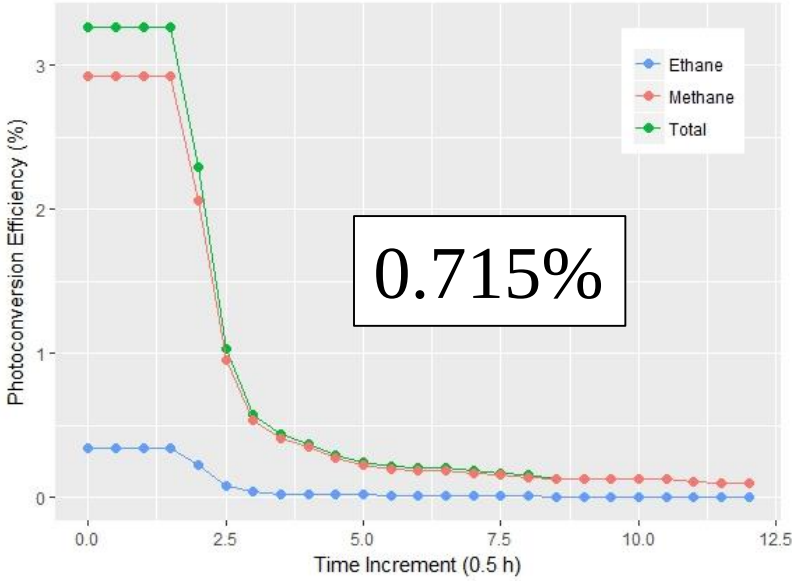
Efficiency of $Cu_{1.00\%}$-$Pt_{0.35\%}$-BT Sample



Actual Data:

3.44135 mmol Methane

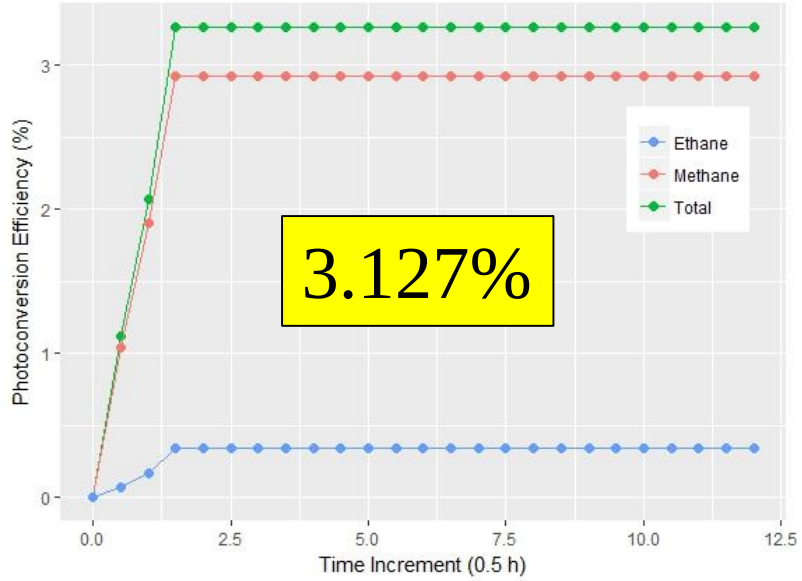
0.15802 mmol Ethane



Ideal Hot-Start Scenario:

4.22402 mmol Methane

0.22223 mmol Ethane



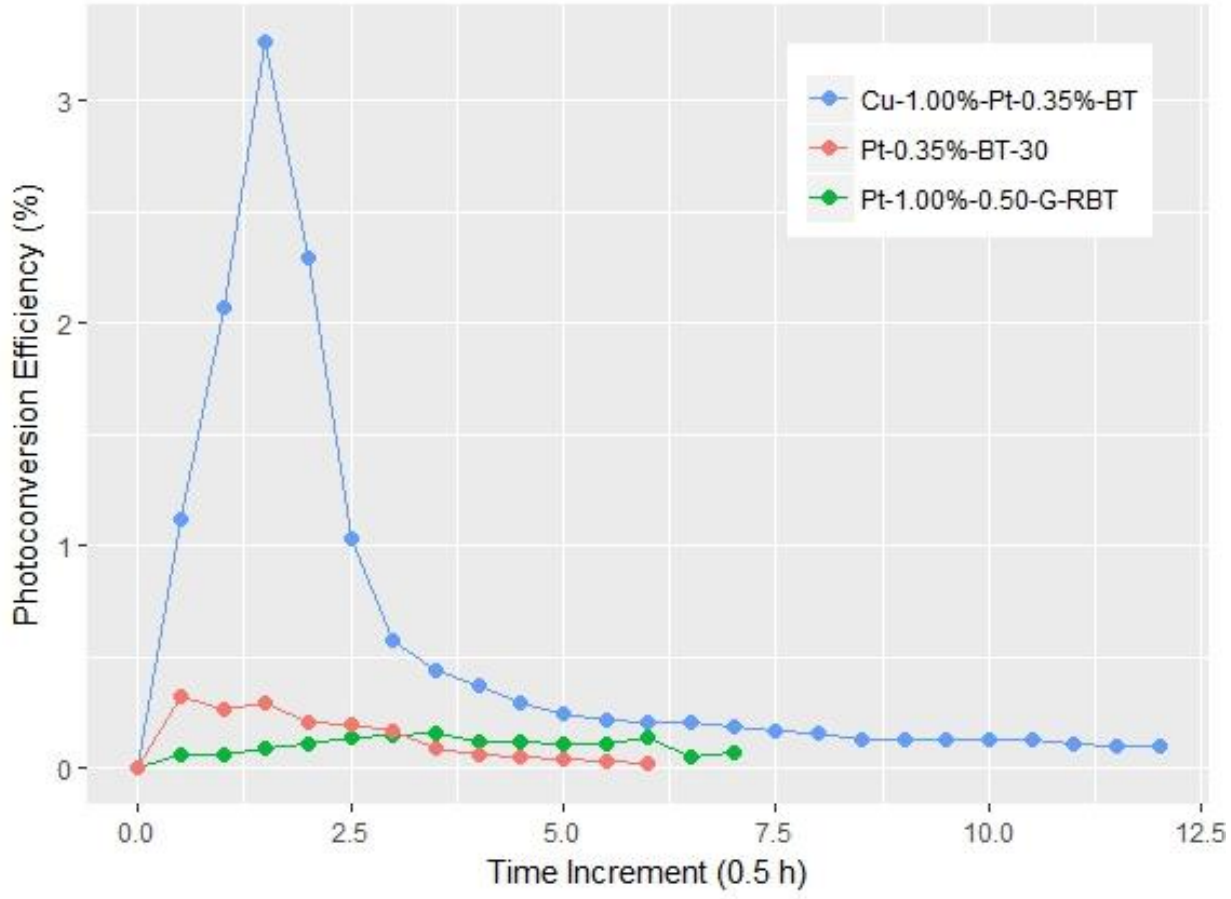
Ideal No-Deactivation Scenario:

18.20805 mmol Methane

1.10939 mmol Ethane

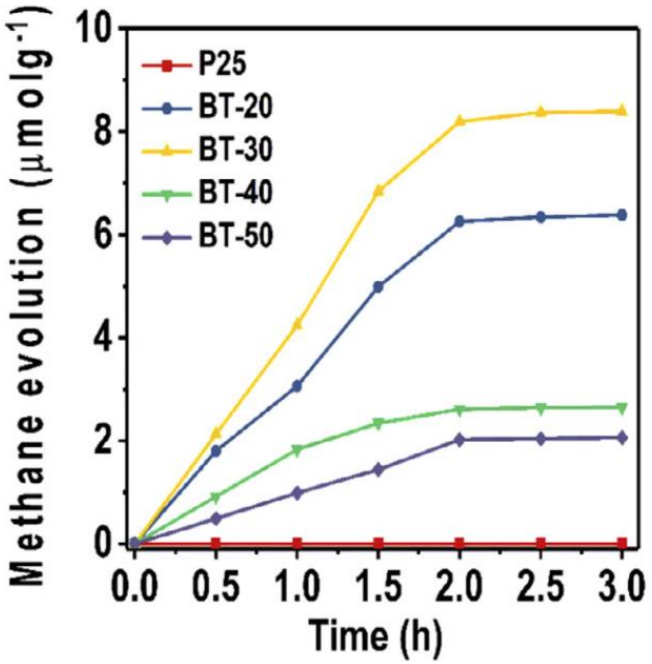
Research

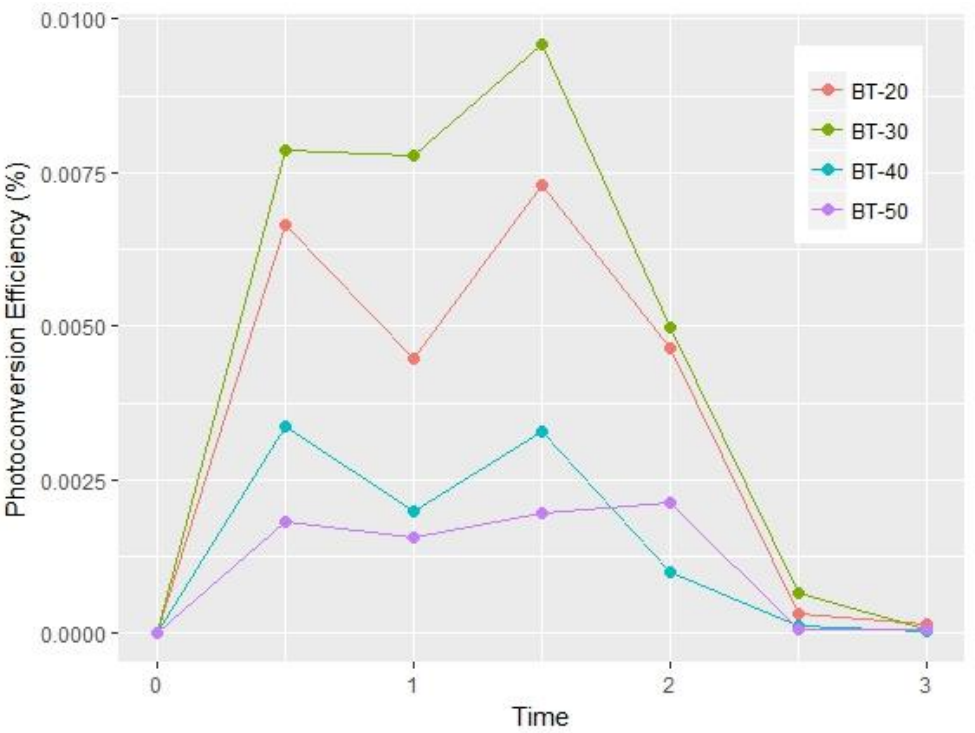
- Gathered data from multiple samples and papers
- Again automated the calculations and plotting

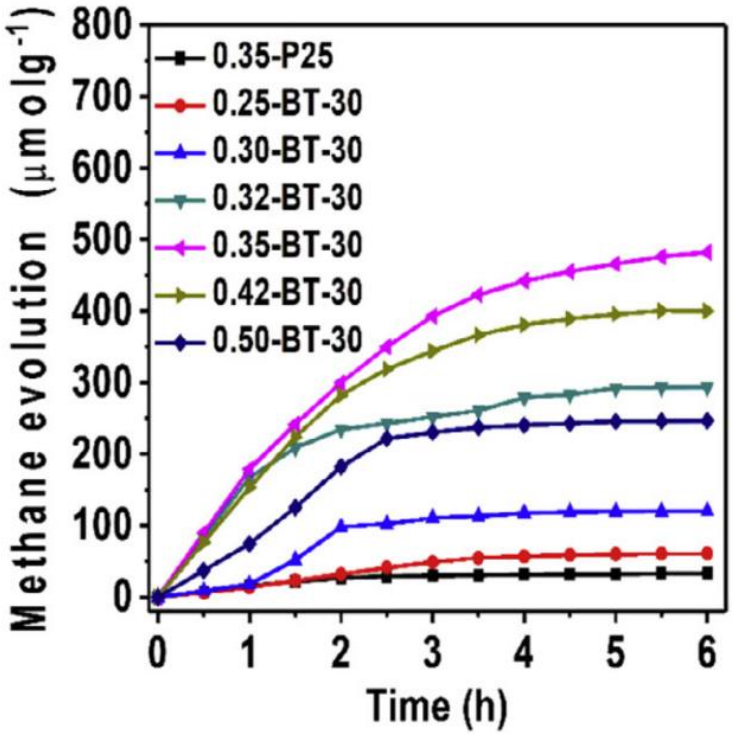


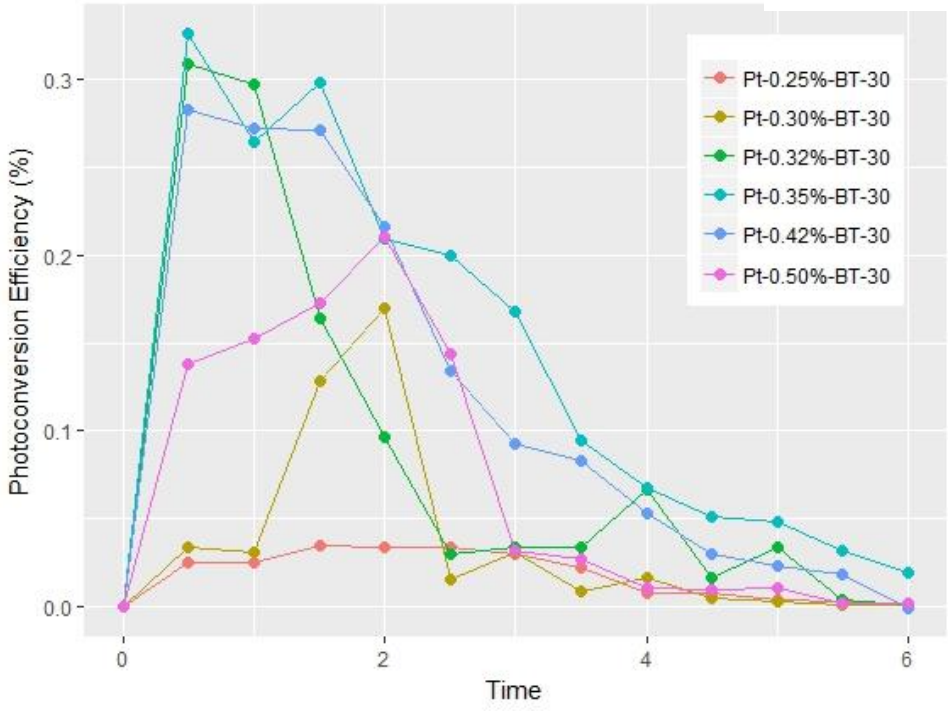
Research

- Dramatic peak drop-offs with only BT or Pt and BT



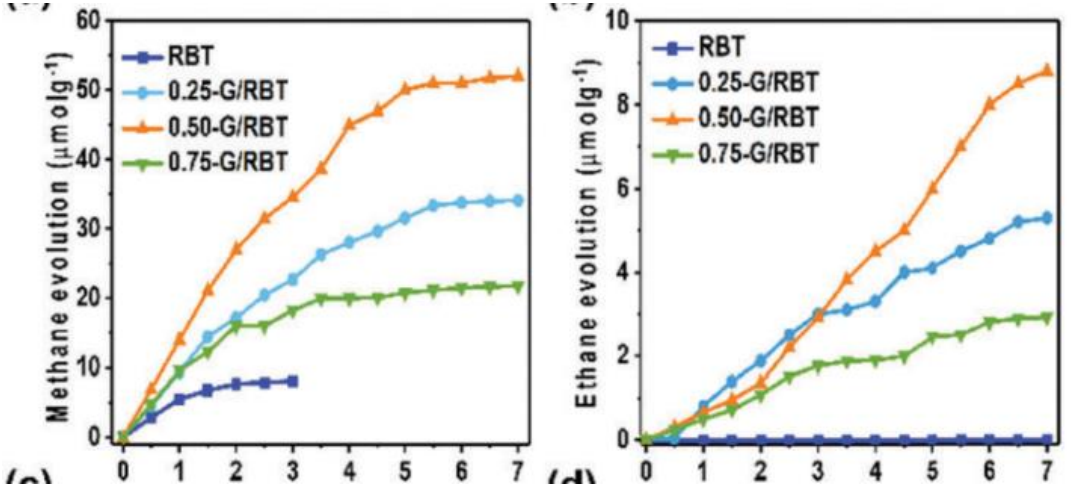


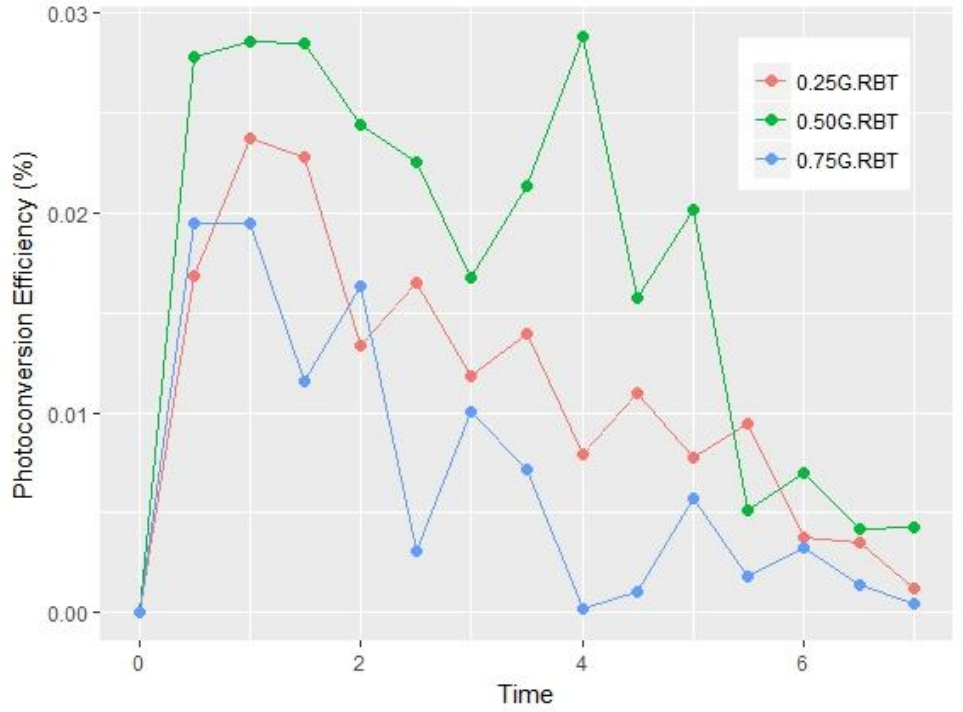




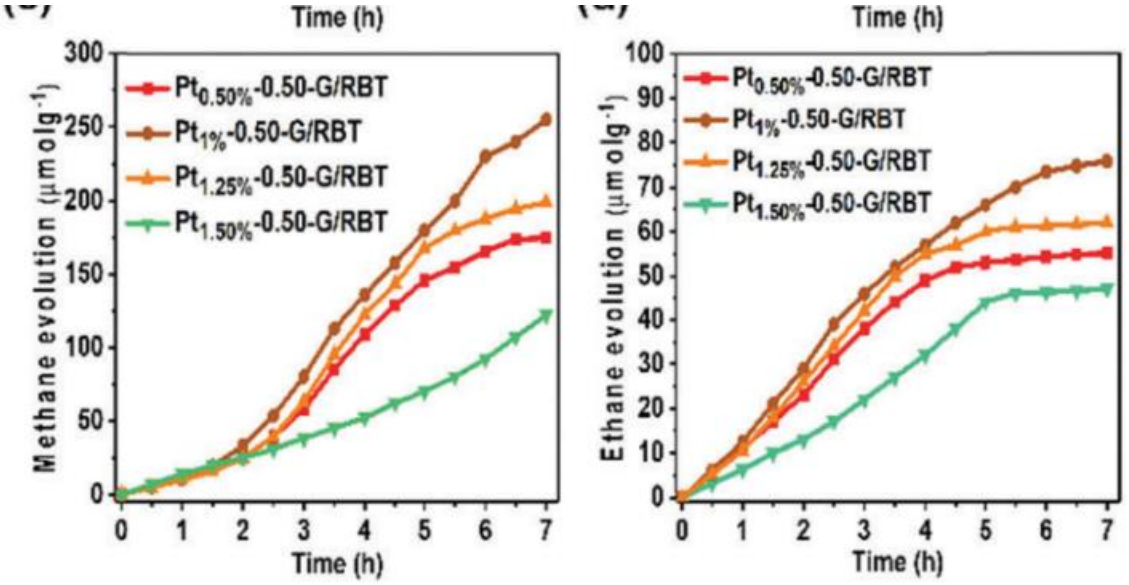
Sorcar et al. Highly enhanced and stable activity of defect-induced titania nanoparticles for solar light-driven CO2 reduction into CH4. *Materials Today* 20, 507-515 (2017).

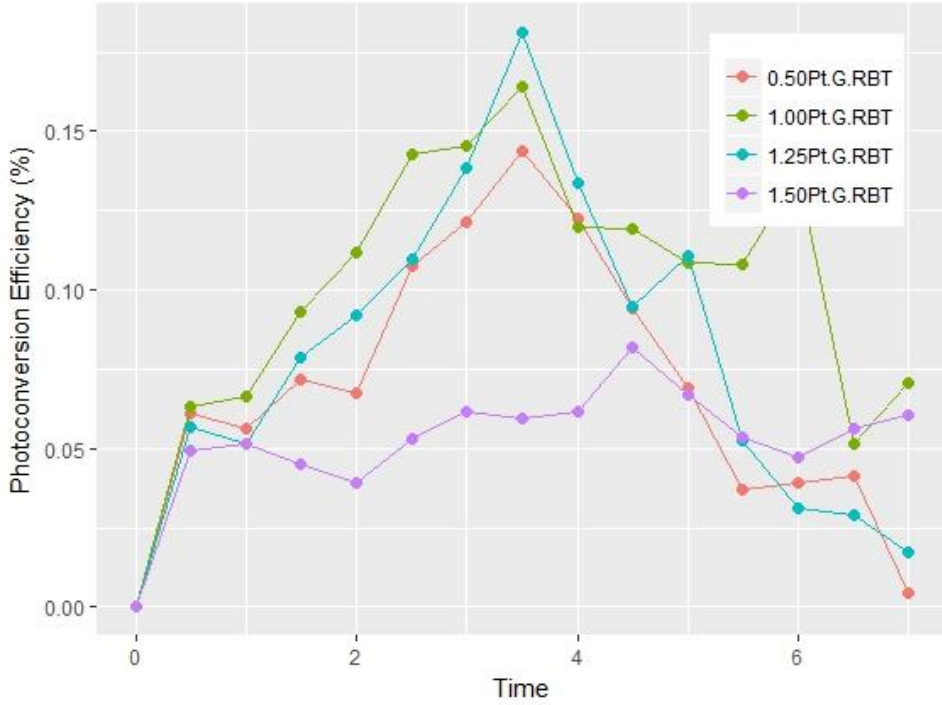
Research





- Peak-drop offs are slower with G-RBT and peaks occur later with Pt-G-RBT





Sorcar et al. High-rate solar-light photoconversion of CO2 to fuel: controllable transformation from C1 to C2 products. *EES* (2018).

Research

- Investigations like these seem to be uncommon
- Continuing to look at the data in this way can provide good insights in how to prevent deactivation in the future

Memories

- Working in the lab, DGIST campus, soccer

Thank You!

- Dr. In for allowing me to work in your lab
- Saurav and Ali for teaching me so much
- EunHee for taking us to lunch every day
- And everyone for being such gracious hosts!