

# Fotokatalyse

Fotokatalytisk Hydrogen Produksjon  
Gjennom Foto-reforming av Hydrokarboner

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# Preface

This study was carried out as a part of a master thesis at the Department of Chemical Engineering at the Norwegian University of Science and Technology.

During this work Magnus Rønning was the acting supervisor, and Charitha Udani the co-supervisor.

My reason for choosing this path was my interest in technology based of off the sun, and the drag towards more environmental friendly quests.

This master thesis has focused on the production of hydrogen from a mixture of alcohol and water, at different concentrations, with added Cu-TiO<sub>2</sub>-catalyst, at various mass and copper loadings. This work would differ from precious work on the reactor in the way that the UVC-light bulbs were changed to UVA, and the alcohol used, from methanol to ethanol, isopropanol and glycerin. The goal was to understand the process, optimize the system for the glycerin experiments and to compare the different alcohols tested with respect to hydroxyl groups and maximum hydrogen production.

I would like to give thanks to my supervisor and co-supervisor for being patient and helping me. Also a thanks to those who helped me along, and gave me the necessary training: Karin Wiggen for BET, Chemisorption and Calcination. Julian Tolchard for XRD, Eirik Pedersen for TPR training, and for the help setting up a program for the pulse chemisorption, Erik for guidance and Sandra Larsson for proofreading.

## **Declaration of compliance**

I declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology (NTNU).

Place and date:

Signature:



# Sammendrag

I løpet av det siste vårsemesteret på masterstudium i industriell kjemi, ble det kjørt en rekke eksperimenter i fotokatalyse, for å undersøke optimale driftsforhold ved ett skifte av alkohol til glyserol. Andre alkoholer ble også testet.

Ekperimentene ble utført under bestråling av UVA, og parametrene som skulle varieres var: kobber lasting, glyserolkonsentrasjon, og masse katalysator per liter reaksjonsvæske.

I de første forsøkene ble en rekke forskjellige alkoholer ble testet. Metanol fungert som en baseline når etanol, iso-propanol og glyserin ble testet. Metanol , etanol og iso-propanol ble funnet å være nesten like gode når hydrogenutviklingen per mol OH ble sammenlignet de tre i mellom.

Ved optimalisering av glyserin eksperimentene ble tre parametre variert. Eksperimentene begynte med at vol% av glyserin ble endret mens massen av katalysator og kobberlastingen ble holdt konstant på henholdsvis 1.5vekt % og 250mg. 1volum% glyserin hadde høyest aktivitet på 0.069 ml H<sub>2</sub>/min.

Den andre serien eksperimenter involverte å endre kobberlastingen på katalysatoren. 1vekt%Cu på katalysatoren hadde den høyeste produksjon på 0.10 ml H<sub>2</sub>/min

Den siste variabelen som ble manipulert var masse katalysator per sats. Hvor volumet på hver sats var 500ml. Resultatene fra denne serien med eksperimenter viste at 250mg av 1vekt%Cu-TiO<sub>2</sub> med 1volum% glyserin overgikk de andre på trenden over reaksjonshastigheter.

Det optimale forholdet mellom massen av katalysator og glyserolkonsentrasjon ble observert til å være:

$$\frac{50mg \text{ 1wt\%Cu} - TiO_2}{1.00 \text{ ml glycerin}}, \sim 1vol\% \text{ glycerin}$$

Den optimale verdien til mange av parameterne ble forandret etter at alkoholen, den organiske offer-komponenten, ble byttet.



# Abstract

During the spring semester in the fifth year of the master's degree in industrial chemistry, a number photocatalytic experiments was performed to investigate the optimal operating conditions for the sugar alcohol, glycerin. The effect of changing the sacrificial agent was also investigated.

The experiments were performed under UVA and the parameters varied was: copper loading, glycerol concentration, and mass of catalyst per liter of reaction liquid.

In the first experiments a range of different alcohols were tested. Methanol served as a baseline when ethanol, iso-propanol and glycerin was tested. Methanol, ethanol and iso-propanol was found to be almost equally good when hydrogen evolution per mol OH was compared.

When optimizing the glycerin experiments, three parameters were varied. Firstly the vol% of glycerin was changed while the mass of catalyst and copper loading was held constant at 1.5wt% and 250mg respectively. 1vol% of glycerin had the highest activity at 0.069 ml H<sub>2</sub>/min.

The second series of experiments involved changing the copper loading of the catalyst. 1wt%Cu on the catalyst had the highest activity of 0.10 ml H<sub>2</sub>/min

The last variable to be manipulated was the variation of the mass of catalyst per batch. Where each batch volume was 500ml. The results from these series of experiments showed that 250mg of 1wt%Cu-TiO<sub>2</sub> with 1vol% glycerin exceeded the others on the reaction rate charts.

The optimal ratio between mass of catalyst and the glycerol concentration was observed to be:

$$\frac{50mg \text{ 1wt\%Cu} - TiO_2}{1.00 \text{ ml glycerin}}, \sim 1vol\% \text{ glycerin}$$

The optimal values for the parameters changed quite a lot when the alcohol, the organic sacrificial agent, was changed.





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## List of symbols and acronyms

<b>Symbol</b>	<b>Meaning</b>	<b>Unit</b>
<b>rpm</b>	Rounds per minute	min <sup>-1</sup>
<b>VOC</b>	Volatile Organic Compound	-
<b>MeOH</b>	Methanol	-
<b>EtOH</b>	Ethanol	-
<b>LMHW</b>	Langemuir-Hinshelwood	-
<b>MS</b>		-
<b>E<sub>g</sub></b>	Band gap energy	Electronvolt (eV)



# Introduction

Today's world is growing, and with it the demand for energy, the requirement for green energy. Most of the supply generated today comes from non-renewable sources, such as natural gas, crude oil and coal. But with the increasing focus on  $\text{CO}_2$ - and  $\text{NO}_x$ -emissions, other alternatives are being investigated.

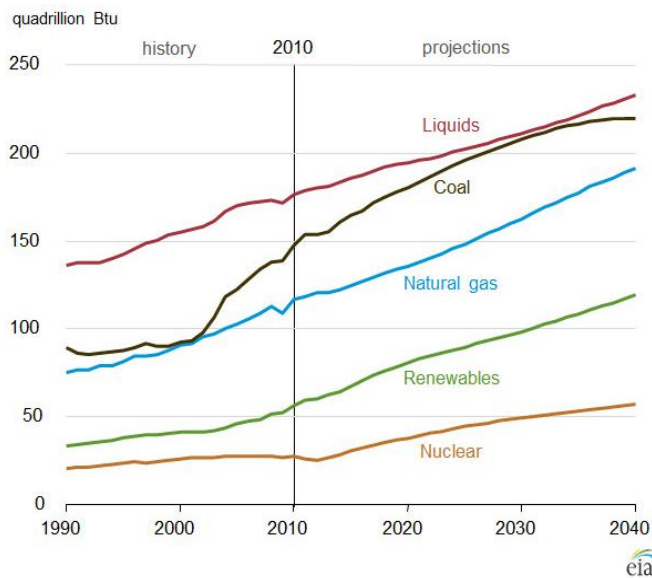


Figure 1: Forecast for fuel energy consumption. (U.S Department of Energy, 2013)

As seen in figure 1, the fuel thought to have the largest increase in consumption is the natural gas, and renewables. But fossil fuels will still be the main contributor of fuel energy.

This increased focus on  $\text{CO}_2$ -emissions has made a whole generation aware of its energy consumption, but left the gas with the blame alone for the climatic changes. The changes seem to correlate to the concentration of  $\text{CO}_2$  in the atmosphere. But the variations seen are not caused only by the  $\text{CO}_2$ -emissions, rather the emissions of a number of heat trapping gasses. There is no escaping fact that the temperature anomalies we see are man-made.

$\text{NO}_x$ -emissions contribute to localized health issues for humans, and is also known to form as acid rain, killing fish stocks by decreasing the pH-values in their natural habitat. All of these factors are contributing to the search for a greener energy source. This project focuses on a green way of producing hydrogen, done without much emissions and from a renewable source. The technology might not be able to sustain a factory alone, but a small plant beside an already existing facility, producing hydrogen via photo-reforming waste alcohols from said factory.



# 1 Theory

## 1.1 Photocatalysis

The word photocatalysis is a combination of photo, which comes from the latin word *photos*, meaning light, and catalysis, which is the principle of accelerating a chemical reaction. The catalyst does this by lowering the activation energy, without being consumed. So a valid formulation of the definition could be: "*A catalyst accelerated photoreaction*".

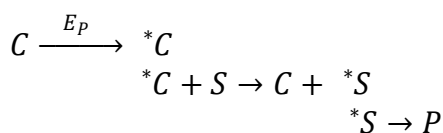
Photocatalysis is the only principle which allows you do drive "uphill" reactions. This is one of the attractive aspects when it comes to photocatalysis. The other side which is equally interesting is the fact that you can use the energy from the sun to power the reaction. You can also use light emitting bulbs to power the system as well, but that would not be nearly as attractive as using the sun.

One can say that photocatalysis, or in our case; heterogeneous photocatalysis is just like catalysis, except the catalyst is activated by photons and not thermal energy.

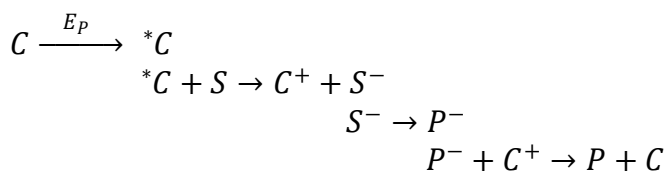
### 1.1.1 Reaction mechanisms

There are two ways a reaction can occur when a catalyst has absorbed light. An electron transfer can occur, either by being an electron acceptor, or an electron donor. Or via energy transfer.

- 1.) Energy transfer, where "C" depicts the catalyst and P the product. S is the reactant in an activated state. Also the \* shows a photosensitized unit.

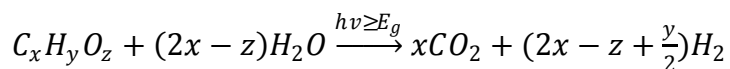


- 2.) Electron donor/acceptor.



(Castellote & Bengtsson, 2011)

An equation that has been found to depict photo-reforming of alcohols rather accurately is seen in the equation that follows:



This makes it possible to closely predict the hydrogen output. Experiments conducted to confirm this used a Pt-TiO<sub>2</sub> with the same preparation method as the catalysts in this paper, except the electron conducting material has been changed from Pt to Cu in this study.

(Patsoura, Kondarides, & Verykios, 2007)

## 1.2 The laws of photochemistry

There are three laws when the subject is photochemistry;

- 1.) Only light which is absorbed by a given molecule may alter the given molecule. Formulated by Grotthus (1817) and Draper (1843).
- 2.) Only one molecule can be activated per adsorbed photon.
- 3.) *"The energy of an absorbed photon must be equal or greater than the weakest bond in the molecule"* (Bolton, 2010).

The first law suggests some overlapping of wavelength ranges from the light entering the system, and the light absorbed by the material initially. This implies knowing which wavelength the material absorbs, and also in what range the radiation source emits.

The second law does not apply to photochemistry involving the use of lasers because of a phenomenon called biphotonic process, where the number of excited molecules are so high that they might absorb an additional photon.

The third law states that it is necessary to compare the threshold wavelengths, which is calculated with the enthalpy from symmetrical bond dissociation (from the weakest bond), and the onset wavelength, which is what you irradiate the reaction liquid with.



To sum up the laws in its bare necessities;

Make sure your species are able to absorb the wavelength you put into your system, and also make sure that there are minimal interference from external sources, like the transparency of the reactor.

In the case of this report, it will be the titanium(IV)oxide that absorbs some of the light to drive the reactions.

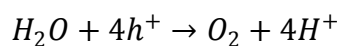
(Pfoertner & Oppenländer, 2012)

### 1.3 Photo-reforming

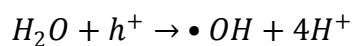
The focus of this project work was on photo-reforming of lower alcohols to produce hydrogen. The bi-products are a source of future research.

Possible reactions present in the reactor;

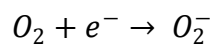
The oxidation of water on the TiO<sub>2</sub> particle;



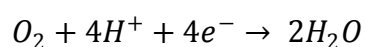
Hydroxyl radical formation at the valence band by water oxidation on the TiO<sub>2</sub> particle;



Superoxide formation at the conductive band by the reduction of oxygen on the TiO<sub>2</sub> particle;

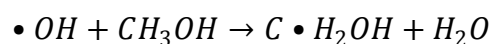


Oxygen returning to water;

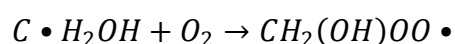


These reactions are a source for better understanding the circumstances inside the reactor. The hydroxyl and superoxide are radicals, meaning they do not follow the octet rule and are therefore extremely reactive.

Next in queue is the simplest of alcohols that were added to the mix; methanol. A possible pathway of the reaction between the hydroxyl radical and the alcohol could be;



Coupled with the oxygen created from water oxidation we get a;



The peroxy, created from the carbon radical, can interact with methanol again in a chain-like process. (Fujishima, Narasinga Rao, & Ohko, 2002)

## 1.4 Titanium(IV)oxide

Titanium(IV)oxide is the most commonly used support in photocatalysis. But in spite of being classified as a support material, it is actually active during the process. The  $TiO_2$  is excellent for absorbing UV-radiation, which is why the most commonly found form of titaniumdioxide is in sunscreen-lotion.

The ability to absorb UV-radiation is the ability harnessed during photocatalysis. The photon excites an electron, creating an electron hole. This in turn affects the reactant in the reaction liquid, and forms an intermediate, which eventually ends up as the desired product.

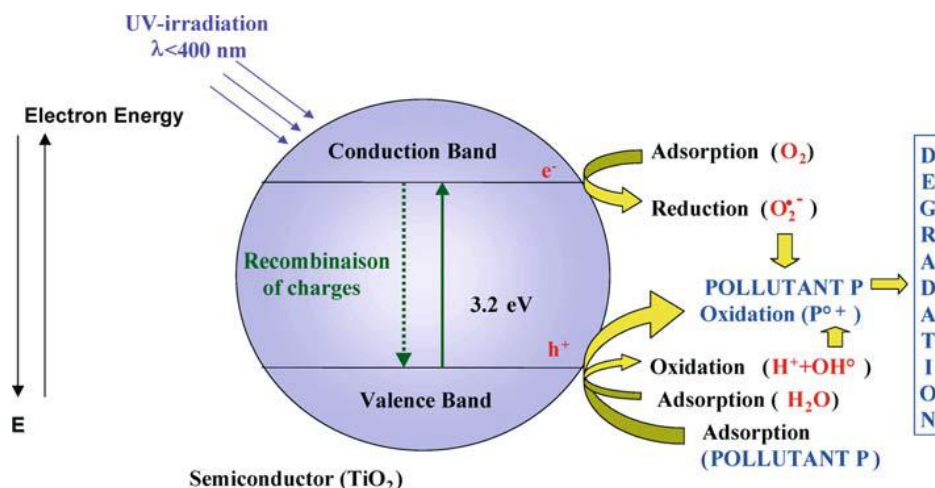


Figure 2: Spherical titanium(IV)oxide particle interactions (Herrmann, 2005).

In the conduction band, we can see that the  $\text{TiO}_2$  particle has the ability to reduce oxygen, making the radical called "superoxide", which is extremely reactive.

The Valence band however oxidizes the water around the particle, creating  $\text{H}^+$  and a hydroxyl radical.

The former is very interesting when it comes to air purification via photocatalysis. The latter is interesting in hydrogen production, which is the focus of this report, and also wastewater purification. The main idea of the two is that the radicals will react with the unwanted compound and preferably render it relatively inert.

There are three different qualities of  $\text{TiO}_2$  that are interesting to compare when speaking of photocatalysis; Anatase, rutile and P25.

Anatase and rutile is a reference to a term used to describe the structure of the titaniumdioxide. While P25 is a reference to a given particle size of the  $\text{TiO}_2$ . This paper has focused on the P25 quality of the titanium(IV)oxide-support, since this arrangement has been proven to be more active under the reaction conditions.

## 1.5 Optimization

To better understand what the indicators for an optimized photocatalytic process looks like, it is necessary to have an understanding of the phenomena in play and also to know how one is supposed to interpret the trends.

From figure 3 we can ascertain that the reaction rates will increase as a 1. order reaction does, but when the system has an excess of either the reactants, or the mass of catalyst, it will level out and act as a 0. order reaction.

The explanation for this, starting with the excess of reactant concentration, is the saturation of hydroxylic adsorption sites on the  $\text{TiO}_2$ . So the most optimized concentration would be just before, or straight after the rate has leveled out.

The same trend appears on the mass of catalyst optimization. In the given reaction liquid, with catalyst mass well in on the plateau, a blocking of UV-radiation takes place. This results in most of the particles not being activated by the light. Which means that you have a reactor where lots of the catalyst is not being used to its fullest potential.

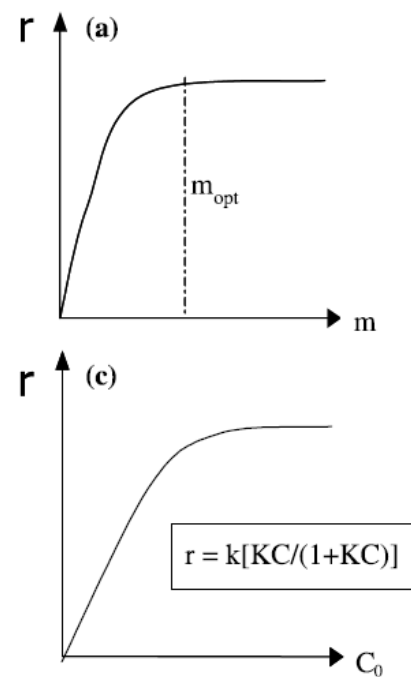


Figure 3: Graphs indicating optimized concentration and mass of catalyst (Herrmann, 2005).

## 1.6 Areas of interest

Some fields under photocatalysis are more researched than others. Some are still in their infant stages, while others are close to being a commercialized process.

### 1.6.1 Wastewater purification

Water purification via photocatalysis still needs research to be of much practical use. The reason as to why photocatalytic oxidation is so attractive when it comes to wastewater, is the increasing complexity of the water, due to organic, toxic and biological compounds.

Examples of species needing reduction is the Chrome(VI), which is devastating to humans in the way that it is carcinogenic and it is also water-soluble. By reducing Chrome(VI) to Chrome(III) which is not water-soluble and no threat towards humans, it could benefit the recipient of the cleansed water.

This subject is relatively new, but the prospects are immensely promising. The technology should be available in the near future.

(Soboleva & Prihod'ko, 2013)

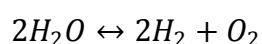
### 1.6.2 Air purification

Air purification is by far the most researched topic. It is commercialized, and sold as an air purifier you have in your home to oxidize VOC, bacteria and pathogens, leaving behind an odorless mixture of H<sub>2</sub>O, CO<sub>2</sub> and remnants of the destroyed compound.

The unit is set up with a filter that contains the catalyst, titanium(IV)dioxide, and a UV lamp in the shorter wavelength range, UVC. The air with the unwanted compounds travels past the lamp, through the filter, comes in contact with the catalyst and becomes oxidized.

### 1.6.3 Water-splitting

Water-splitting is a relatively new area. Much research is needed to be able to put it to practical use.



Popularly called "Artificial Photosynthesis", the idea is to split, as the name suggests, the water molecule into hydrogen and oxygen. Potentially creating one of the cleanest sources of fuel.

## 2 Experimental

The experiments were carried out on the rig in K5 at the third floor in room 17. The reactor was running for between 12 to 24 hours for each of the experiments.

The consistency of the results have been upheld throughout the experiments by using the same equipment to measure the quantities of liquids in the reactor, the same weight for weighting the catalyst, the same position in the reactor (marked by pen) and also the set point of the stirrer is fixed. These steps should be sufficient to obtain a reproducible result.

### 2.1 Catalyst preparation

The catalyst was prepared by incipient wetness impregnation, then the catalyst was dried overnight at 70 degrees Celsius. After the drying, it was crushed to a finer powder, to ensure homogeneous calcination throughout the catalyst mass. After calcining the catalyst for 4 hours at 200°C, with a ramping of 5°C/min, it was cooled down and brought back to the lab for more crushing.

The goal was to have a particle size of less than 53µm. This was achieved through repeated crushing and sieving, then mortaring the mass that did not go through the fine mesh.

#### 2.2.1 Incipient Wetness Impregnation

The IWI technique is based on empirical observations for when the support looks sufficiently "wet". After measuring out the required amount of distilled water to fill the pores of the support, TiO<sub>2</sub> P25, the precursor, CuN<sub>2</sub>O<sub>6</sub>:3H<sub>2</sub>O, was added and stirred until dissolved. The solubility of the precursor in water is 2670g/l at 20°C. This means that the maximal wt%Cu you could have in your catalyst would be ~70wt%.

When the solution looked homogeneous, the support was added bit by bit. First a small amount to control the consistency of the mix, then the TiO<sub>2</sub> was added in the same fashion as baking bread; half the support in, then half of the remaining, then half of the remaining, etc.

## 2.2 The set up

The set up consists of a reactor, a container which allows the exposure with different wavelengths and a connected MicroGC to quantify the hydrogen output.



**Figure 4: The set up with the reactor inside. Before UVA-exposure (MeOH).**

An argon flow at 10 cc/min through the reactor, which translates to a valve opening on the Mass flow controller (MFC) of 6.8% (6.4% after calibration), bringing any hydrogen produced with it to the MicroGC. The outlet of the reactor is also heated, to avoid having any liquid water entering the MicroGC, as it withdraws samples from the ventilation pipe.

The MicroGC destroys the samples in order to analyze them, so the effluent from the MicroGC goes back into the ventilation pipe, and out over the roof. The fluorescent tubes can be changed to the desired wavelength for exposure. The focus of this report has been UVA, which has a wavelength of between 320-400nm.

A known fact is that rubber cannot withstand UV-radiation over long periods of time, and still be flexible as new; so to prevent the decay of the rubber tubes transporting the argon and the product stream, the tubes have been wrapped in aluminum foil.

## 2.3 Reactor

The reactor is a glass cylinder with a volume of just a bit more than one liter, with a reusable rubber seal between the lid and container. The lid has two exit points with grooves on them, to secure gas in/out lines and prevent leakage.

The reactor is then further sealed by applying a locking mechanism to keep the lid and container tightly fixed against each other with the rubber seal in between.

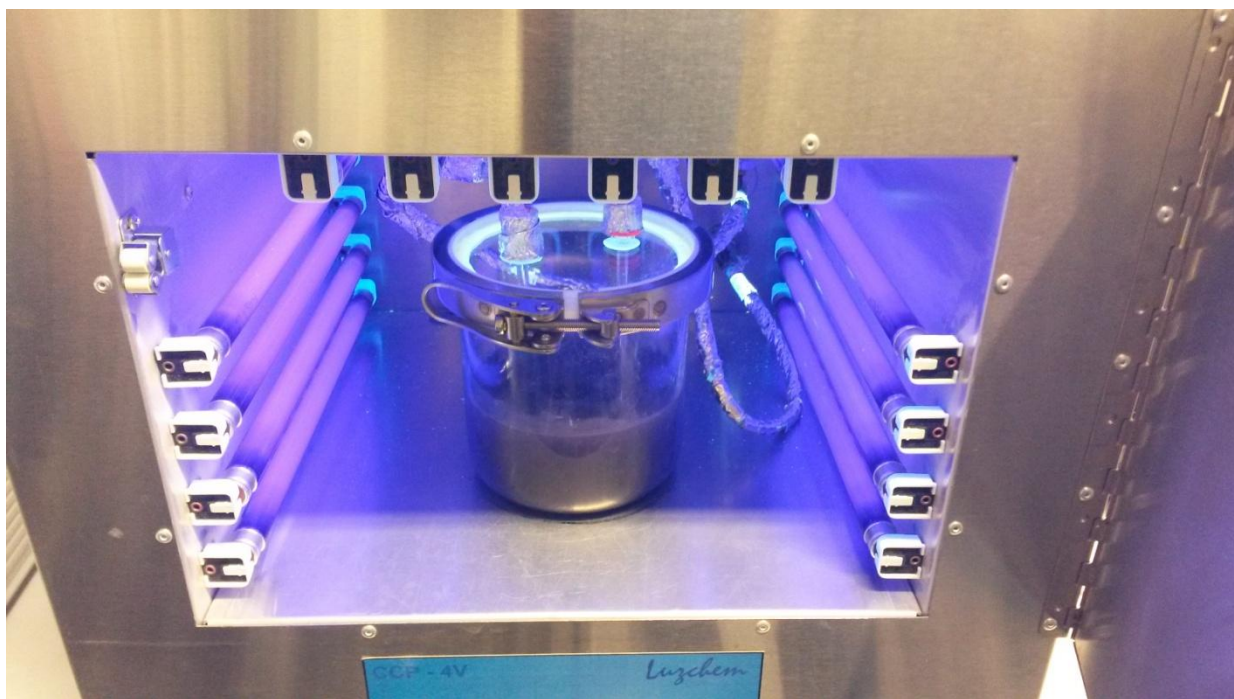


Figure 5: Reaction in progress. UVA lights activated (MeOH).

From figure 5, one can see how the reactor is placed in every experiment, as well as an almost immediate color change in the reaction liquid (After <16 minutes).



### 3. Results and discussion

#### 3.1 Particle size

Last semester a paper was written, by the author, comparing the effect of copper loading against the hydrogen evolution. The optimized parameters for photocatalysis with methanol using the copper catalyst were: 250mg, 1.5wt%Cu-TiO<sub>2</sub> and 50vol% of alcohol. The effect the particle size has on the reaction rate was not tested until this year. The catalysts were crushed, then sieved through a mesh with an opening of 53µm.

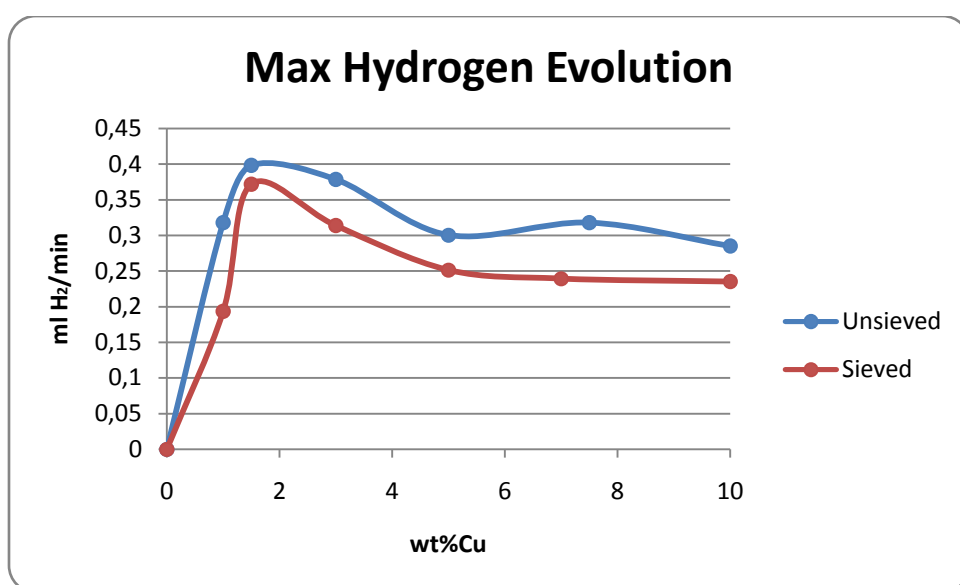


Figure 6: Sieved copper catalysts Vs. Unsieved

Unexpected as it is, the smaller particle size seem to have lower peak activity than the catalyst that has not been sieved. The largest difference can be seen at 1wt%Cu. The smallest change is unexpectedly found at 1.5wt%, because this catalyst was the only one that was sieved. This means that the interval between the two 1.5wt%Cu catalysts is caused by the fact that two different people made those catalysts.

Even though there is a slight difference in activity of the two sieved samples, it does not explain that the unsieved sample at 1wt%Cu shows a 64% higher activity than the sieved sample. However, being made by different people might have had an effect on the outcome.

## 3.2 Alcohols

The chosen alcohols were: Methanol, ethanol, iso-propanol and glycerin. The reason for choosing these alcohols was to study the effect of increasing the length of the carbon chain. The glycerin was added to see what happens when one decides to add three hydroxyl groups into the mix.

The catalyst used for the various experiments was the one optimized for methanol. This was discovered last fall to be 250mg of 1.5wt%Cu-TiO<sub>2</sub> in 500ml of reaction liquid where the alcohol stood for 50vol%.

The alcohols will be compared in various ways to point out the differences.

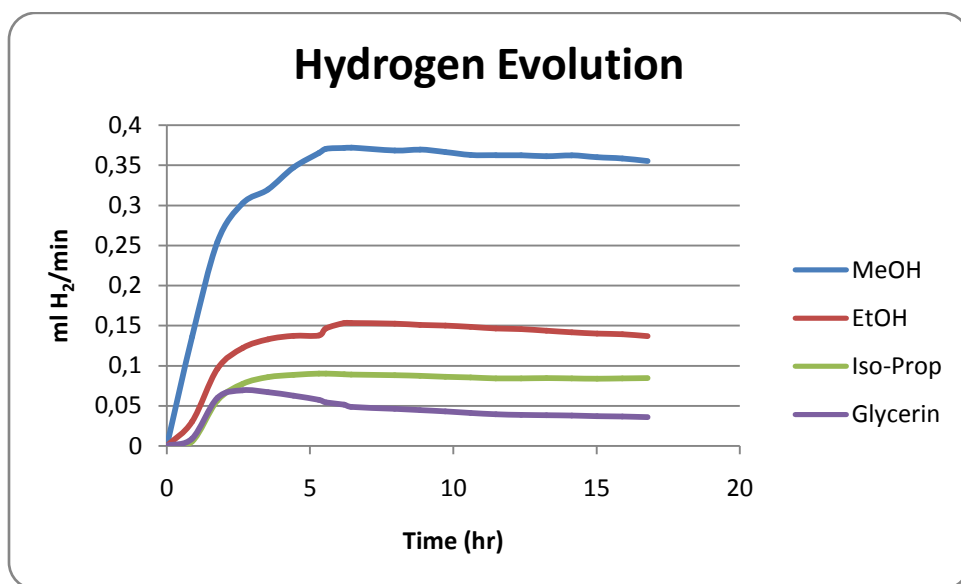


Figure 7: Compared hydrogen evolution for the different alcohols tested.

In figure 7 the different alcohols were compared with respect to hydrogen evolution. The glycerin sample ran at 1vol%, since the 50% and 25% experiments did not produce any detectable amount of hydrogen.

The figure illustrates that the increasing size of the molecule makes it more difficult to dehydrogenate the alcohol, implying that one has to go through several reaction steps to extract all of the hydrogen, the larger the molecule becomes.

(Patsoura, Kondarides, & Verykios, 2007)

These results can be plotted together in a different way, by comparing the peak in hydrogen evolution, together with the number of carbon atoms found in said alcohol.

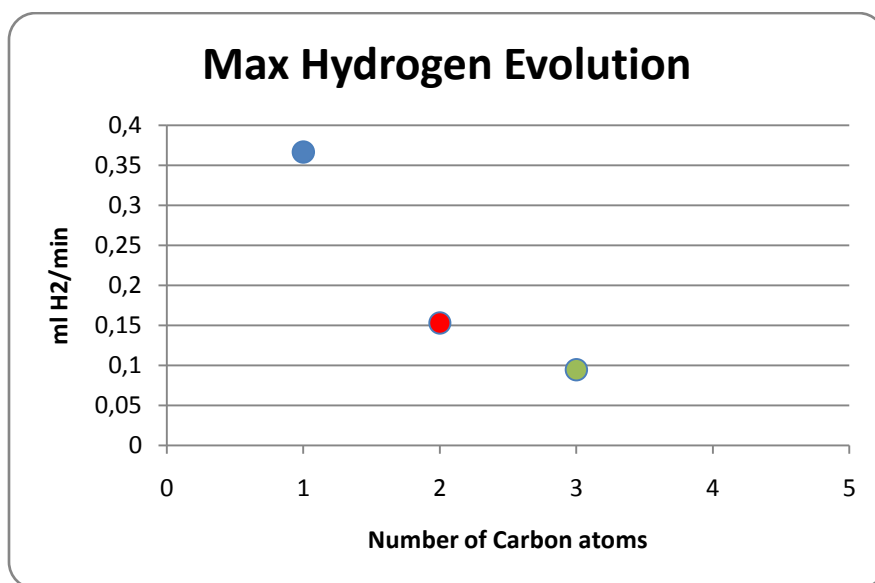


Figure 8: Plot of max hydrogen evolution against increased carbon content in said alcohols.

The representation of quantities in figure 8 is not "fair", but speaks in favor of the previously mentioned theory, that dehydrogenation is harder to complete for larger alcohols. It is true that one would produce less hydrogen with 250ml of alcohol, when the number of carbon atoms in the compound is increased; When compared to number of mol of hydroxyl-groups, however, the figures should prove more equal.

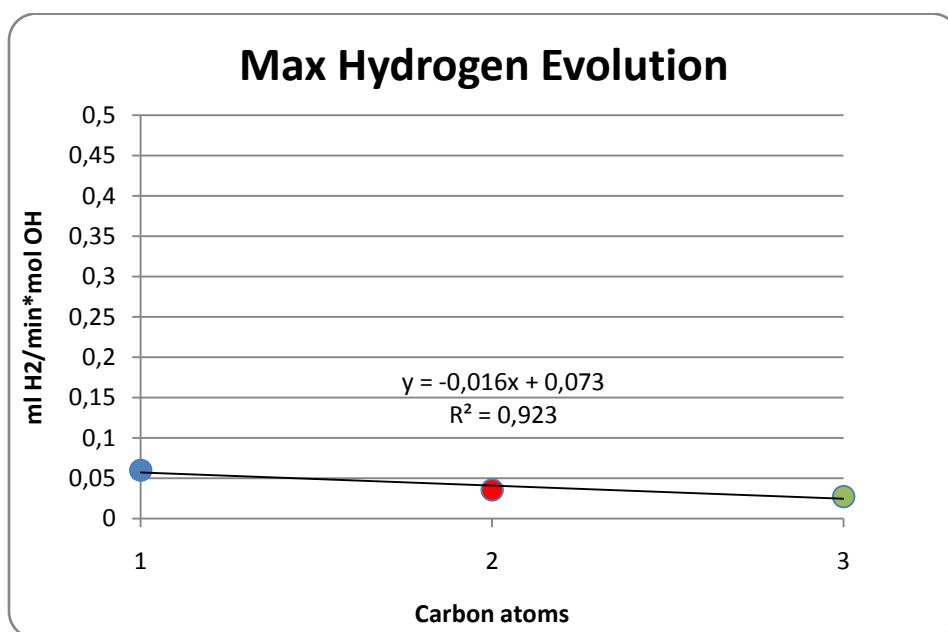


Figure 9: Comparing the hydrogen production per mol OH.

In figure 9, methanol, ethanol and iso-propanol is plotted as blue, red and green, respectively, displaying the hydrogen production per mol of hydroxyl groups. The slope is at -0.016 which is not ideal; Expected it to be closer to 0 so that the results easily can be grounded in theory.

The experiments for Ethanol and iso-propanol are not optimized, this is one reason for the differences being bigger than they should. Looking at only ethanol and iso-propanol together, they produce a slope of -0.0082, which brings the experiments closer to their roots in theory.

Furthermore the consistency of the experiments were checked, seeing how there are two pairs of parallels. The expected value of the differences of methanol and iso-propanol experiments were -0.011 and 0.0040, respectively. With associated standard deviation of 0.0080 and 0.0013, respectively. The unit for these parameters are ml H<sub>2</sub>/min.

### 3.3 Optimizing glycerin parameters

To properly compare the results, we have to optimize the experiments when it comes to hydrogen evolution by manipulating the process parameters such as; concentration of glycerin, copper loading on the catalyst and mass of catalyst.

#### 3.3.1 Volume percent

The experiments started with a mix of 1:1 of alcohol and water. The reaction liquid was much thicker than the one where methanol was involved. The results from the runs with 50- and 25vol% resulted in a non-detectable amount of hydrogen. The only apparent connection to this was the viscosity. As seen in appendix A the color change as observed in previous experiments are apparent; This indicates that there are some kind of reaction happening. The experiments failed to produce any detectable amount even after 24 hours.

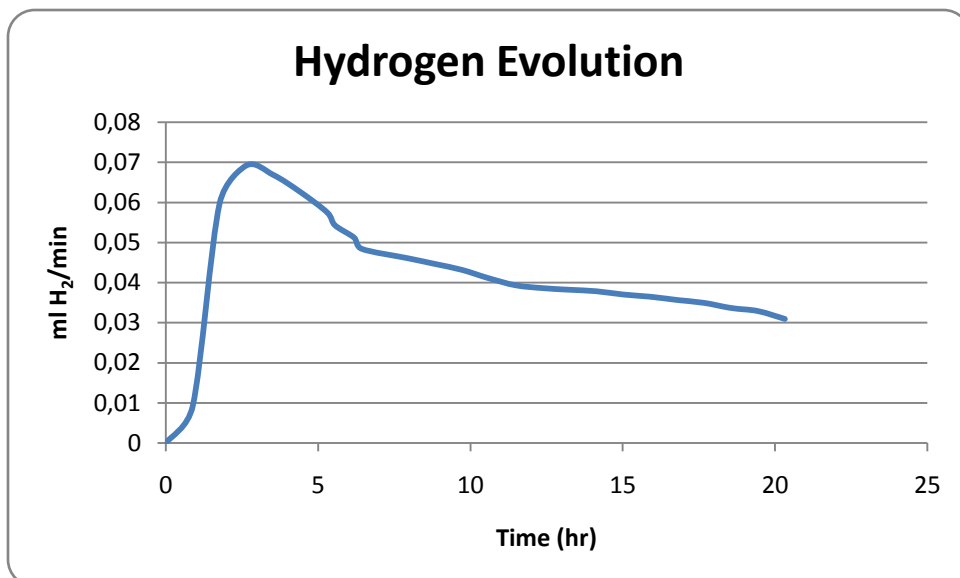


Figure 10: 1vol% glycerin, 1.5wt%Cu and 250mg catalyst.

Figure 10 shows hydrogen evolution for the best vol% conditions. This is relatively high compared to the methanol experiments. At 1 vol%, compared to 50vol% in methanol experiments, this glycerin run manages to achieve 1/4 of the product. This is at stage 1 of the optimization.

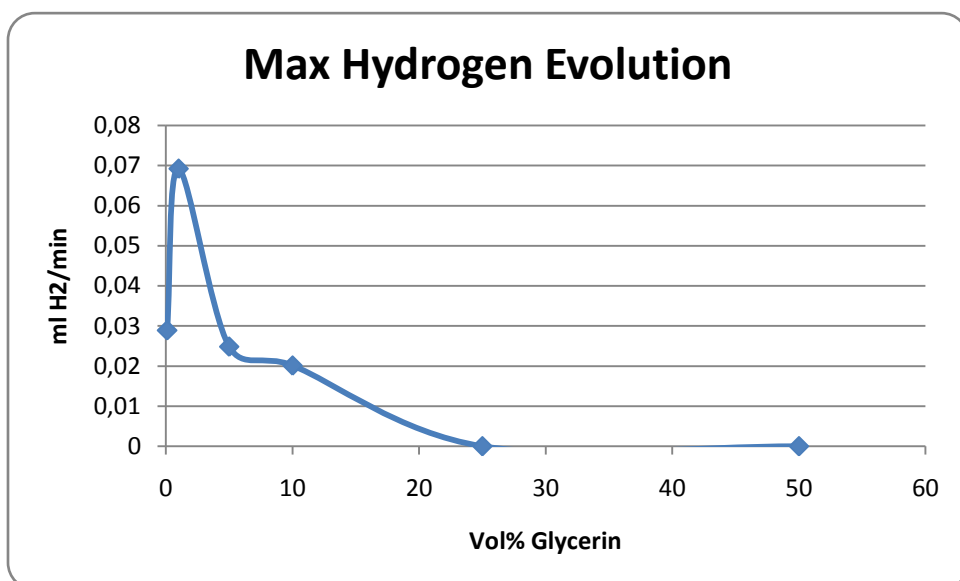


Figure 11: Hydrogen Evolution peaks plotted against vol% of glycerin

In figure 11 one can see that the graph looks nothing like expected. If we blame the viscosity for causing problems early on, and look at the rapid growth of the initial reaction rate, it appears to be a 2. order reaction initially, converging towards a 1. order reaction after.

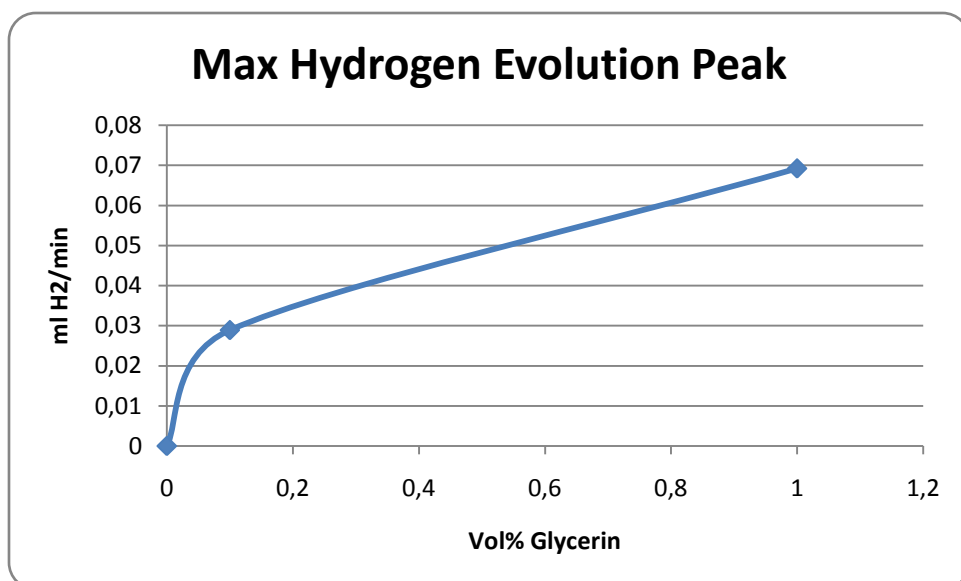


Figure 12: First two data points compared in a plot before viscosity sets in.

To be sure about the observed behavior of the reaction rate, with the increasing concentration of glycerin, a study should be performed where a solvent is added to counteract the viscosity changes due to the high glycerin content.

### 3.3.2 Copper loading

The loading of metal on the catalyst improves the electron transport of the catalyst, but also it screens titanium(IV)oxide preventing irradiation being absorbed. A balance between the two is necessary to achieve the best results.

The copper loading experiments were performed at 1 vol% of glycerin and with 250mg of catalyst. From earlier work, the need to modify the copper loading has been coupled with the irradiation source. The change from UVC to UVA changed the optimal copper loading from 5wt% to 1.5wt% in the case with methanol. However, this needs further study to observe if the trend continues. Since the copper loading also affects the speed of the electron transport, and glycerin has three hydroxyl groups, it is necessary to gather some data points to see how those parameters coincide.

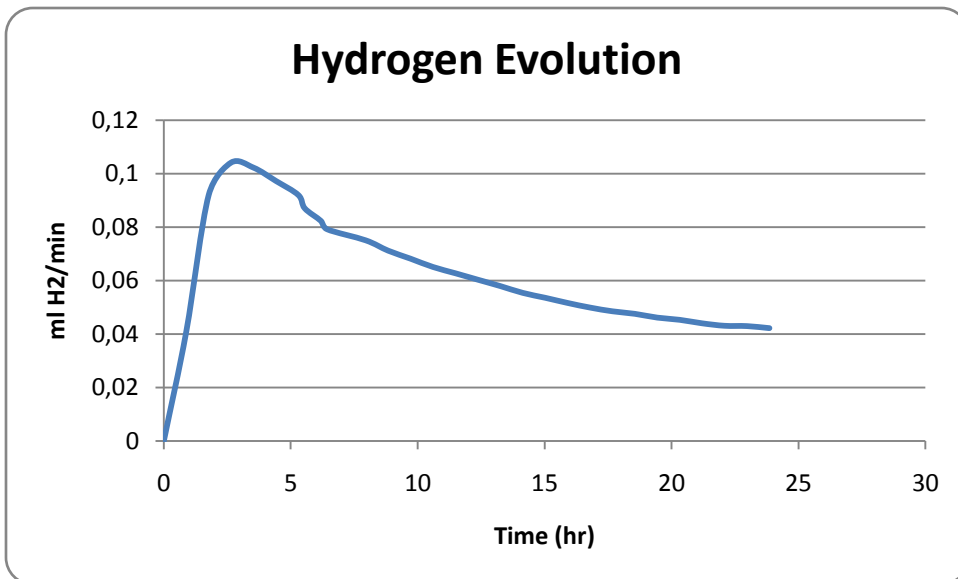


Figure 13: 1wt%Cu-TiO<sub>2</sub>, 250mg.

Figure 13 is the frontrunner among the copper loading experiments. It appears that the glycerin reaction favors lower copper loading than that of the methanol. To see the glycerin reach as high as 0.10 ml H<sub>2</sub>/min is pleasant. Especially since the concentration is as low as 1vol%.

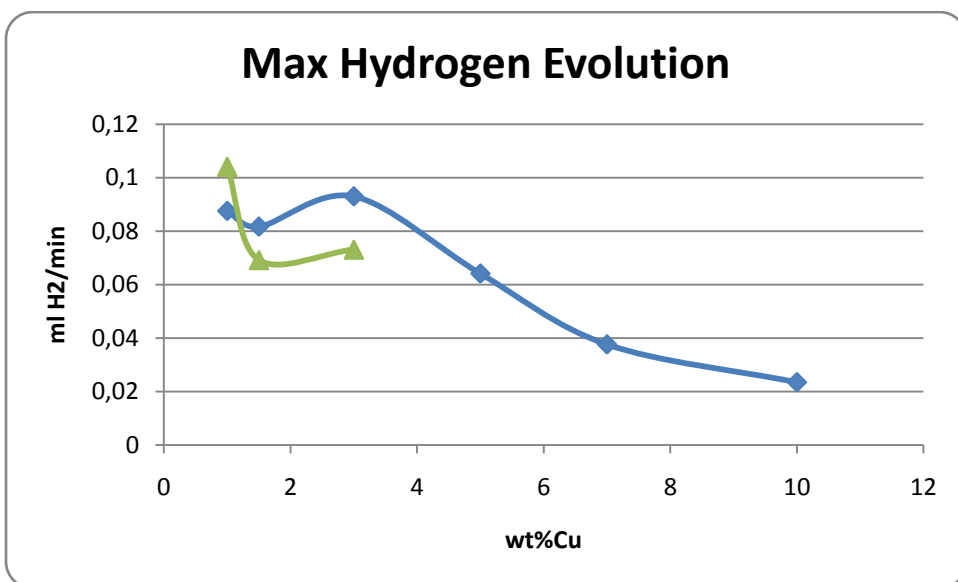


Figure 14: Hydrogen Evolution peaks plotted against copper loading.

In this range of experiments an issue presented itself. The results seemed incorrect, and on that notion the mass flow controller was double-checked. The flow of argon was off by 0.7ml/min.

The green line is the three best experiments executed after the calibration of the controller. So the blue is a valid representation of the behavior when increasing the copper loading, but the green trend has the correct value at its data points.

The largest different is found at 1wt%. This might be caused by the low vol% of glycerin as mentioned in the previous discussion. When dealing with 1vol%, the margin of error is incredibly small.

### 3.3.3 Mass of catalyst

Moving on to the last part of the experiments, the mass of catalyst. From the theory chapter we have established that the optimal amount of catalyst is at two points on the graph, and that the reaction rate will level out as the catalyst particles start blocking the irradiation from each other. Many of the experiments here were also victims of the slightly off MFC.

The run shown in figure 13 had the highest activity of these series of experiments after the MFC was calibrated. The amount of catalyst is equal to that of the optimized methanol experiments. Compared to the methanol experiments, where the activity decrease is significant at increased mass of catalyst, glycerin shows the opposite behavior. To illustrate this, the experiment with the lowest mass of catalyst is brought fourth for inspection.

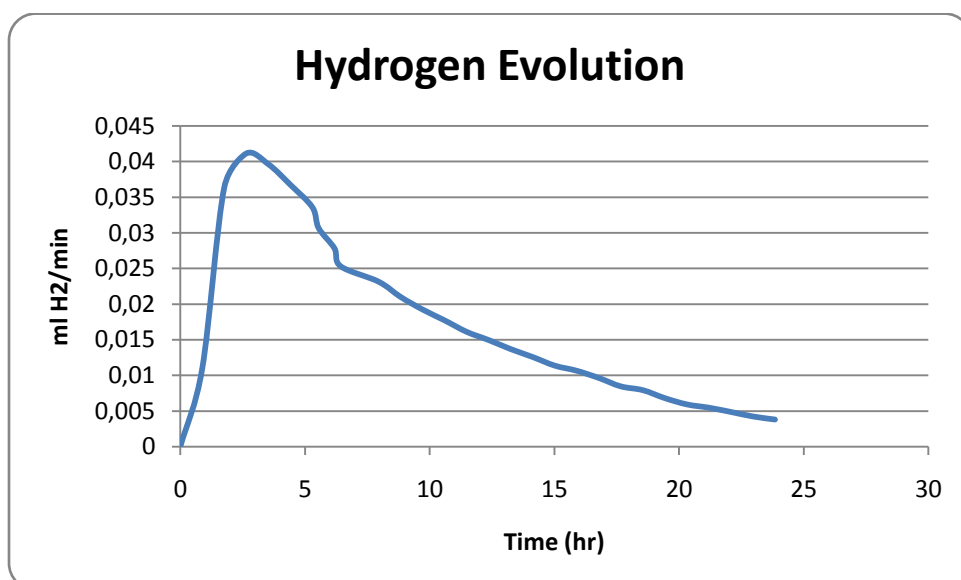


Figure 15: 50mg of 1wt%Cu-TiO<sub>2</sub>.



In figure 15 we can see the activity drop that was mentioned above. It is quite fast compared to the run in Figure 13. In the appendix section we can compare to the experiment done with 500mg of catalyst. This one confirms that the hydrogen evolution settles higher than what it does with a lower mass of catalyst.

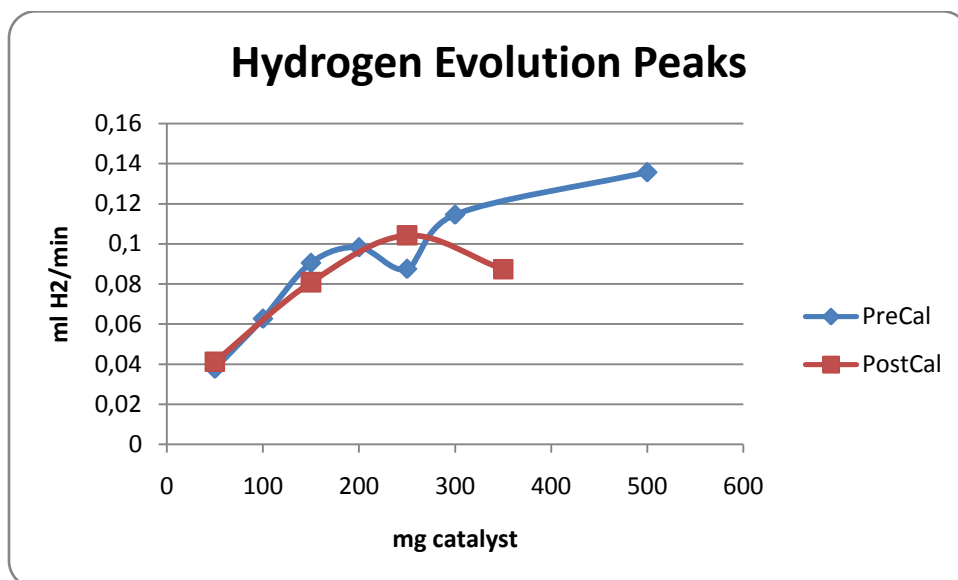


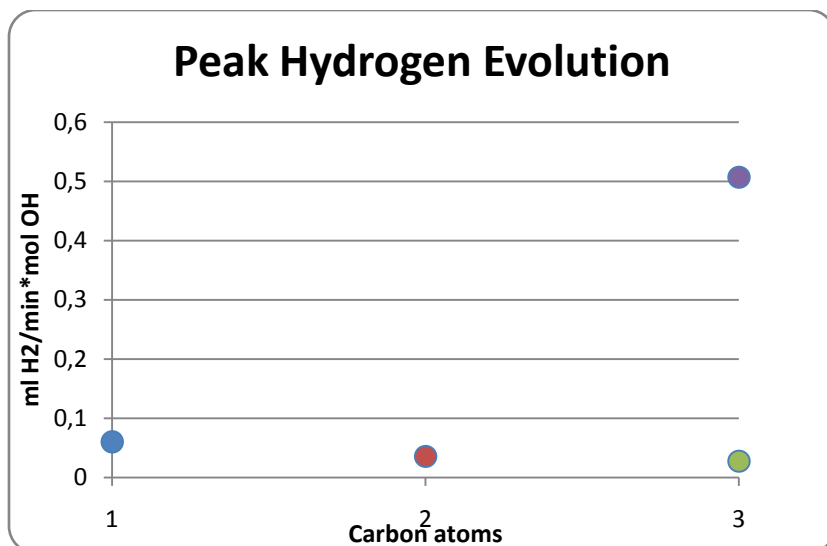
Figure 16: Hydrogen Evolution peaks plotted against mass of catalyst.

In figure 16 the data points are gathered for comparison. A large difference at 250mg, this is addressed earlier in the paper, and is likely caused by a strong sensitivity to the glycerin concentration. This is of course caused by the low concentration to begin with, and the imperfections of measuring out the required amount of glycerin.

At 50mg catalyst we see that the difference is quite small. At 0.038 ml H<sub>2</sub> /min before calibration, versus 0.041 ml H<sub>2</sub>/min after.

One does expect the activity to reach its maximum, as mentioned in the theory chapter. However, the said theory seems to fit the methanol experiments better than those containing glycerin. The optimization for alcohols containing several hydroxyl group might need different charts to be able to compared properly.

Now that all parameters has been optimized as much as the current situation allows, the results can be compared to the optimized methanol experiments. The best comparison would be the hydrogen production per mol of hydroxyl groups.



Figur 17: Comparing effectiveness of the different alcohols. Methanol, ethanol, iso-propanol and glycerin shown as blue, red, green and purple, respectively.

Figure 17 indicates that glycerin is approximately 10 times more efficient than methanol. One would expect it to only be 3 times that of methanol, which is not the case here. The reason for this is that glycerin is more efficient in exploiting the electron holes made by the excitation of the catalyst. The efficiency of utilizing these holes increases with the number of hydroxyl groups (M., J., & S. B., 2007).

Also, the optimal mass of catalyst chosen for methanol was slightly below where it reached maximum hydrogen production. These conditions contributes to methanol producing only 1/10 hydrogen per mol OH compared to glycerin. indicating that the methanol experiments still have some potential for further optimization.

The hydrogen production per mol hydroxyl groups comparison proves to be a helpful tool when measuring the efficiency of the experiments. A larger quantity of experiments and optimization of those experiments is needed to establish a good baseline for comparison.

### 3.4 Reproducibility

To ensure that the results are useful for future works, reproducibility has to be established. This was achieved by following the same process every time an experiment was conducted. The same measuring cylinder was used when concentrations were made, and the same type of syringe was used to properly measure out small quantities whenever that was needed. The speed of the magnetic stirrer was constant throughout the experiments, and the reactor was handled with gloves to prevent deposition of fingerprints.

## 4 Future prospects

- 1.) Hydrogen production is limited when it comes to using glycerol as the sacrificial agent, which seems to be caused by the increase in viscosity. To properly measure what the effect of increased alcohol concentration has on the reaction rate. When using only water, the effect of viscosity becomes apparent already at 5vol%. To counteract the increase of viscosity, one could use another solvent with a lower density than water.
- 2.) The reason for the color change in the reaction liquid is still unknown. To investigate this, a MS could be applied in situ. With the glycerin experiments the color change was still apparent, but the sediment in the reactor was black, instead of the blue/purple color from earlier experiments. The different color of the sediment might be caused by a variation of catalyst preparation, stopping the copper leaching off the catalyst and appearing as ions with a charge of 1+, before rinsing with water, and 2+, after tap water is introduced.
- 3.) Change the wavelength of the fluorescent tubes and optimize the methanol parameters for said wavelengths. This to see if the trend of optimal copper loading changes with the wavelength. The closer the irradiation source is to visible light, the lower the energy is absorbed, and the less copper can be added on the catalyst, as to not to screen the active part of the catalyst. This might explain the need to decrease the copper loading as the irradiation source nears visible light.
- 4.) Sample the methanol concentration of ongoing experiments to monitor the amount of methanol in the reaction liquid as hydrogen is produced. This will give a richer understanding of the deactivation mechanisms of the experiments.

## 5 Conclusion

The experiments with the sieved and unsieved samples of Cu-TiO<sub>2</sub>, with methanol as the electron donor, showed that the catalysts that were not sieved showed a slightly higher activity. However, due to the catalyst being made by two different persons, separated by a time span of over 4 months, one cannot draw a valid conclusion from this.

The different alcohols showed an overall lower activity than that of methanol. This was expected, seeing how photocatalytic reactions depend on the hydroxyl group(s) in said alcohol. Since the methanol molecule is smaller than that of ethanol and iso-propanol, one gets more mol hydroxyl groups with methanol at 50vol% than the other two. This means in practice that one needs larger quantities of alcohol, the higher the carbon content becomes, to get the same results as the experiments with methanol.

In theory there should be no difference in hydrogen production per mol OH added to the mix. In this case however, there seem to be a slight difference. When plotted together they produce a slope of -0.016 when it should be zero. This is attributed to the fact that the experiment was not optimized for each of the alcohols except methanol.

The glycerin was the focus of this paper. It was expected to produce more hydrogen seeing how the compound has 3 hydroxyl groups compared to methanol which only has 1. One parameter was varied while the other two were kept constant. The optimal concentration of glycerin was found to be 1vol%. At  $\geq 25\text{vol}\%$  the microGC did not detect any hydrogen, even though the liquid changed color, indicating activity. This was explained to be caused by the increased viscosity due to the high content of the sugar alcohol.

The second parameter to be optimized was the copper loading. This was tested twice, and the trend seemed to be that the lower copper loading gave the highest activity. The copper loading which gave the best electron conduction for glycerin, without screening too much of the titanium(IV)oxide, was 1wt%.

The third and last parameter to optimize was the mass of catalyst. The optimal mass is 250mg, same as that of the methanol experiments. The increased mass of catalyst would not be worth the trade-off.

Comparing the efficiency through plots of hydrogen production per mol of hydroxyl groups should prove useful for optimizing these experiments in the future.

To sum the results for glycerin optimization up:

$$\frac{50\text{mg } 1\text{wt}\% \text{Cu} - \text{TiO}_2}{1.00 \text{ ml glycerin}}, \sim 1\text{vol}\% \text{ glycerin}$$

## Literature

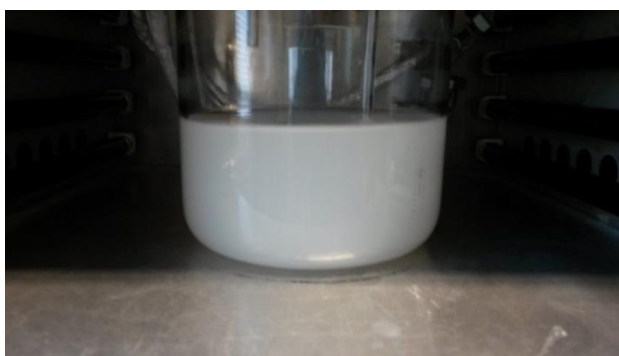
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# Appendix

## Appendix A - Color and odor change

A color change from light green to purple was observed in the reaction liquid shortly after being on stream. The remaining powder after decanting the liquid out of the reactor however, was dark in color. During the experiments fall 2013 some of the copper leached off the catalyst and attached itself on the reactor walls, displaying a blue color as the  $\text{Cu}^{2+}$  ions are stable in a solution of water.

Before irradiating the reactor with UVA rays:



**Figure A1: Reactor with  $\text{CuTiO}_2$  catalyst and 25% glycerin before activation by UVA.**

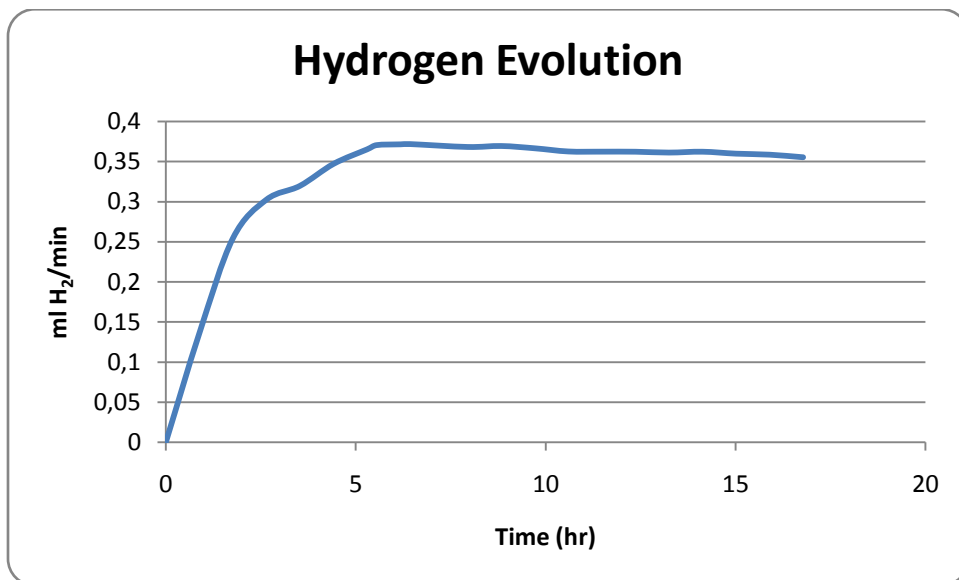
After 24h on stream:



**Figure: A2: Reactor with  $\text{CuTiO}_2$  catalyst and 25% glycerin after ~24h of UVA exposure.**

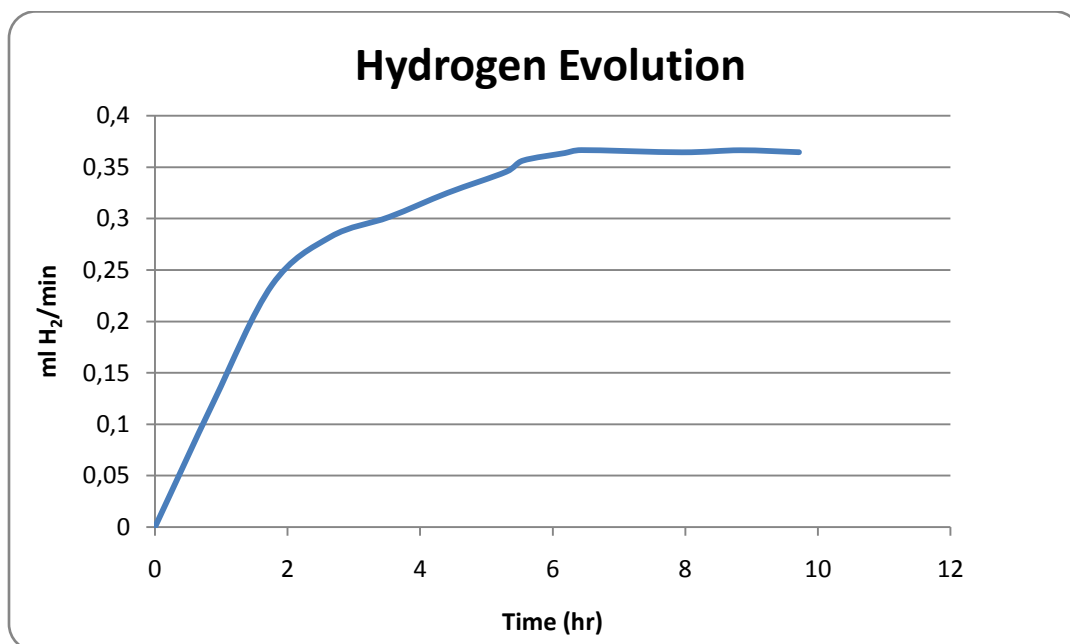
The odor of the glycerin and water solutions also changed after being on stream. From relatively odorless to unpleasant; Indicating the presence of volatile components being formed during the photo reforming. Not knowing specifically what these components were, the best HSE action was to actively use local fume hoods and keeping the reactor sealed until it was to be emptied. The surface of the reactor where the liquid touches the glass has had its properties changed. If water hits that area it only partially wets the surface.

Appendix B1 - 50vol%MeOH, 1.5wt%Cu-TiO<sub>2</sub>, 250mg  
(Before computer malfunctioned)



Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,1359
1,7667	0,25432
2,65	0,30246
3,5333	0,3197
4,4167	0,34708
5,3	0,36517
5,55	0,37046
6,1833	0,37144
6,4333	0,37175
7,95	0,36816
8,8333	0,36935
9,7167	0,3665
10,6	0,36254
11,4833	0,36231
12,3667	0,36223
13,25	0,36117
14,1333	0,36223
15,0167	0,35982
15,9	0,35853
16,7833	0,35532

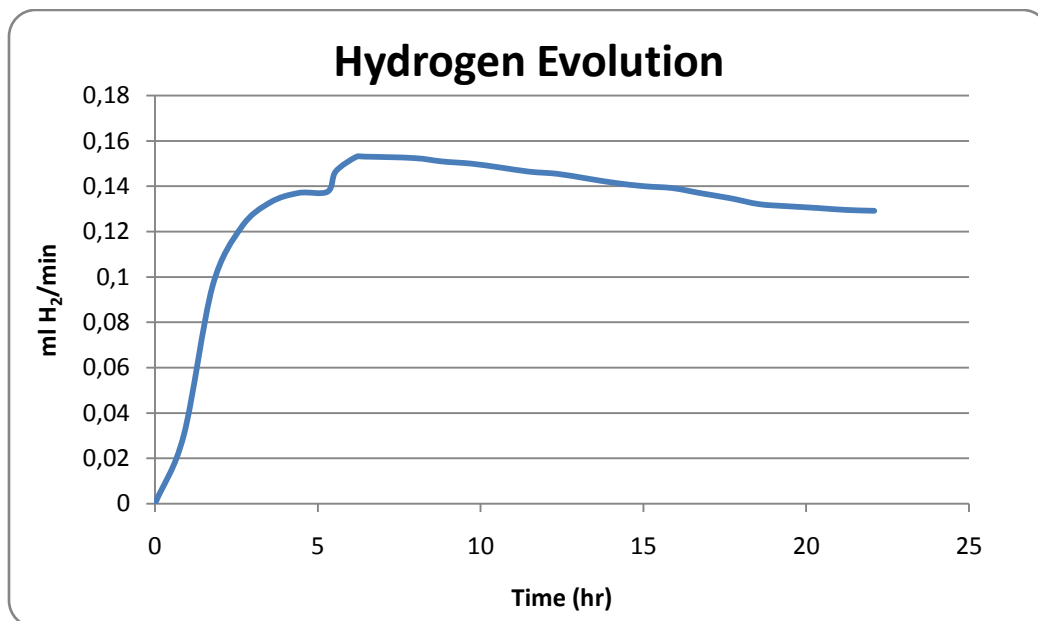
Appendix B2 - 50vol%MeOH, 1.5wt%Cu-TiO<sub>2</sub>, 250mg  
(After replacing the computer)



Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,12166
1,7667	0,23551
2,65	0,28224
3,5333	0,30151
4,4167	0,32501
5,3	0,34552
5,55	0,35632
6,1833	0,3637
6,4333	0,36656
7,95	0,36442
8,8333	0,36641
9,7167	0,36451

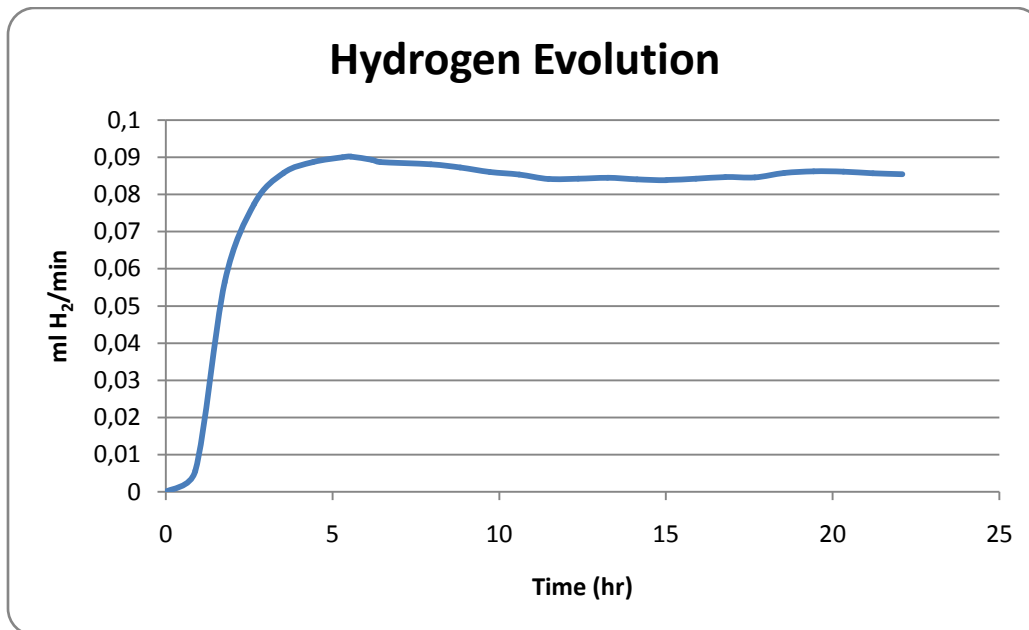


Appendix B3 - 50vol%EtOH, 1.5wt%Cu-TiO<sub>2</sub>, 250mg



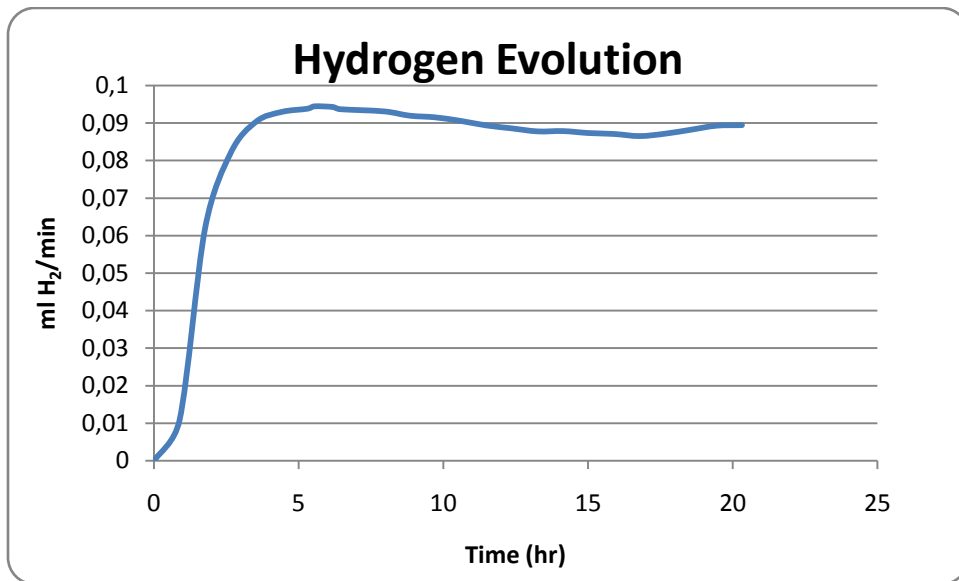
Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,03016
1,7667	0,09591
2,65	0,12185
3,5333	0,1328
4,4167	0,13702
5,3	0,13758
5,55	0,14651
6,1833	0,15296
6,4333	0,15303
7,95	0,1524
8,8333	0,15088
9,7167	0,14993
10,6	0,14824
11,4833	0,14641
12,3667	0,14542
13,25	0,14342
14,1333	0,14142
15,0167	0,13999
15,9	0,13913
16,7833	0,13684
17,6667	0,13467
18,55	0,13207
19,4333	0,13115
20,3167	0,1304
21,2	0,12953
22,0833	0,12914

Appendix B4 - 50vol% Iso-propanol, 1.5wt% Cu-TiO<sub>2</sub>, 250mg  
 (Before computer malfunction)



Time (hr)	H <sub>2</sub> (ml/min)		
0	0	13,25	0,08447
0,8833	0,00561	14,1333	0,08405
1,7667	0,05642	15,0167	0,08384
2,65	0,07737	15,9	0,08423
3,5333	0,08575	16,7833	0,08466
4,4167	0,08867	17,6667	0,08456
5,3	0,08997	18,55	0,08574
5,55	0,09016	19,4333	0,08619
6,1833	0,0893	20,3167	0,08612
6,4333	0,08873	21,2	0,08568
7,95	0,0881	22,0833	0,08539
8,8333	0,08722		
9,7167	0,08602		
10,6	0,08532		
11,4833	0,08415		
12,3667	0,08419		

Appendix B5 - 50vol% Iso-propanol, 1.5wt% Cu-TiO<sub>2</sub>, 250mg  
 (After replacing the computer)



Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,0108
1,7667	0,06199
2,65	0,08204
3,5333	0,09039
4,4167	0,09297
5,3	0,09382
5,55	0,09446
6,1833	0,09428
6,4333	0,0937
7,95	0,09311
8,8333	0,09197
9,7167	0,09152
10,6	0,09057
11,4833	0,08937
12,3667	0,08858
13,25	0,08778
14,1333	0,08786
15,0167	0,08734
15,9	0,08709
16,7833	0,08653
17,6667	0,08717
18,55	0,08822
19,4333	0,0893
20,3167	0,08944

## Appendix B6 - 50vol% Glycerin, 1.5wt% Cu-TiO<sub>2</sub>, 250mg

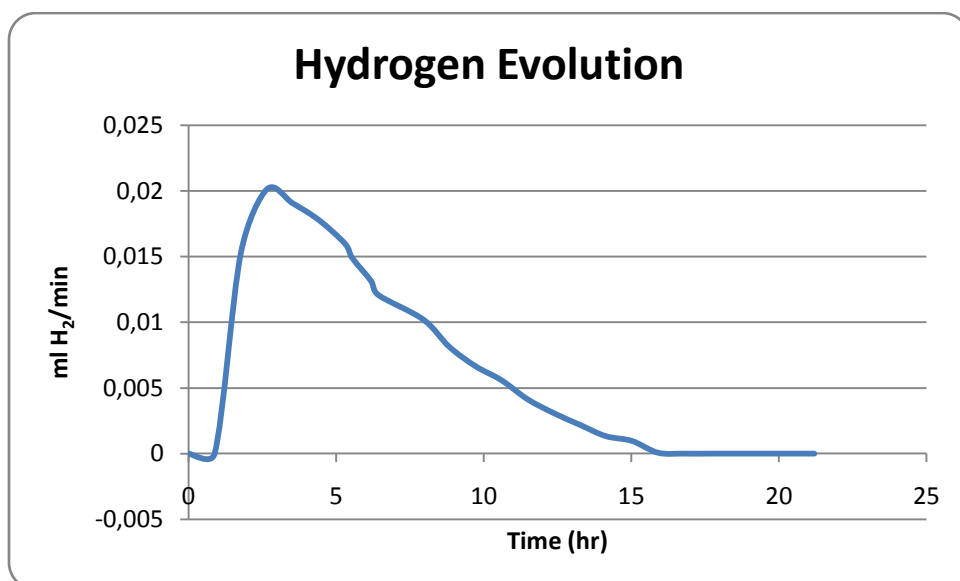
The experiment did not produce any detectable amount of hydrogen. The author postulates that this is directly related to the high viscosity of the mixture due to the high glycerin content.

The change of color was just as intense as the rest of the experiments with different alcohols, with a slightly softer/lighter purple compared to the others.

## Appendix C1 - 25vol% Glycerin, 1.5wt% Cu-TiO<sub>2</sub>, 250mg

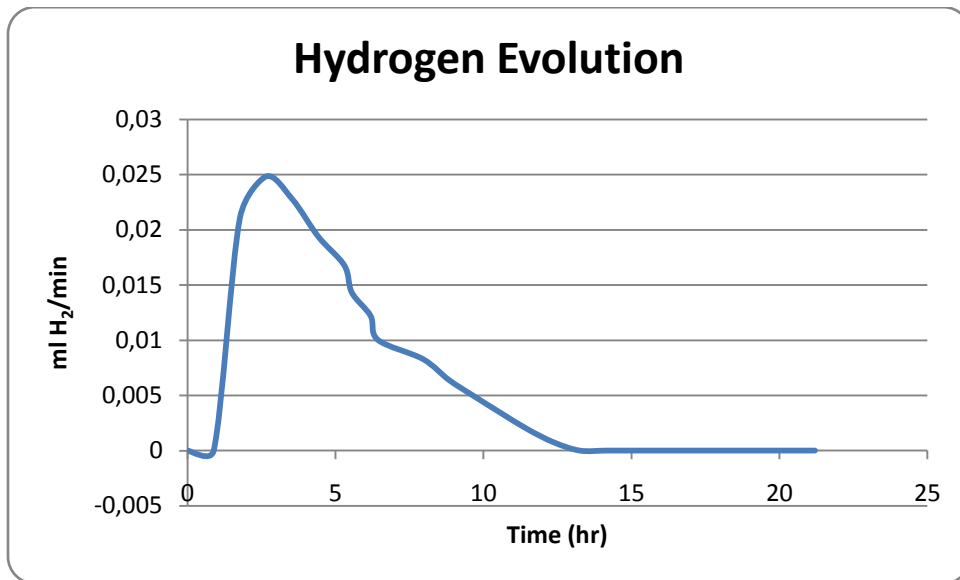
Same outcome as the run with 50vol% glycerin. This did not produce any Hydrogen.

Appendix C2 - 10vol% Glycerin, 1.5wt% Cu-TiO<sub>2</sub>, 250mg



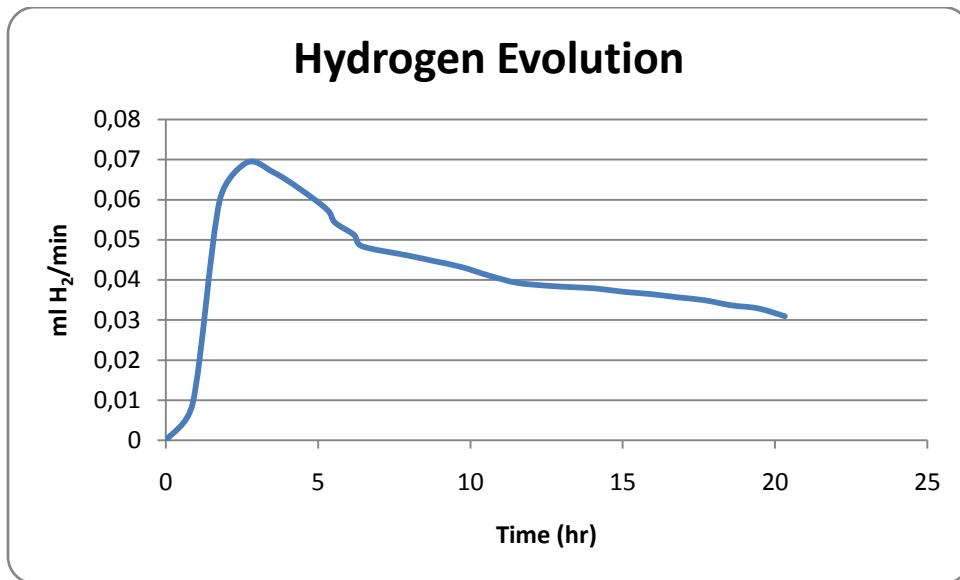
Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0
1,7667	0,01523
2,65	0,02012
3,5333	0,01905
4,4167	0,01778
5,3	0,01598
5,55	0,01488
6,1833	0,01314
6,4333	0,01207
7,95	0,01021
8,8333	0,00813
9,7167	0,00666
10,6	0,00559
11,4833	0,00414
12,3667	0,00309
13,25	0,0022
14,1333	0,00133
15,0167	0,00097
15,9	0,00007

Appendix C3 - 5vol% Glycerin, 1.5wt% Cu-TiO<sub>2</sub>, 250mg



Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0
1,7667	0,02105
2,65	0,02482
3,5333	0,02278
4,4167	0,01937
5,3	0,01675
5,55	0,01431
6,1833	0,0122
6,4333	0,01002
7,95	0,00829
8,8333	0,00639
9,7167	0,00486
10,6	0,00338
11,4833	0,00194
12,3667	0,00075
13,25	0

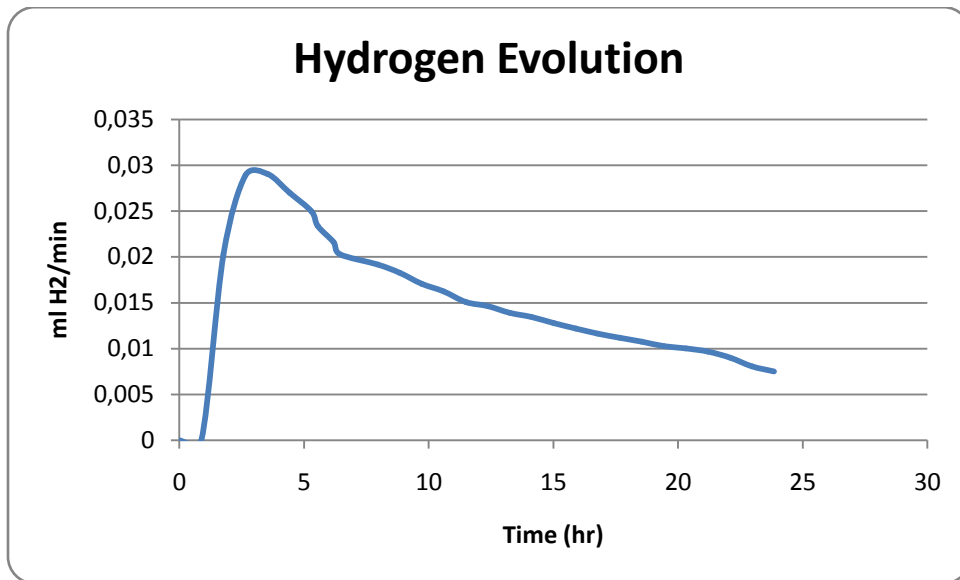
Appendix C4 - 1 vol% Glycerin, 1.5 wt% Cu-TiO<sub>2</sub>, 250mg



Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,00921
1,7667	0,05972
2,65	0,06918
3,5333	0,06678
4,4167	0,06253
5,3	0,05742
5,55	0,05426
6,1833	0,05115
6,4333	0,04837
7,95	0,04603
8,8333	0,04461
9,7167	0,04314
10,6	0,04105
11,4833	0,03929
12,3667	0,03859
13,25	0,03818
14,1333	0,03781
15,0167	0,03699
15,9	0,03645
16,7833	0,03563
17,6667	0,03491
18,55	0,03364
19,4333	0,03287
20,3167	0,03091

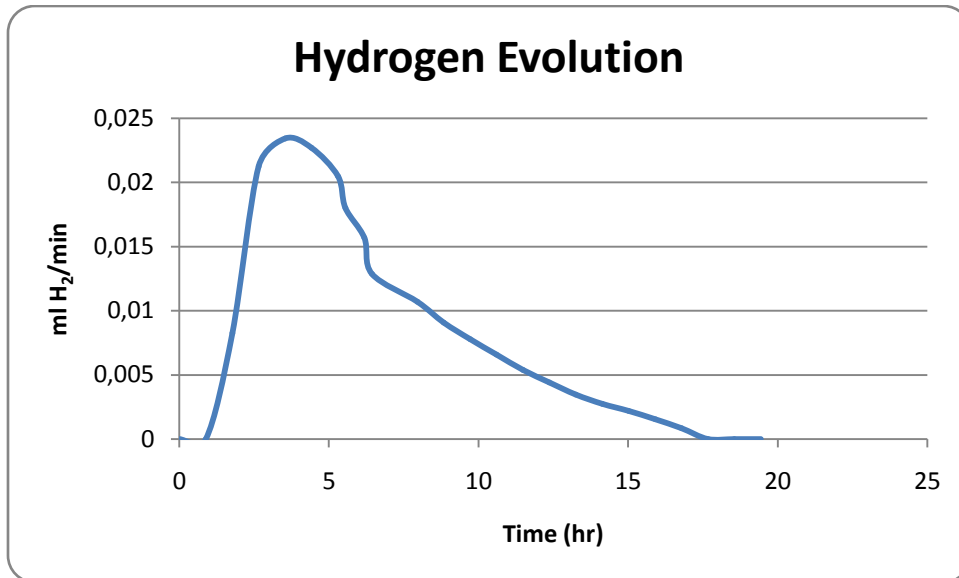


Appendix C5 - 0.1vol% Glycerin, 1.5wt% Cu-TiO<sub>2</sub>, 250mg



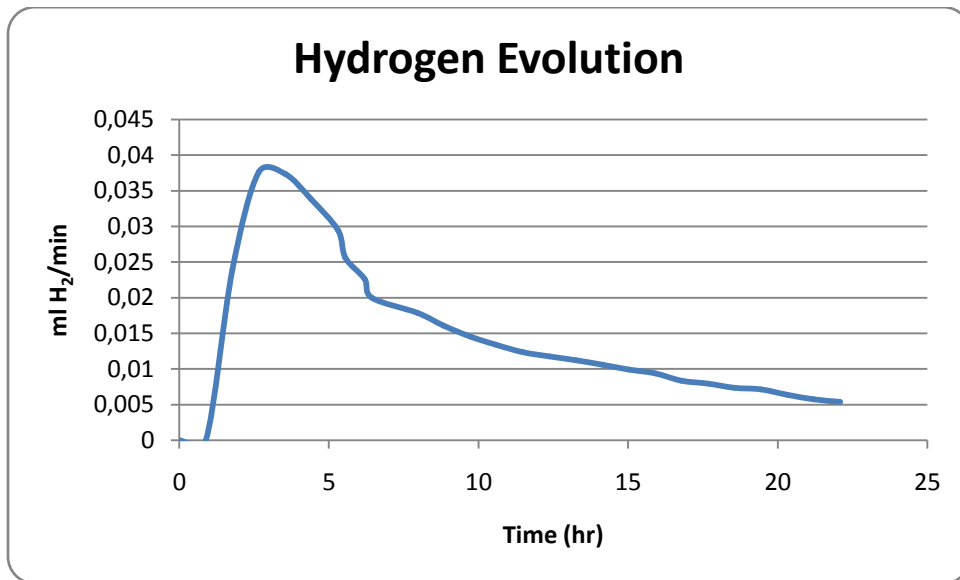
time (hr)	H2 (ml/min)
0	0
0,8833	0
1,7667	0,02023
2,65	0,02891
3,5333	0,02904
4,4167	0,02699
5,3	0,02497
5,55	0,02334
6,1833	0,02162
6,4333	0,02029
7,95	0,01915
8,8333	0,01826
9,7167	0,01707
10,6	0,01623
11,4833	0,01506
12,3667	0,01462
13,25	0,01388
14,1333	0,01343
15,0167	0,01277
15,9	0,01219
16,7833	0,01161
17,6667	0,01115
18,55	0,01073
19,4333	0,01027
20,3167	0,01
21,2	0,00966
22,0833	0,00901
22,9666	0,00805
23,8499	0,00751

## Appendix D1 - 10wt%Cu-TiO<sub>2</sub>, 250mg, 1vol%Glycerin



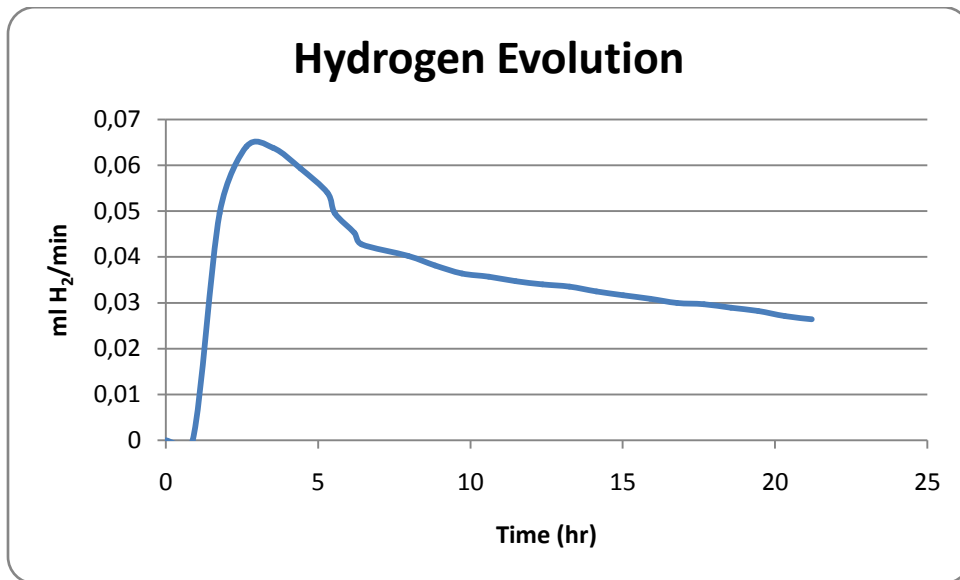
Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0
1,7667	0,00826
2,65	0,02126
3,5333	0,02342
4,4167	0,0227
5,3	0,02048
5,55	0,01801
6,1833	0,01568
6,4333	0,01287
7,95	0,0107
8,8333	0,00908
9,7167	0,00777
10,6	0,00657
11,4833	0,00539
12,3667	0,00441
13,25	0,00345
14,1333	0,00273
15,0167	0,00218
15,9	0,00153
16,7833	0,00083
17,6667	0

## Appendix D2 - 7wt%Cu-TiO<sub>2</sub>, 250mg, 1vol% Glycerin



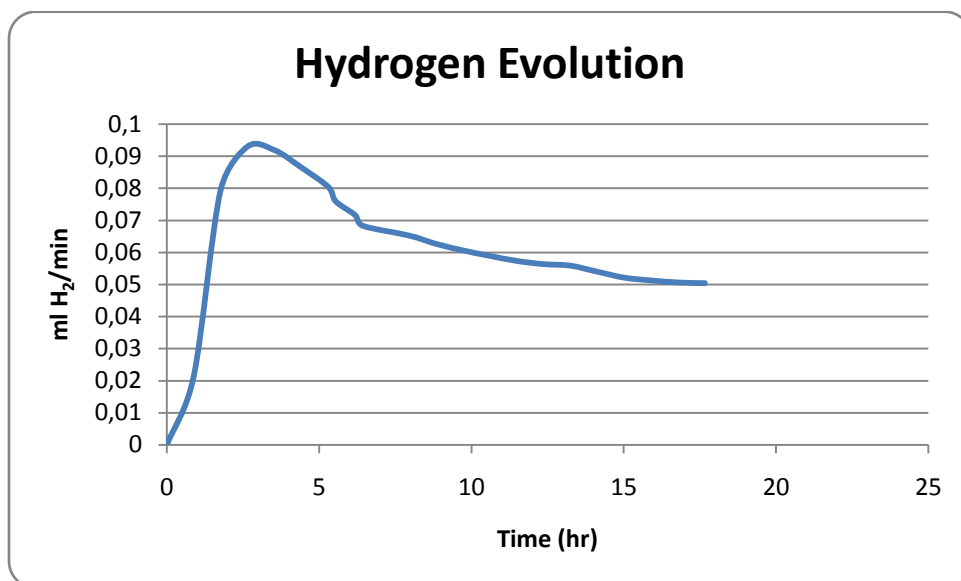
time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0
1,7667	0,0239
2,65	0,03758
3,5333	0,03735
4,4167	0,03375
5,3	0,02943
5,55	0,02557
6,1833	0,02265
6,4333	0,01995
7,95	0,01788
8,8333	0,01604
9,7167	0,01455
10,6	0,01335
11,4833	0,01235
12,3667	0,01176
13,25	0,01123
14,1333	0,01059
15,0167	0,0099
15,9	0,00937
16,7833	0,00833
17,6667	0,00791
18,55	0,00733
19,4333	0,00713
20,3167	0,00638
21,2	0,00573
22,0833	0,00539
22,9666	0,0047

## Appendix D3 - 5wt% Cu-TiO<sub>2</sub>, 250mg, 1vol% Glycerin



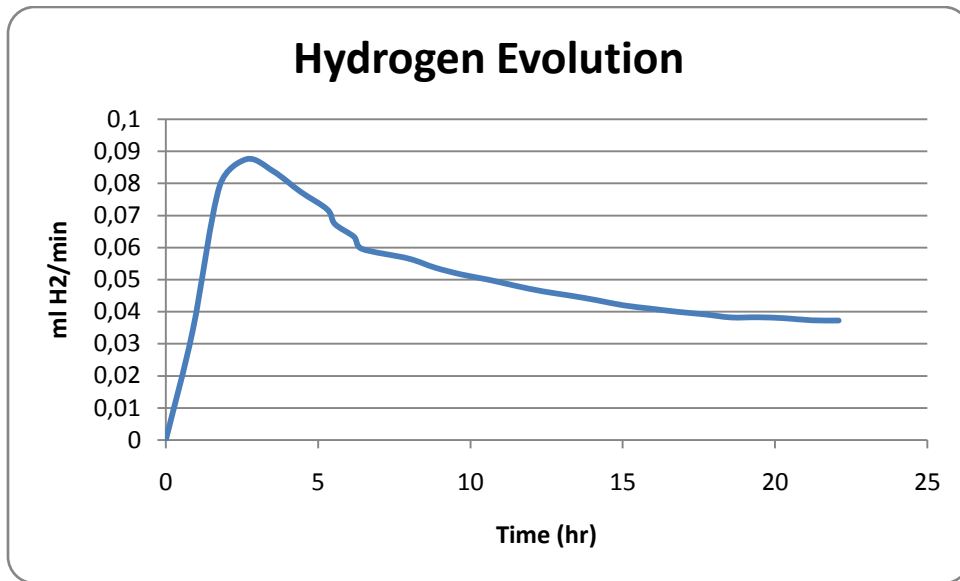
Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0
1,7667	0,04951
2,65	0,06408
3,5333	0,06378
4,4167	0,05931
5,3	0,05399
5,55	0,04952
6,1833	0,04526
6,4333	0,04276
7,95	0,0402
8,8333	0,03815
9,7167	0,03637
10,6	0,03565
11,4833	0,03466
12,3667	0,034
13,25	0,03351
14,1333	0,03247
15,0167	0,03165
15,9	0,03088
16,7833	0,02995
17,6667	0,02969
18,55	0,0289
19,4333	0,02818
20,3167	0,02705
21,2	0,0264

## Appendix D4 - 3wt% Cu-TiO<sub>2</sub>, 250mg, 1 vol% Glycerin



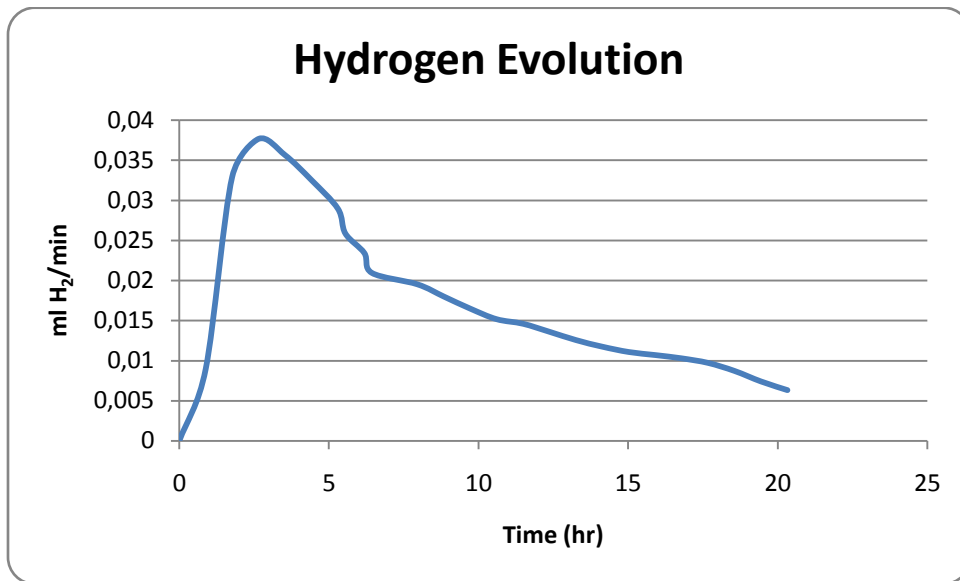
Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,02142
1,7667	0,07937
2,65	0,09297
3,5333	0,09185
4,4167	0,08644
5,3	0,08038
5,55	0,07585
6,1833	0,07161
6,4333	0,06828
7,95	0,06524
8,8333	0,06266
9,7167	0,06061
10,6	0,0589
11,4833	0,05733
12,3667	0,05633
13,25	0,05585
14,1333	0,05397
15,0167	0,05212
15,9	0,05125
16,7833	0,05062
17,6667	0,0504

## Appendix D5 - 1wt% Cu-TiO<sub>2</sub>, 250mg, 1vol% Glycerin



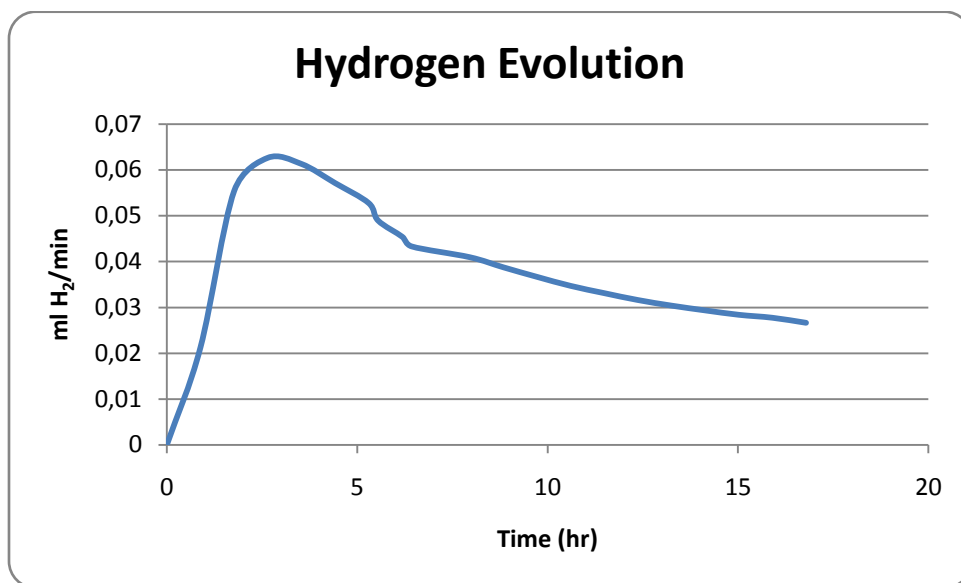
time (hr)	H2 (ml/min)
0	0
0,8833	0,03414
1,7667	0,07915
2,65	0,08751
3,5333	0,08371
4,4167	0,07739
5,3	0,07183
5,55	0,0673
6,1833	0,06327
6,4333	0,05959
7,95	0,05658
8,8333	0,05372
9,7167	0,05156
10,6	0,04994
11,4833	0,04804
12,3667	0,04634
13,25	0,04503
14,1333	0,04359
15,0167	0,04198
15,9	0,04096
16,7833	0,03996
17,6667	0,03918
18,55	0,0382
19,4333	0,03825
20,3167	0,03795
21,2	0,03731
22,0833	0,03724
22,9666	0,03602
23,8499	0,03474

## Appendix E1 - 50mg, 1wt% Cu-TiO<sub>2</sub>, 1vol% Glycerin



Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,00896
1,7667	0,03289
2,65	0,03764
3,5333	0,03562
4,4167	0,0325
5,3	0,02893
5,55	0,02584
6,1833	0,02341
6,4333	0,02094
7,95	0,01952
8,8333	0,018
9,7167	0,01649
10,6	0,01517
11,4833	0,0146
12,3667	0,0136
13,25	0,01257
14,1333	0,01174
15,0167	0,01108
15,9	0,0107
16,7833	0,01029
17,6667	0,00972
18,55	0,00872
19,4333	0,00741
20,3167	0,00633

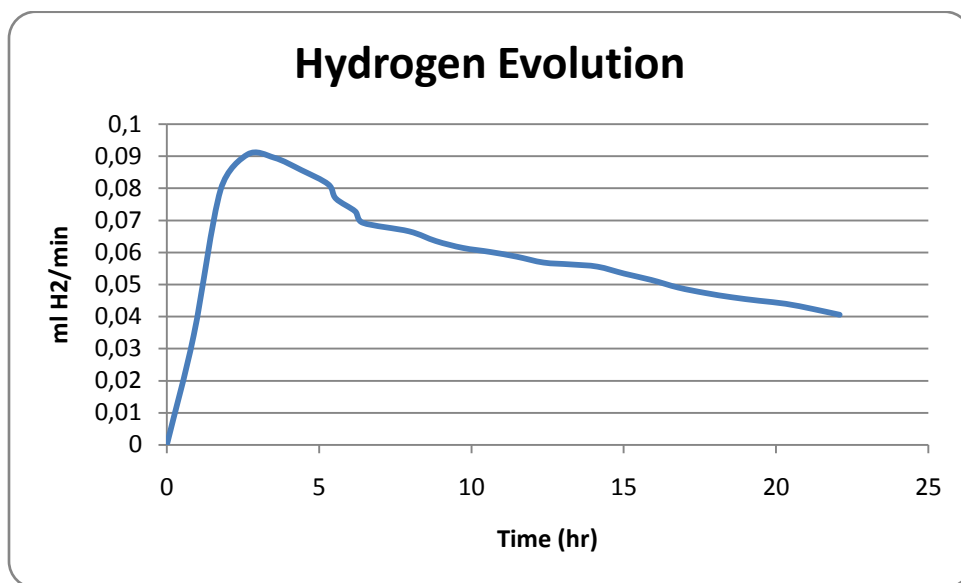
## Appendix E2 - 100mg, 1wt%Cu-TiO<sub>2</sub>, 1vol%Glycerin



Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,02127
1,7667	0,05537
2,65	0,06263
3,5333	0,0613
4,4167	0,05713
5,3	0,05276
5,55	0,04892
6,1833	0,0454
6,4333	0,04329
7,95	0,04096
8,8333	0,03875
9,7167	0,03667
10,6	0,0347
11,4833	0,03311
12,3667	0,03161
13,25	0,03039
14,1333	0,02935
15,0167	0,02839
15,9	0,02774
16,7833	0,02664

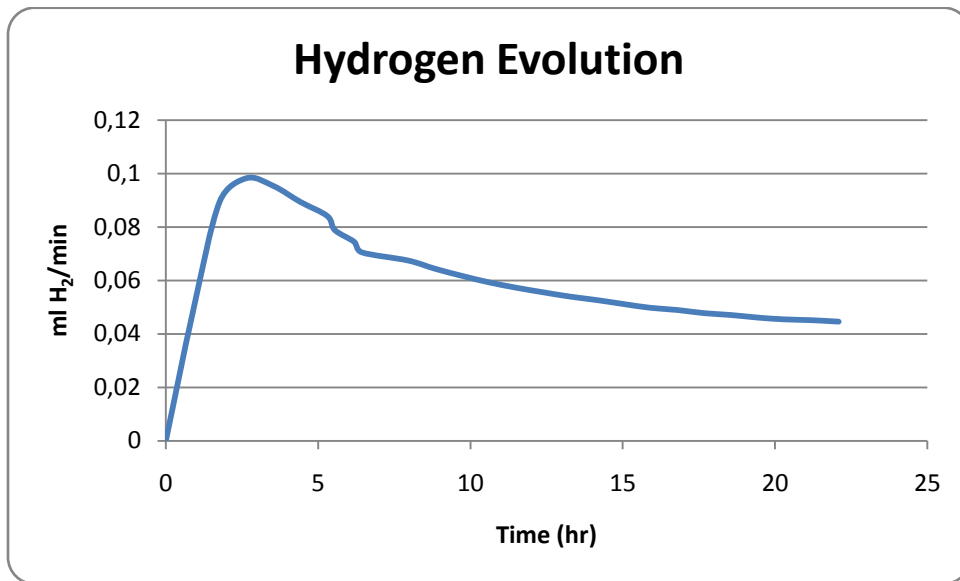


## Appendix E3 - 150mg, 1wt%Cu-TiO<sub>2</sub>, 1vol%Glycerin



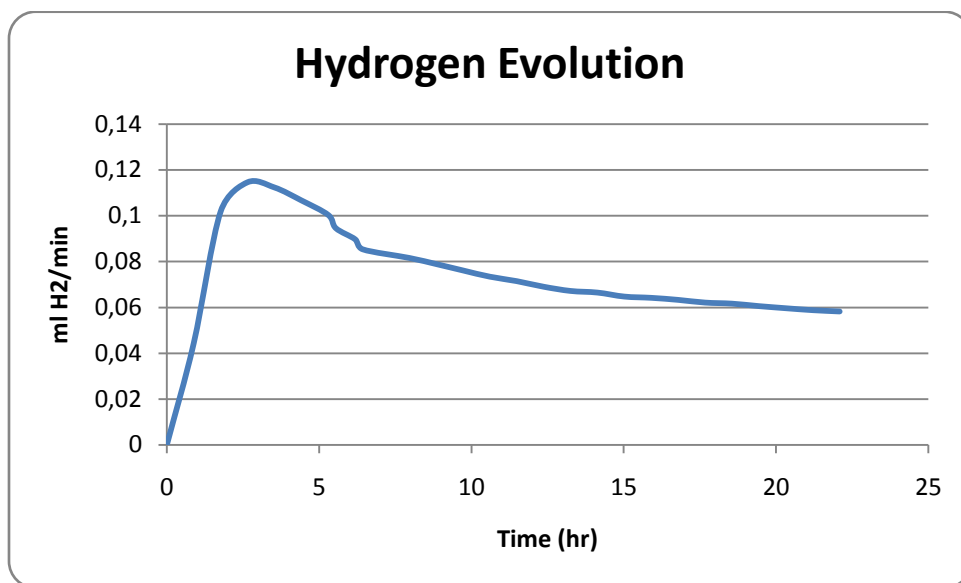
time (hr)	H <sub>2</sub> (ml/min)		
		<b>13,25</b>	0,05623
<b>0</b>	<b>0</b>	<b>14,1333</b>	0,05553
<b>0,8833</b>	0,03416	<b>15,0167</b>	0,05335
<b>1,7667</b>	0,07952	<b>15,9</b>	0,05139
<b>2,65</b>	0,09048	<b>16,7833</b>	0,04902
<b>3,5333</b>	0,08944	<b>17,6667</b>	0,04734
<b>4,4167</b>	0,0856	<b>18,55</b>	0,04598
<b>5,3</b>	0,08116	<b>19,4333</b>	0,04492
<b>5,55</b>	0,07673	<b>20,3167</b>	0,04396
<b>6,1833</b>	0,07274	<b>21,2</b>	0,04235
<b>6,4333</b>	0,0692	<b>22,0833</b>	0,04054
<b>7,95</b>	0,06653	<b>22,9666</b>	0,03879
<b>8,8333</b>	0,06349	<b>23,8499</b>	0,0374
<b>9,7167</b>	0,06136		
<b>10,6</b>	0,06013		
<b>11,4833</b>	0,05863		
<b>12,3667</b>	0,0568		

## Appendix E4 - 200mg, 1wt%Cu-TiO<sub>2</sub>, 1vol%Glycerin



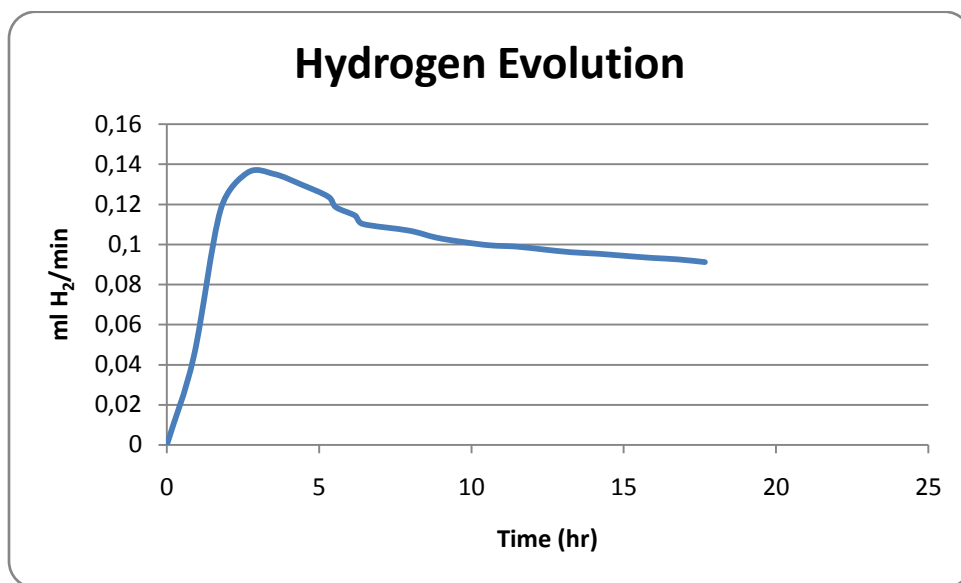
Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,04797
1,7667	0,08945
2,65	0,09826
3,5333	0,09533
4,4167	0,08937
5,3	0,08409
5,55	0,07882
6,1833	0,07443
6,4333	0,07052
7,95	0,06747
8,8333	0,06439
9,7167	0,06173
10,6	0,05932
11,4833	0,05733
12,3667	0,05562
13,25	0,054
14,1333	0,05269
15,0167	0,0512
15,9	0,04979
16,7833	0,04897
17,6667	0,04778
18,55	0,04709
19,4333	0,04612
20,3167	0,04545
21,2	0,04515
22,0833	0,0446
22,9666	0,04373
23,8499	0,04299

## Appendix E5 - 300mg, 1wt%Cu-TiO<sub>2</sub>, 1vol%Glycerin



time (hr)	H2 (ml/min)
0	0
0,8833	0,04436
1,7667	0,1018
2,65	0,11457
3,5333	0,1123
4,4167	0,10666
5,3	0,10028
5,55	0,09451
6,1833	0,08967
6,4333	0,08531
7,95	0,08158
8,8333	0,07892
9,7167	0,07611
10,6	0,07339
11,4833	0,07145
12,3667	0,069
13,25	0,06717
14,1333	0,06646
15,0167	0,06471
15,9	0,06416
16,7833	0,06327
17,6667	0,06209
18,55	0,06163
19,4333	0,06055
20,3167	0,05963
21,2	0,05878
22,0833	0,05821
22,9666	0,05749
23,8499	0,0563

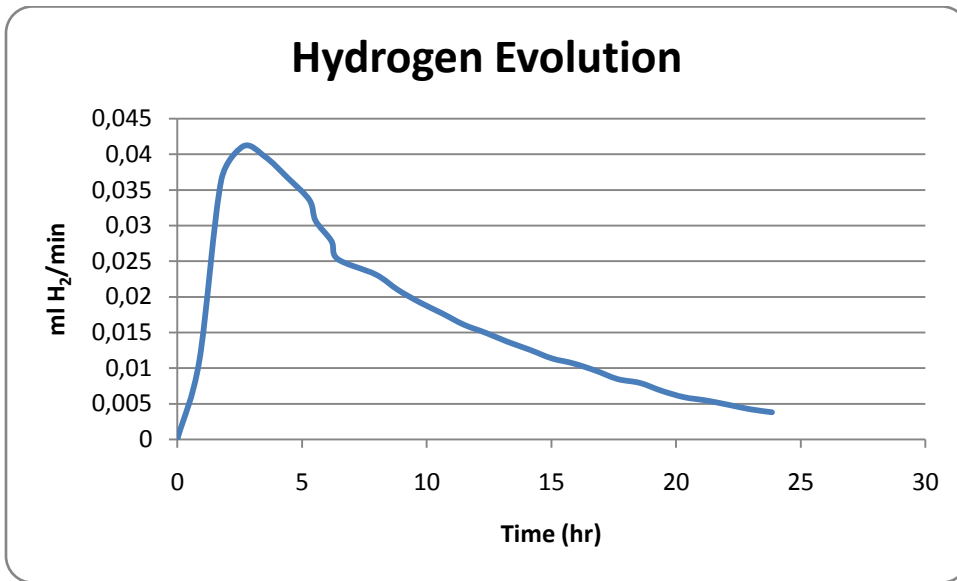
## Appendix E6 - 500mg, 1wt%Cu-TiO<sub>2</sub>, 1vol%Glycerin



Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,04398
1,7667	0,11729
2,65	0,13572
3,5333	0,13501
4,4167	0,1298
5,3	0,12374
5,55	0,11851
6,1833	0,1143
6,4333	0,11016
7,95	0,10684
8,8333	0,10339
9,7167	0,10117
10,6	0,09951
11,4833	0,09886
12,3667	0,09744
13,25	0,09608
14,1333	0,09533
15,0167	0,09428
15,9	0,09326
16,7833	0,09249
17,6667	0,09113

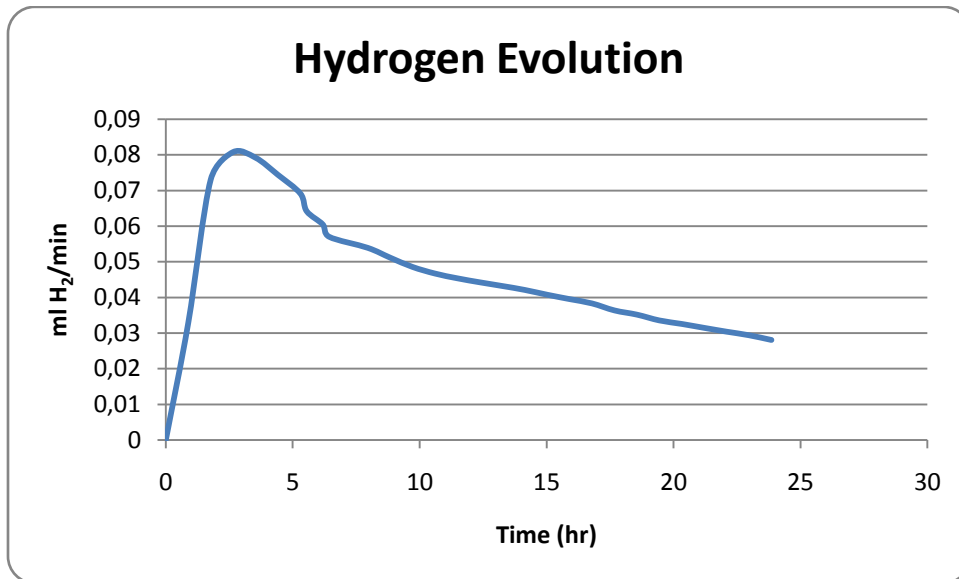
# Appendix F1 - 50mg, 1wt% Cu-TiO<sub>2</sub>, 1vol% Glycerin

After MFC calibration



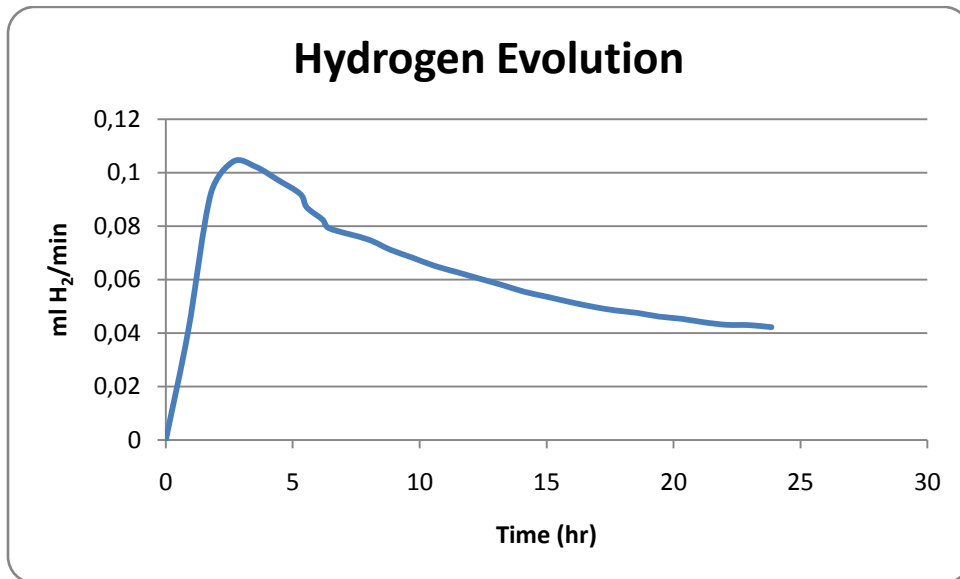
Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,01101
1,7667	0,03641
2,65	0,04113
3,5333	0,03962
4,4167	0,03673
5,3	0,03357
5,55	0,03065
6,1833	0,02782
6,4333	0,0253
7,95	0,02315
8,8333	0,02101
9,7167	0,01924
10,6	0,01772
11,4833	0,01611
12,3667	0,01496
13,25	0,01369
14,1333	0,01258
15,0167	0,01137
15,9	0,01065
16,7833	0,00964
17,6667	0,00846
18,55	0,00793
19,4333	0,00681
20,3167	0,00593
21,2	0,00547
22,0833	0,00487
22,9666	0,00424
23,8499	0,00381

Appendix F2 - 150mg, 1wt% Cu-TiO<sub>2</sub>, 1vol% Glycerin  
After MFC calibration



Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,03283
1,7667	0,07298
2,65	0,08075
3,5333	0,07916
4,4167	0,07435
5,3	0,0691
5,55	0,06414
6,1833	0,06043
6,4333	0,05699
7,95	0,05389
8,8333	0,05114
9,7167	0,04853
10,6	0,04668
11,4833	0,04534
12,3667	0,04422
13,25	0,04319
14,1333	0,04209
15,0167	0,04074
15,9	0,03951
16,7833	0,0383
17,6667	0,03634
18,55	0,03516
19,4333	0,03354
20,3167	0,03255
21,2	0,03145
22,0833	0,03038
22,9666	0,02938
23,8499	0,02805

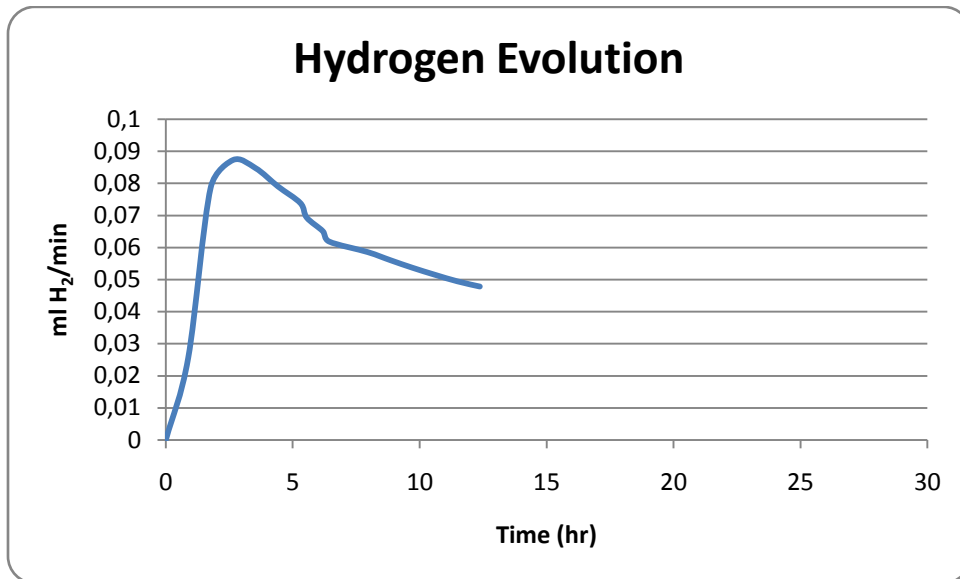
Appendix F3 - 250mg, 1wt%Cu-TiO<sub>2</sub>, 1vol%Glycerin  
After MFC calibration



Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,04089
1,7667	0,09197
2,65	0,10413
3,5333	0,10223
4,4167	0,09725
5,3	0,09197
5,55	0,08702
6,1833	0,08234
6,4333	0,07918
7,95	0,07505
8,8333	0,07119
9,7167	0,06819
10,6	0,06508
11,4833	0,06273
12,3667	0,06032
13,25	0,05795
14,1333	0,0554
15,0167	0,05357
15,9	0,05163
16,7833	0,04991
17,6667	0,04851
18,55	0,04756
19,4333	0,04615
20,3167	0,04532
21,2	0,04401
22,0833	0,04309
22,9666	0,04297
23,8499	0,0422

# Appendix F4 - 350mg, 1wt% Cu-TiO<sub>2</sub>, 1vol% Glycerin

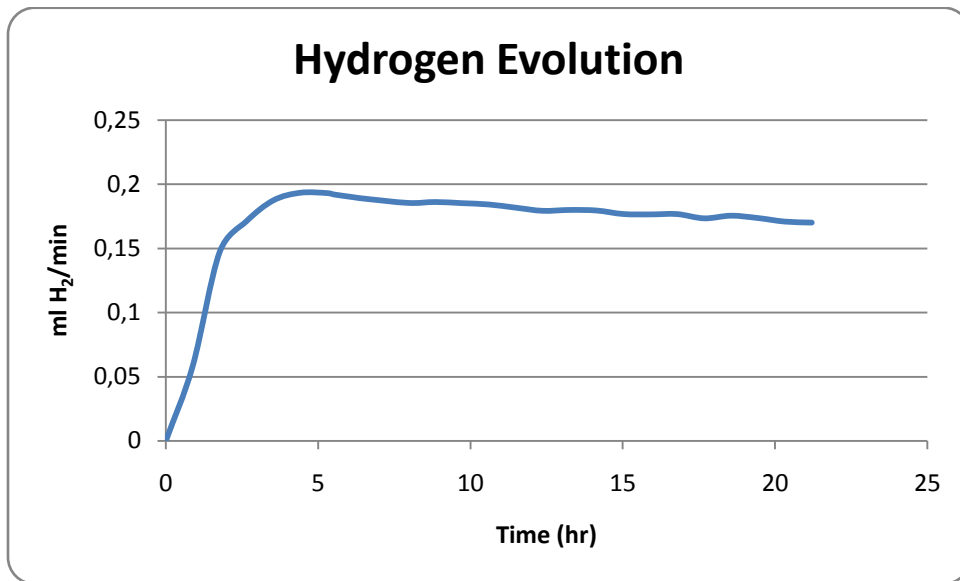
After MFC calibration



Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,02565
1,7667	0,07861
2,65	0,08723
3,5333	0,08469
4,4167	0,07898
5,3	0,07379
5,55	0,06927
6,1833	0,06504
6,4333	0,06181
7,95	0,05853
8,8333	0,05604
9,7167	0,05364
10,6	0,05146
11,4833	0,04942
12,3667	0,0478

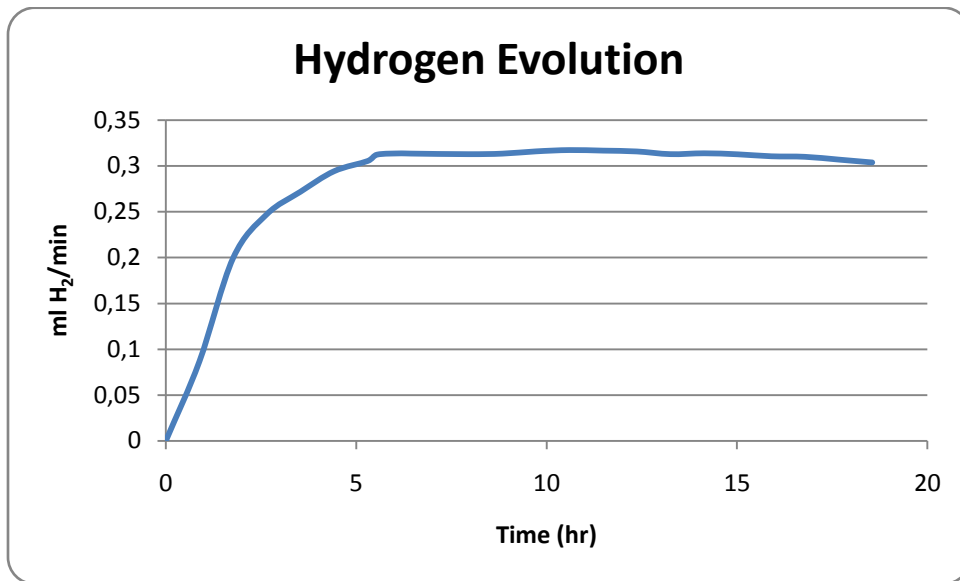


Appendix G1 - 1wt% Cu-TiO<sub>2</sub>, 250mg, 50vol% MeOH, d<sub>p</sub><53μm



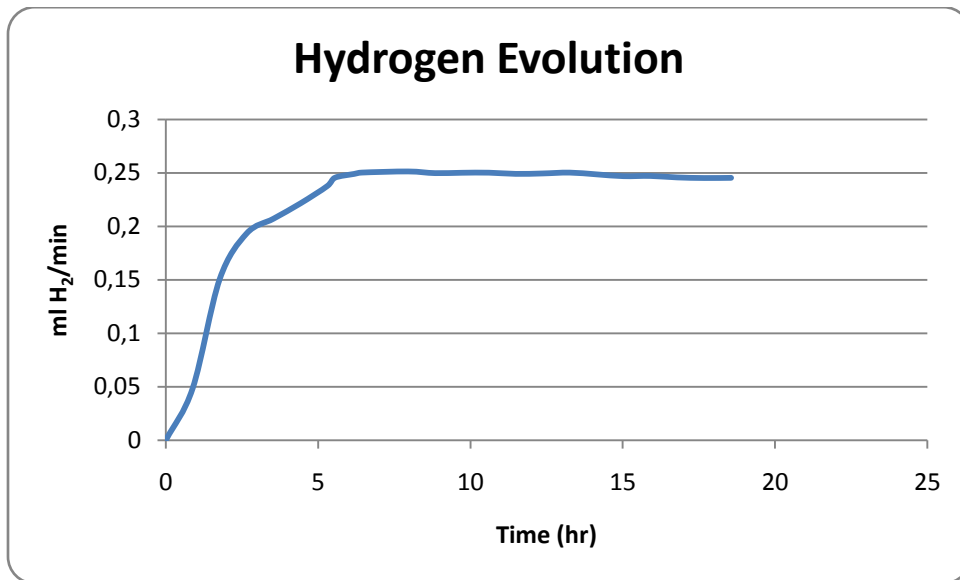
Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,0584
1,7667	0,14712
2,65	0,17122
3,5333	0,18747
4,4167	0,19335
5,3	0,19306
5,55	0,19188
6,1833	0,18978
6,4333	0,18896
7,95	0,18542
8,8333	0,18614
9,7167	0,18524
10,6	0,18421
11,4833	0,18171
12,3667	0,17928
13,25	0,17994
14,1333	0,17951
15,0167	0,17676
15,9	0,17648
16,7833	0,17671
17,6667	0,17341
18,55	0,17548
19,4333	0,17365
20,3167	0,17089
21,2	0,17008

Appendix G2 - 3wt% Cu-TiO<sub>2</sub>, 250mg, 50vol% MeOH, d<sub>p</sub><53μm



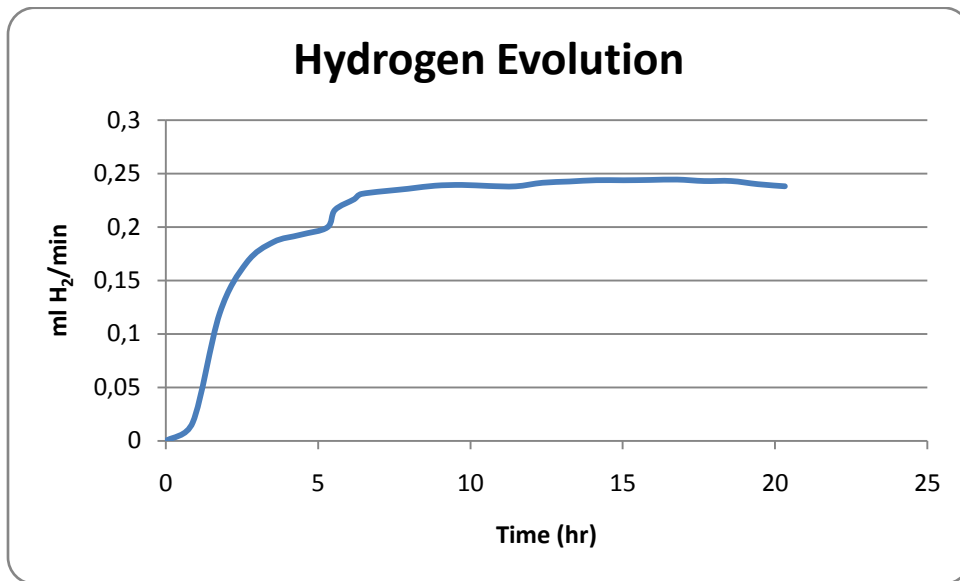
Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,08683
1,7667	0,19938
2,65	0,24711
3,5333	0,27167
4,4167	0,29409
5,3	0,30526
5,55	0,31223
6,1833	0,31356
6,4333	0,31333
7,95	0,3127
8,8333	0,31327
9,7167	0,31576
10,6	0,31719
11,4833	0,31656
12,3667	0,31567
13,25	0,31272
14,1333	0,31367
15,0167	0,31255
15,9	0,31041
16,7833	0,30983
17,6667	0,30678
18,55	0,30364

Appendix G3 - 5wt% Cu-TiO<sub>2</sub>, 250mg, 50vol% MeOH, d<sub>p</sub><53μm



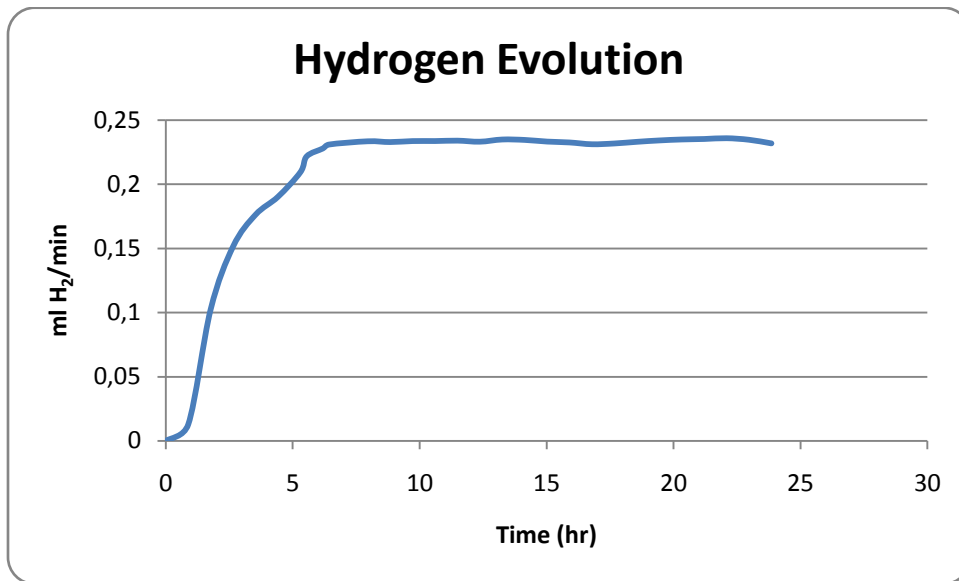
Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,04878
1,7667	0,15065
2,65	0,19337
3,5333	0,20727
4,4167	0,22157
5,3	0,23783
5,55	0,24561
6,1833	0,24917
6,4333	0,25042
7,95	0,25145
8,8333	0,2499
9,7167	0,25025
10,6	0,25032
11,4833	0,2492
12,3667	0,24959
13,25	0,25039
14,1333	0,24873
15,0167	0,24705
15,9	0,24725
16,7833	0,24586
17,6667	0,24533
18,55	0,24548

Appendix G4 - 7wt% Cu-TiO<sub>2</sub>, 250mg, 50vol% MeOH, d<sub>p</sub><53μm



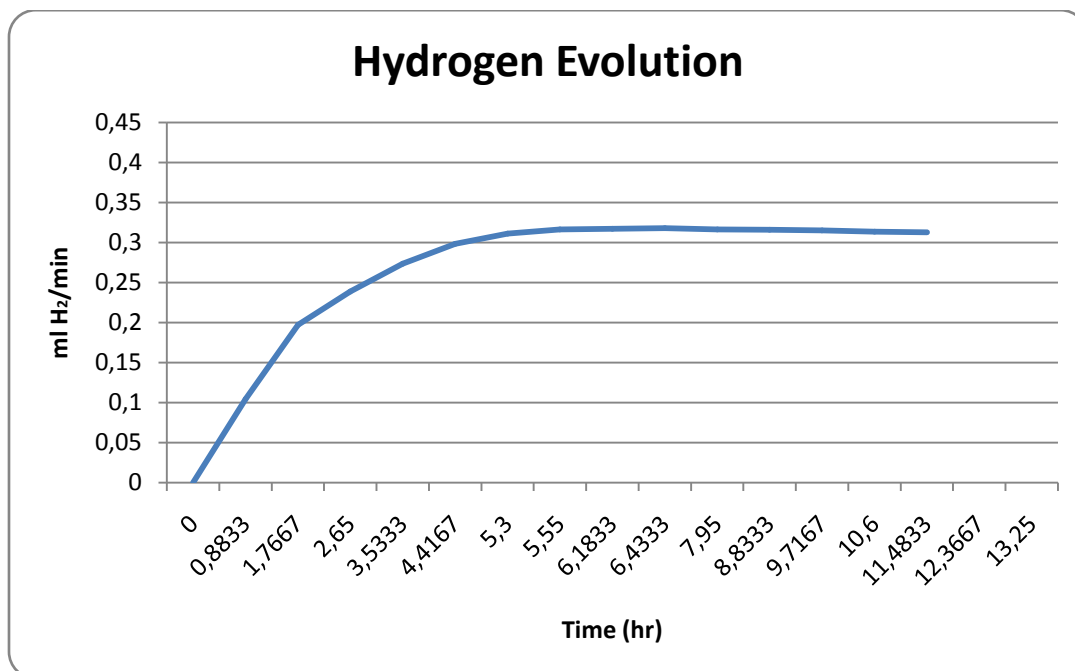
Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,01725
1,7667	0,11917
2,65	0,16657
3,5333	0,18594
4,4167	0,19266
5,3	0,19964
5,55	0,2159
6,1833	0,22592
6,4333	0,23095
7,95	0,2357
8,8333	0,23856
9,7167	0,23929
10,6	0,23832
11,4833	0,238
12,3667	0,24133
13,25	0,2425
14,1333	0,24374
15,0167	0,24366
15,9	0,24395
16,7833	0,24431
17,6667	0,24293
18,55	0,24297
19,4333	0,23999
20,3167	0,23803

Appendix G5 - 10wt% Cu-TiO<sub>2</sub>, 250mg, 50vol% MeOH, d<sub>p</sub><53μm



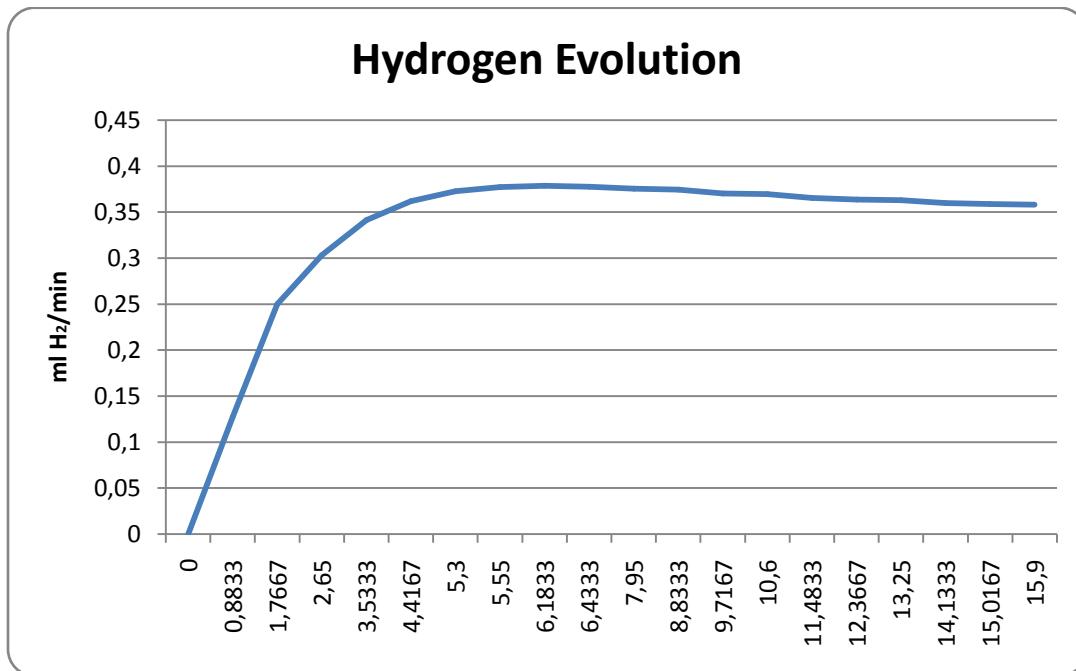
Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,0129
1,7667	0,10262
2,65	0,15162
3,5333	0,17633
4,4167	0,1903
5,3	0,20949
5,55	0,22186
6,1833	0,22795
6,4333	0,23106
7,95	0,23356
8,8333	0,23296
9,7167	0,23374
10,6	0,23375
11,4833	0,23406
12,3667	0,23326
13,25	0,23496
14,1333	0,23462
15,0167	0,23334
15,9	0,23265
16,7833	0,23126
17,6667	0,23187
18,55	0,23315
19,4333	0,23424
20,3167	0,23498
21,2	0,23536
22,0833	0,23596
22,9666	0,23475
23,8499	0,23193

Appendix H1 - 1wt% Cu-TiO<sub>2</sub>, 250mg, 50vol% MeOH, d<sub>p</sub>=N/A



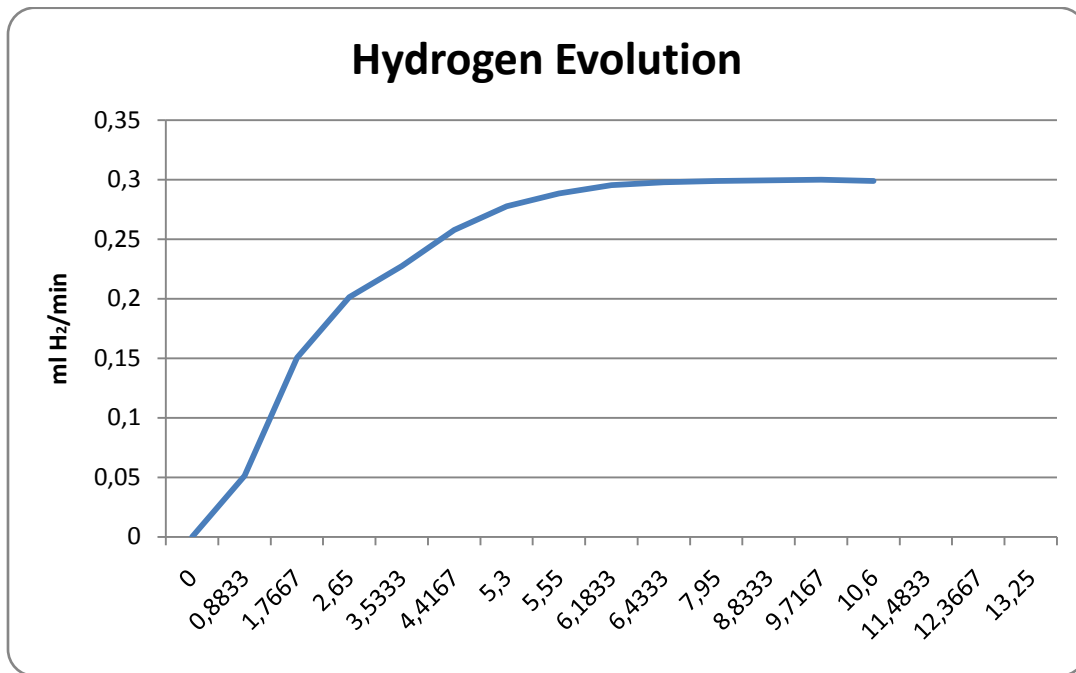
Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,10452
1,7667	0,19711
2,65	0,23865
3,5333	0,27342
4,4167	0,29842
5,3	0,31128
5,55	0,31649
6,1833	0,31713
6,4333	0,31784
7,95	0,31629
8,8333	0,3157
9,7167	0,31517
10,6	0,31347
11,4833	0,31274

Appendix H2 - 3wt%Cu-TiO<sub>2</sub>, 250mg, 50vol%MeOH, d<sub>p</sub>=N/A



Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,12753
1,7667	0,24977
2,65	0,30294
3,5333	0,34145
4,4167	0,3617
5,3	0,37268
5,55	0,37727
6,1833	0,37847
6,4333	0,37753
7,95	0,37534
8,8333	0,37441
9,7167	0,37011
10,6	0,36936
11,4833	0,36536
12,3667	0,3637
13,25	0,363
14,1333	0,35969
15,0167	0,35861
15,9	0,35795

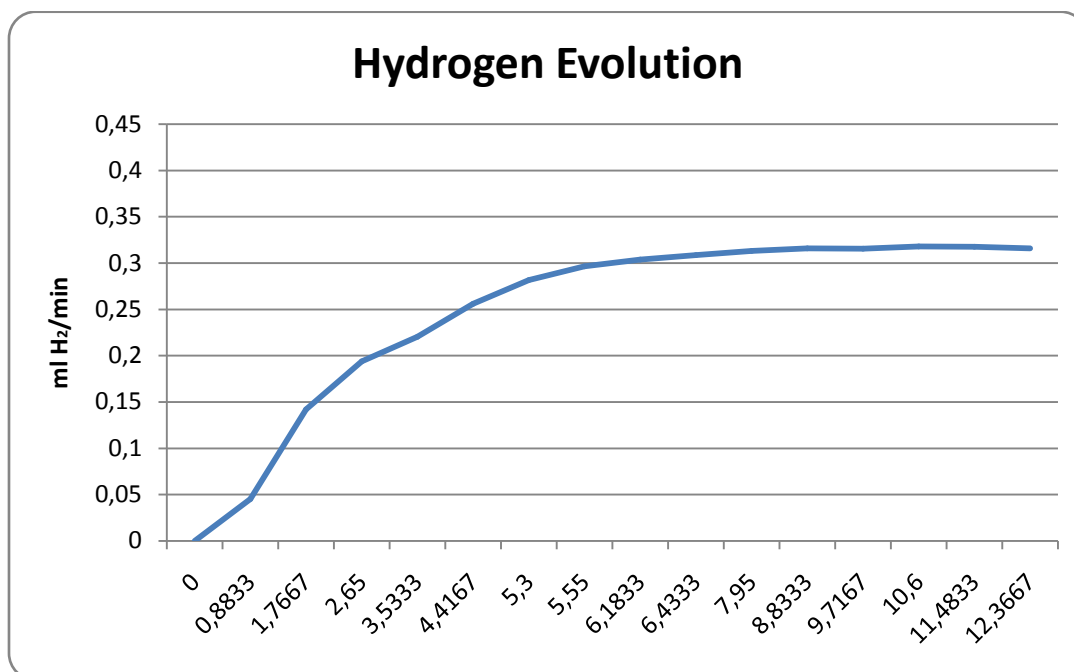
Appendix H3 - 5wt% Cu-TiO<sub>2</sub>, 250mg, 50vol% MeOH, d<sub>p</sub>=N/A



Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,05134
1,7667	0,15051
2,65	0,2013
3,5333	0,22726
4,4167	0,25763
5,3	0,2774
5,55	0,28837
6,1833	0,29521
6,4333	0,29775
7,95	0,2988
8,8333	0,29915
9,7167	0,2998
10,6	0,29883

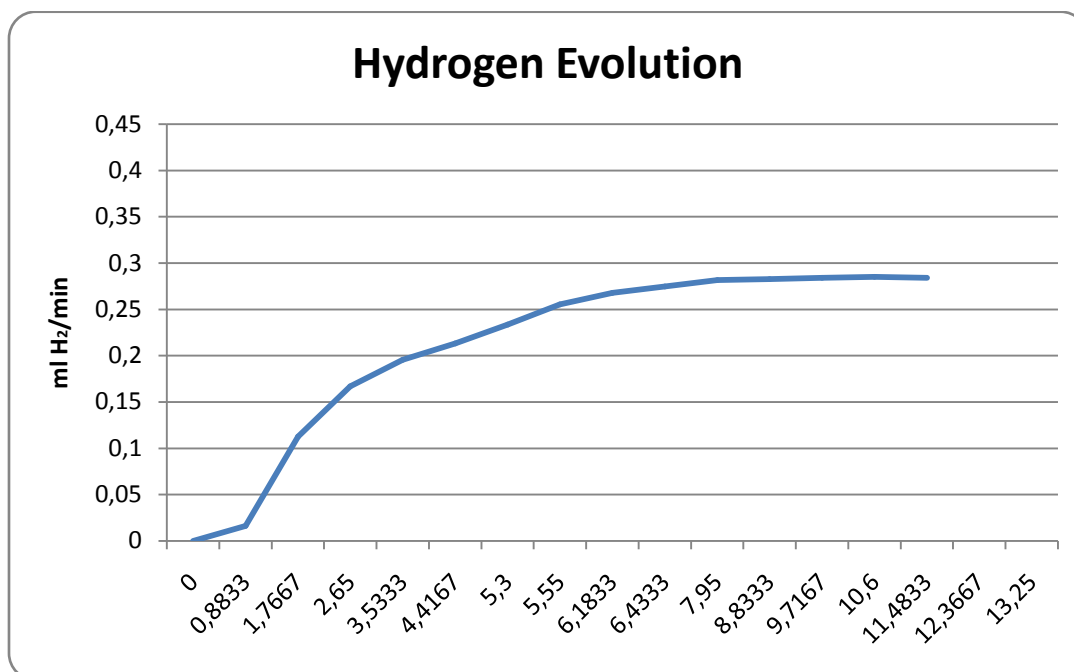


Appendix H4 - 7.5wt% Cu-TiO<sub>2</sub>, 250mg, 50vol% MeOH, d<sub>p</sub>=N/A



Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,04499
1,7667	0,14184
2,65	0,19394
3,5333	0,22056
4,4167	0,25608
5,3	0,28156
5,55	0,29642
6,1833	0,30354
6,4333	0,30851
7,95	0,31306
8,8333	0,31574
9,7167	0,31544
10,6	0,31771
11,4833	0,31738
12,3667	0,31591

Appendix H4 - 10wt% Cu-TiO<sub>2</sub>, 250mg, 50vol% MeOH, d<sub>p</sub>=N/A



Time (hr)	H <sub>2</sub> (ml/min)
0	0
0,8833	0,01614
1,7667	0,11251
2,65	0,16669
3,5333	0,19559
4,4167	0,21309
5,3	0,23336
5,55	0,25534
6,1833	0,26778
6,4333	0,27451
7,95	0,28166
8,8333	0,28264
9,7167	0,28397
10,6	0,285
11,4833	0,28403

## Appendix I - HSE-risk assessment analysis and matrix

### MATRIX FOR RISK ASSESSMENTS at NTNU

<b>CONSEQUENCE</b>	Extremely serious	<b>E1</b>	<b>E2</b>	<b>E3</b>	<b>E4</b>	<b>E5</b>
	Serious	<b>D1</b>	<b>D2</b>	<b>D3</b>	<b>D4</b>	<b>D5</b>
	Moderate	<b>C1</b>	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>
	Minor	<b>B1</b>	<b>B2</b>	<b>B3</b>	<b>B4</b>	<b>B5</b>
	Not significant	<b>A1</b>	<b>A2</b>	<b>A3</b>	<b>A4</b>	<b>A5</b>
		Very low	Low	Medium	High	Very high
		<b>LIKELIHOOD</b>				

Principle for acceptance criteria. Explanation of the colours used in the risk matrix.

Colour	Description
Red	Unacceptable risk. Measures must be taken to reduce the risk.
Yellow	Assessment range. Measures must be considered.
Green	Acceptable risk Measures can be considered based on other considerations.

#### Potential undesirable incident/strain

Identify possible incidents and conditions that may lead to situations that pose a hazard to people, the environment and any materiel/equipment involved.

#### Criteria for the assessment of likelihood and consequence in relation to fieldwork

Each activity is assessed according to a worst-case scenario. Likelihood and consequence are to be assessed separately for each potential undesirable incident. Before starting on the quantification, the participants should agree what they understand by the assessment criteria:

#### Likelihood

Minimal 1	Low 2	Medium 3	High 4	Very high 5
Once every 50 years or less	Once every 10 years or less	Once a year or less	Once a month or less	Once a week

## Consequence

Grading	Human	Environment	Financial/material
<b>E</b> Very critical	May produce fatality/ies	Very prolonged, non-reversible damage	Shutdown of work >1 year.
<b>D</b> Critical	Permanent injury, may produce serious serious health damage/sickness	Prolonged damage. Long recovery time.	Shutdown of work 0.5-1 year.
<b>C</b> Dangerous	Serious personal injury	Minor damage. Long recovery time	Shutdown of work < 1 month
<b>B</b> Relatively safe	Injury that requires medical treatment	Minor damage. Short recovery time	Shutdown of work < 1week
<b>A</b> Safe	Injury that requires first aid	Insignificant damage. Short recovery time	Shutdown of work < 1day



The unit makes its own decision as to whether opting to fill in or not consequences for economy/materiel, for example if the unit is going to use particularly valuable equipment. It is up to the individual unit to choose the assessment criteria for this column.

### Risk = Likelihood x Consequence

Please calculate the risk value for “Human”, “Environment” and, if chosen, “Economy/materiel”, separately.

### About the column ”Comments/status, suggested preventative and corrective measures”:

Measures can impact on both likelihood and consequences. Prioritise measures that can prevent the incident from occurring; in other words, likelihood-reducing measures are to be prioritised above greater emergency preparedness, i.e. consequence-reducing measures.

NTNU	Hazardous activity identification process	Prepared by	Number	Date	
		HSE section	HMSRV-26/01	09.01.2013	
HSE		Approved by	Page	Replaces	
		The Rector	1 out of 1	01.12.2006	

**Unit: IKP**

**Date: 02.10.2013**



**Participants in the identification process (including their function):**

*Eirik Tolgensbakken (Student), Magnus Rønning (Supervisor), Charitha Udani (Co-supervisor)*

**Short description of the main activity/main process:**

Synthesis of photocatalyst.

ID no.	Activity/process	Responsible person	Existing documentation	Existing safety measures	Laws, regulations etc.	Comment
S1	Degaussa P25 TiO <sub>2</sub> handling	Magnus Rønning	Material safety data sheet	Closed fume hood	AML §4-5, HMSRV-12/13, HMSR-39, HMSR-40, Kjemikalieforskriften	Googles, gloves
S2	Measuring methanol	Magnus Rønning	Material safety data sheet	Closed fume hood	AML §4-5, HMSRV-12/13, HMSR-39, HMSR-40, Kjemikalieforskriften	Googles, gloves
S3	Calcination	Magnus Rønning	Manuals	Closed fume hood	AML §4-5, HMSRV-12/13, HMSR-39, HMSR-40, Kjemikalieforskriften	Googles, thermo gloves

NTNU	Hazardous activity identification process	Prepared by	Number	Date	
		HSE section	HMSRV-26/01	09.01.2013	
HSE		Approved by	Page	Replaces	
		The Rector	1 out of 1	01.12.2006	

**Unit: IKP**

**Date: 02.10.2013**



**Participants in the identification process (including their function):**

*Eirik Tolgensbakken (Student), Magnus Rønning (Supervisor), Charitha Udani (Co-supervisor)*

**Short description of the main activity/main process:**

Photoreforming of methanol and necessary calibration

ID no.	Activity/process	Responsible person	Existing documentation	Existing safety measures	Laws, regulations etc.	Comment
P1	Activity measurements using UVA	Magnus Rønning	Material safety data sheet, manuals	UV-protecting goggles	HMSR-32, strålevernloven, strålevernforskriften, manualer, prosedyrer	
P2	Measuring methanol	Magnus Rønning	Material safety data sheet	Local fume hood	AML §4-5, HMSRV-12/13, HMSR-39, HMSR-40, Kjemikalieforskriften	
P3	Hydrogen for calibration of the MicroGC and reactivation	Magnus Rønning	Material data safety sheet	Hanhelds gas detector	AML §4-5, HMSRV-12/13, HMSR-39, HMSR-40, Kjemikalieforskriften	

NTNU	Hazardous activity identification process	Prepared by	Number	Date	
		HSE-section	HMSRV2601	09.01.2013	
HSE		Approved by	Page	Replaces	
	The Rector	1 out of 1	01.12.2006		

**Unit:** IKP

**Date:** 02.10.2013

**Participants in the identification process (including their function):**

*Eirik Tolgensbakken (Student), Magnus Rønning (Supervisor), Charitha Udani (Co-supervisor)*

**Short description of the main activity/process:**

*Characterization of catalyst*

ID no.	Activity/Process	Responsible person	Existing documentation	Existing safety measures	Laws, regulations etc.	Comment
CC1	Use of hydrogen for chemisorption	Magnus Rønning	Manuals, Material safety data sheet	Closed fume hood, leak test, handheld gas detectors	AML §4-5, HMSRV-12/13, HMSR-39, HMSR-40, Kjemikalieforskriften	
CC2	Use of N <sub>2</sub> O for pulse chemisorption	Magnus Rønning	Manuals, Material safety data sheet	Closed fume hood, leak test, handheld gas detectors	AML §4-5, HMSRV-12/13, HMSR-39, HMSR-40, Kjemikalieforskriften	

Unit: **IKP**

Date: **03.10.2013**

Line manager:

Participants in the risk assessment (including their function):

Eirik Tolgensbakken (Student), Magnus Rønning (Supervisor), Charitha Udani (Co-supervisor)

ID no.	Activity from the identification process form	Potential undesirable incident/strain	Likelihood:	Consequence:			Risk value	Comments/status Suggested measures
			Likelihood (1-5)	Human (A-E)	Environment (A-E)	Economy/material (A-E)		
P1	Activity measurements using UVA	Exposure to UV radiation	5	A			5A	Skin is exposed for max 10 sec per day
P2	Measuring methanol	Spilling and splashing	4	A			4A	Use goggles, gloves and lab coat
P3	Hydrogen for calibration of the <u>MicroGC</u> and reactivation	Gas leak, explosion	1	D			1D	Use gas detectors
S1	<u>Degussa P25 TiO<sub>2</sub></u> handling	Inhalation of dust	3	A			3A	Keep away from airways
S2	<u>Copper(II) nitrate</u> handling	Skin exposure	1	B			1B	Use gloves
S3	<u>Calcination</u>	Heat exposure, gas leak	2	B			2B	Wait for cooling, use <u>thermogloves</u>
CC1	<u>Use of hydrogen for chemisorption</u>	Gas leak, explosion	1	D			1D	Leak test
CC2	<u>Use of N<sub>2</sub>O for chemisorption</u>	Gas leak, long term exposure	1	B			1B	Test for leaks, No detectors for N <sub>2</sub> O.

**Likelihood, e.g.:**

1. Minimal
2. Low
3. Medium
4. High
5. Very high

**Consequence, e.g.:**

- A. Safe
- B. Relatively safe
- C. Dangerous
- D. Critical
- E. Very critical

**Risk value (each one to be estimated separately):**

**Human = Likelihood x Human Consequence**

**Environmental = Likelihood x Environmental consequence**

**Financial/material = Likelihood x Consequence for Economy/material**