Converting Cellulosic Biomass to Liquid Fuels using Sulfur Doped Titanium Dioxide Photocatalyst in Aqueous Solutions

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Abstract

Liquid acids are commonly used to catalyze the hydrolysis of lignocellulose biomass. Liquid acids suffer from low recyclability and their use results in reactor corrosion. Sulfonate based organic solids offer better recyclability, but bear the drawback of low solubility of cellulose. Ideally, a catalyst is wanted that can catalyze hydrolysis in water and offer good solubility of cellulose. This research tested sulfur doped titanium dioxide as a catalyst for cellulose hydrolysis. Initial research shows that titanium dioxide doped with varying amounts of sulfur does result in oil being produced in varying environmental conditions. Initial structure analysis via x-ray diffraction shows that the structure of titanium dioxide changes as it is doped with sulfur. The recyclability of titanium dioxide has not yet been fully tested as initial structure analysis shows that post-reaction, the catalyst becomes impure, mixing with the cellulose, and the best cleaning method has not been found yet. Initial reactions were performed with 1 g of cellulose and 0.5 g of one of three catalysts in 100 ml of water in a round bottom flask exposed to one of three forms of light.

Terms & Abbreviations

TiO_2 – Titanium dioxide. A photocatalyst commonly used as a pigment and UV blocker that is also used to clean water.
S-TiO_2 – Sulfur doped titanium dioxide. Titanium dioxide doped with sulfur.
2S-TiO_2 – Titanium dioxide doped with double the amount of sulfur.
XRD – X-Ray Diffraction. A method of determining the crystal structure of a solid with x-ray scattering.
Photocatalyst – A catalyst that works when exposed to specific bands of light.
Anatase – A crystal structure of TiO_2 that is preferred to be used due to it's reactivity.
Calcination – A process of heating a metal with an oxygen.

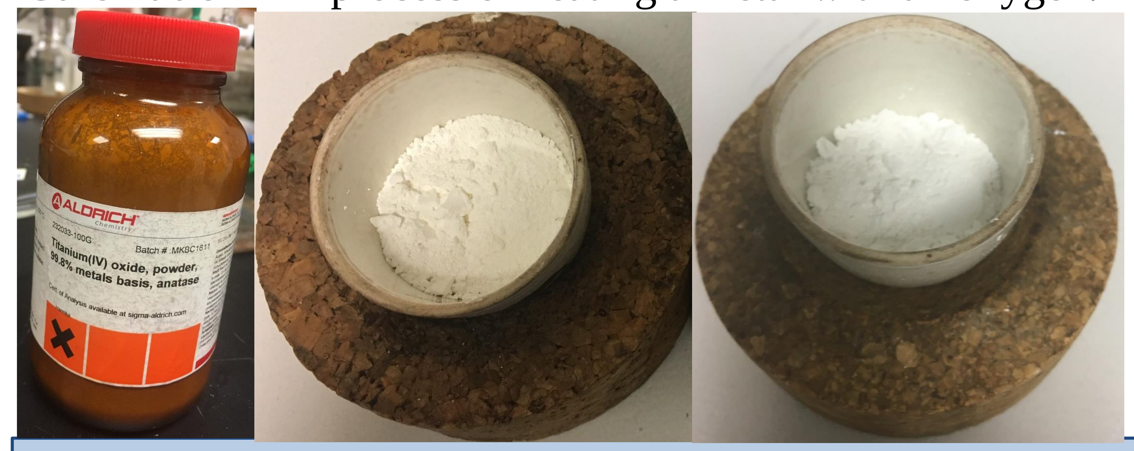


Figure 1 (From left to right): *TiO_2, S-TiO_2, 2S-TiO_2*

Methods

Catalyst Synthesis

S-TiO_2 was synthesized by adding 1 ml of 1.87×10^{-3} M solution of sulfur in benzene to 10 g of 99% anatase TiO_2. It is then ground in a mortar and pestle and calcinated for a total of 9 hours at 200˚C. During the first 5 hours, the solid is removed from the oven to be ground in the mortar and pestle every hour. 2S-TiO_2 was synthesized in the same method, however with a 3.74×10^{-3} M solution.

Reactions

Reactions were performed using 1 g of cellulose and 0.5 g of one of three catalysts added to 100 ml of water in a round bottom flask. Three different light conditions were tested. No light was tested by covering the flask in tin foil. A 150 W light bulb was used to test incandescent light. A 26 W UV bulb was used to test UV Light. To keep the light contain, the flask was wrapped with tin foil as seen in ***Figure 2***. The reactions were kept at 100˚C for 4 hours.

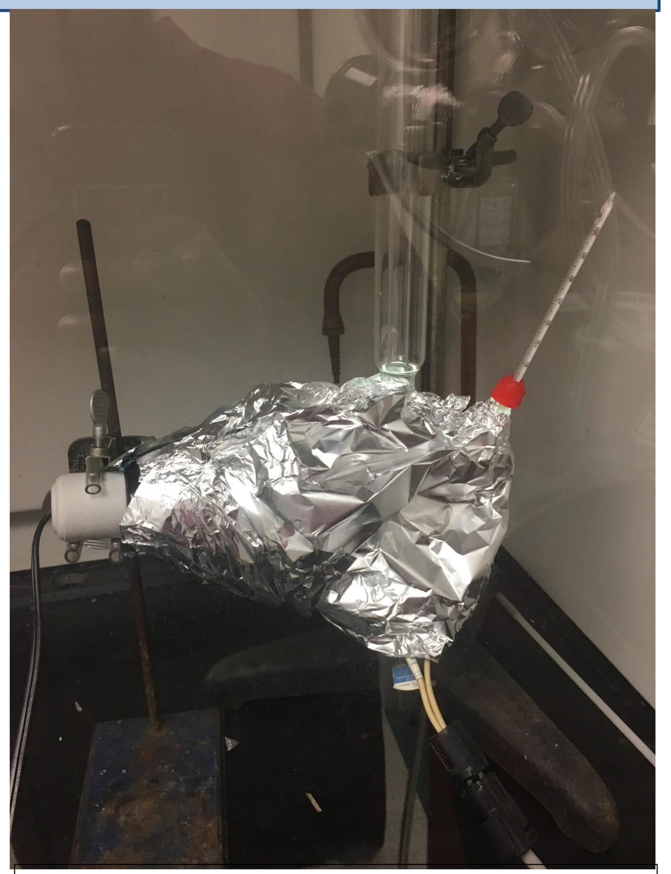


Figure 2: *Reactor Set-Up*

Results

Oil Results

After 9 initial reactions, four situations produced oil. 0.011 g of oil were produced when no light was used and the catalyst was 2S-TiO_2. 0.041 g of oil were produced when incandescent light was used and the catalyst was TiO_2. 0.040 g of oil were produced when incandescent light was used and the catalyst was 2S-TiO_2. 0.032 g of oil were produced when UV light was used and the catalyst was S-TiO_2. In the other 5 scenarios, no oil was produced.

Oil Production (in grams)		Catalyst		
		TiO_2	S-TiO_2	2S-TiO_2
Light	No Light	No Oil	No Oil	0.011 g
	150W Bulb	0.041 g	No Oil	0.040 g
	UV Bulb	No Oil	0.032 g	No Oil

Figure 3: *Oil Production of the initial 9 reactions*

Structure Analysis

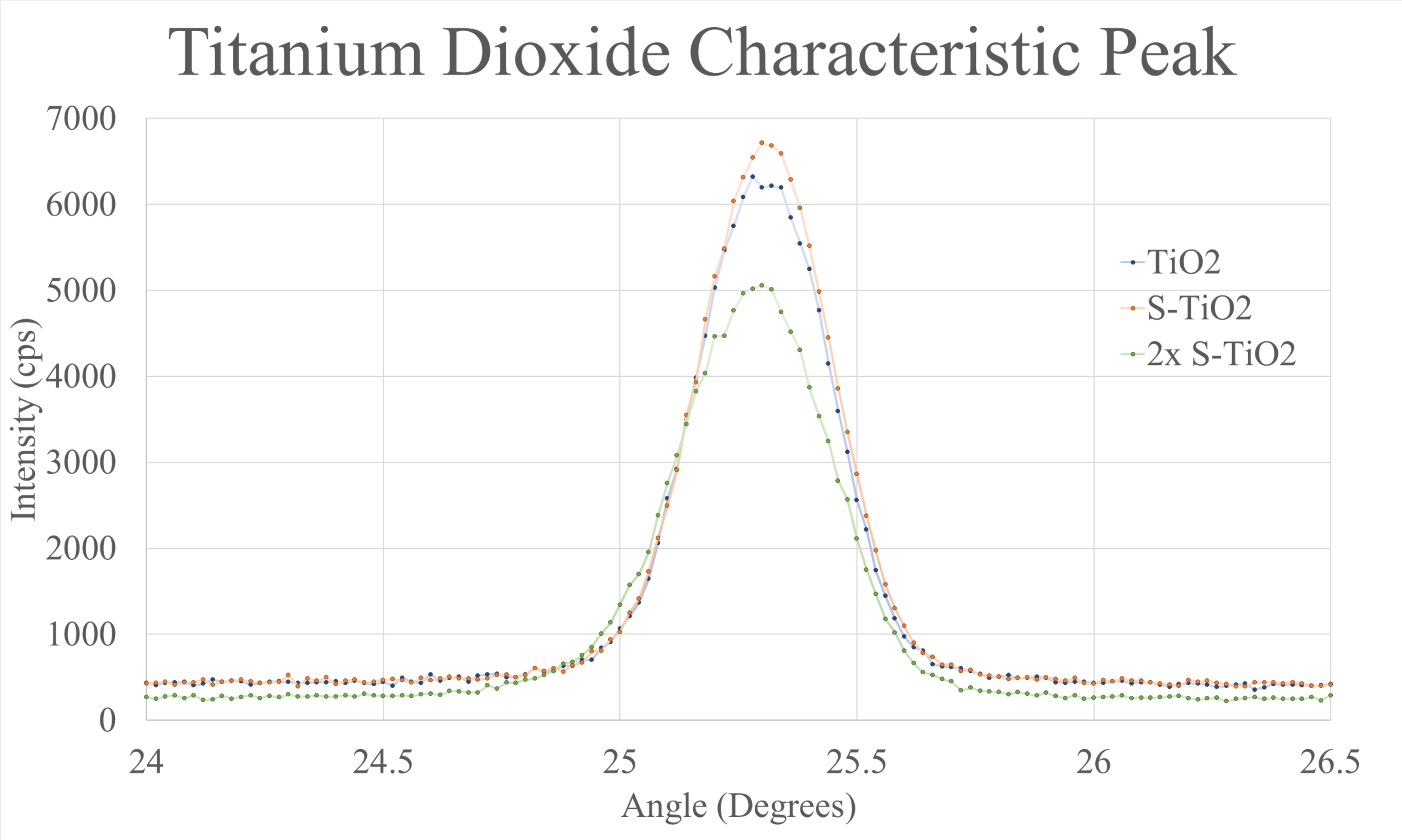
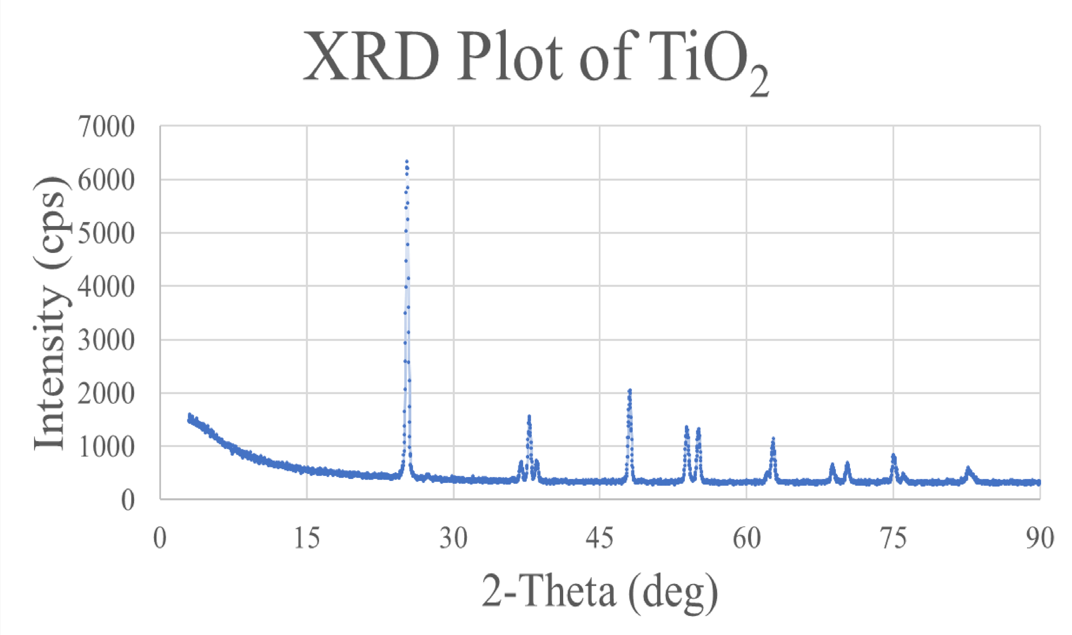


Figure 4 (Above): *Zoom in on the characteristic peak of TiO_2 solids for each catalyst.*
Figure 5 (right): *Whole XRD Plot of TiO_2*



Using the XRD, intensity graphs were obtained for each catalyst, along with sulfur, and post reaction solids. Titanium dioxide has a characteristic peak at an angle of around 25.3 degrees. ***Figure 4*** shows this peak for all three catalysts used. This peak is in the same location for all three catalysts, however the intensity varies. S-TiO_2 had the strongest intensity, while 2S-TiO_2 had the lowest intensity. This was true for all peaks. S-TiO_2 had the highest intensity for every peak, while 2S-TiO_2 had the lowest intensity for every peak. The plot for 99% anatase TiO_2 can be see in ***Figure 5***. All of the sulfur doped variants had peaks in the same locations, but had higher or lower intensities as previously discussed.

Recyclability

The resulting post reaction solid is impure and is likely a mixture of the catalyst and cellulose. XRD showed that the post reaction solid had peaks at the same place of 99.9% anatase titanium dioxide, but were significantly lower intensities (approximately 2000 counts per second versus approximately 6250 counts per second). The impure solid also had additional peaks at around 16 degrees and 23 degrees.

Discussion

Oil Results

Based on previous reactions, it was expected that 2S-TiO_2 would produce oil, but did not. The oil has not yet been characterized so it is possible that in some of the situations that did not produce oil, oil was produced, but the temperature and speed that the rotary evaporator was used at caused the oil to evaporate unknowingly. These reactions will be run again to collect more oil to find the density to aid in cellulose into oil conversion calculations.

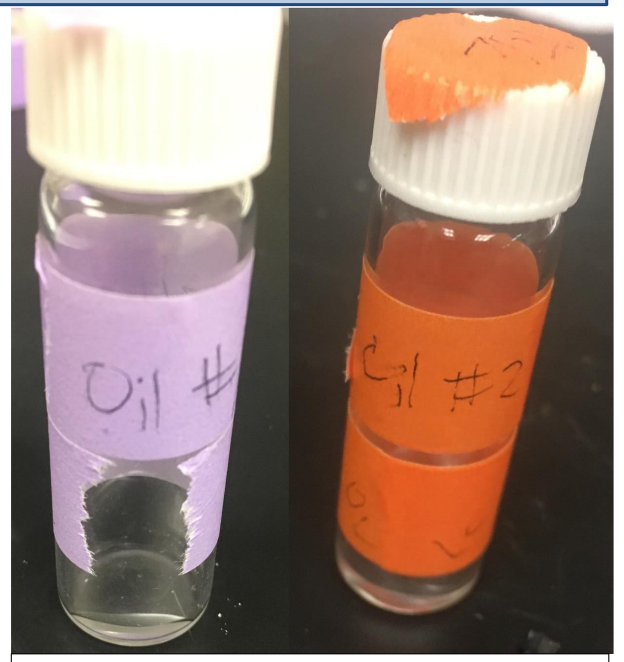


Figure 6: *Oil Samples*

Structure Analysis

Though it is clear that the structure does change as sulfur is added, it is not clear how the structure does change. Previous research proposes that for S-TiO_2 sulfonate groups form on the crystal surface and some sulfur is imbed into the crystal structure[1]. The XRD data obtained by this research is still being used to try to model how the crystal structure changes as sulfur is added.

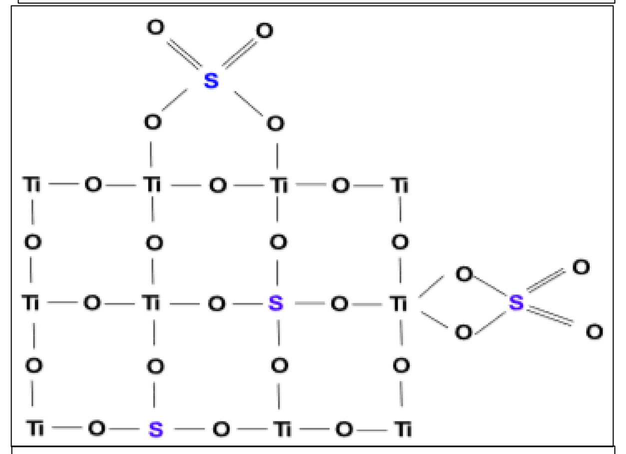


Figure 7: *Structure proposed by L.G. Devi and R. Kavitha[1]*

Recyclability

The XRD will be used to look at the structure of cellulose to see if the two new peaks found in the impure, post-reaction solid come from cellulose. It is also possible that titanium dioxide reacts with the cellulose or water to form a different compound.

Applications

Biomass is a renewable energy source used in the production of biofuels. As of 2013, approximately 220 billion tons of biomass was produced. Of this biomass 70 – 95% of it was lignocellulose which contains about 40 – 50% cellulose[2]. Commercially, glucose, a product of cellulose hydrolysis, is important in the production of fuels, chemicals, polymers, and solvents. Cellulose hydrolysis is typically catalyzed with high concentration sulfuric acid or other liquid acid. These liquid acid catalysts have poor recyclability and the large amount of waste it produces must be treated. Liquid acid catalysts also result in the need of maintenance for reactors as they cause reactor corrosion.

This research attempts to find a solid acid catalyst alternative for this hydrolysis for biofuel production. Solid acid catalysts typically offer more recyclability and separation, however come at the cost of lower conversions. Sulfonated based organic solid acids had high catalytic activities resulting in higher conversion rates, but result in a low solubility of cellulose in aqueous solutions. S-TiO_2 is an attempt to take the best aspects of these two catalysts types as a sulfonated inorganic solid catalyst.

Acknowledgements

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Resources

1. L. Gomathi Devi, R. Kavitha. "Enhanced photocatalytic activity of sulfur doped TiO_2 for the decomposition of phenol: A new insight into the bulk and surface modification." *Materials Chemistry and Physics* 143 (2014): 1300-1308. Print
2. Yao-Bing Huang, Yao Fu. "Hydrolysis of cellulose to glucose by solid acid catalysts." RCS Green Chemistry 15 (2013): 1095-1111. Print