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## PHOTOCATALYTIC TRANSFORMATION OF ORGANIC COMPOUND IN PHOTOCHEMICAL REACTOR

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### **ABSTRACT**

The photocatalytic and photochemical reactions of naturally occurring phenolic compounds from lignin that can make usable products via photoreactions. The specific goals of the research are to determine the molecular reaction networks of organic phenolic compounds derived from lignin (isoeugenol, eugenol, and vanillin) in solution under the following conditions: 1) heterogeneous photocatalytic oxidation; 2) photochemical oxidation. Other specific goals include investigating the relationship between photochemical oxidation yield and oxygen pressure, as well as the non-water solvent used..

***Keywords: photocatalytic, photochemical, reactions, photoreactions, molecules***

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### **I. INTRODUCTION**

Biomass is defined as "any material of recent biological origin, such as plant materials, agricultural produce, and even animal waste." Biomass is known as a rich carbon and energy source. It is renewable and thus long-term. Biomass has the ability to reduce greenhouse gas emissions as well. In addition to the practical properties of biomass, it is vital to remember that it possesses "excess functionality" such as oxygen-containing groups in addition to carbon and hydrogen. These characteristics make it a good source for fuels and chemicals. Currently, just 5% of chemicals are made from renewable resources. A large range of goods could be produced if biomass compounds are successfully converted. It has been demonstrated that there is a growing interest in bio-based products. In only eleven years, the global revenues of biotechnology products increased by \$5,600 million dollars. By 2090, the US bio-based sector hopes to achieve bio-based output of more than 90% for organic chemicals, up to 50% for liquid fuels, and 99 percent for materials such as bioplastics. These objectives are feasible and attainable provided biomass is given the necessary attention.

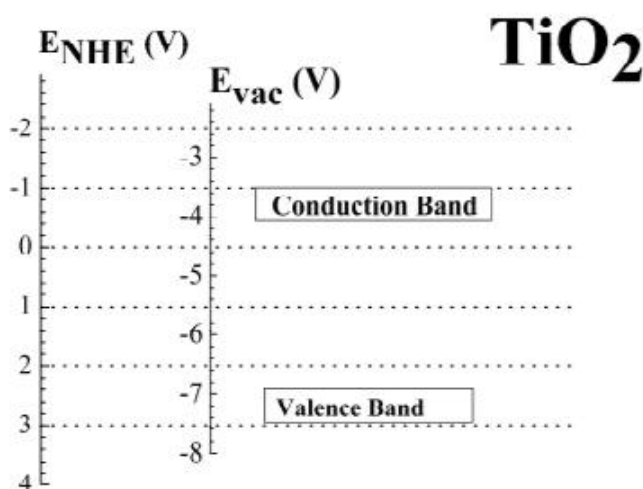
These compounds' chemical identities were confirmed using typical experimental techniques such as thin layer chromatography (TLC), high performance liquid chromatography (HPLC), infrared spectroscopy (IR), and mass spectrometry (MS). Other researchers discovered that when isoeugenol is photooxidized, it creates "dimeric" compounds that are physically similar to the parent lignin structure. Five different solvents were utilised, resulting in a wide range of compounds, including dehydroisoeugenol (DHDIE). Other researchers used atmospheric pressure, room temperature, a light source, and, in contrast to our research, an organic photosensitizer dye to synthesise vanillin from isoeugenol. The yield of vanillin was discovered to be proportional to the concentration of the substrate, isoeugenol. Photocatalytic oxidation has been used to remove eugenol and guaiacol from paper mill wastewater contaminants at low concentrations. Another technique of lignin degradation is catalytic oxidation in alkaline environments to produce vanillin.

### **II. PHOTOCATALYSIS AND PHOTOCHEMISTRY**

The purpose of this research is to employ sustainable ways to manufacture useable products (lignin-based compounds) from biomass in order to contribute to the “green” chemical community. It is obvious that oxidation is what links isoeugenol with vanillin. As a result, it's critical to grasp the differences between photocatalytic and photochemical oxidation of those compounds, as well as how each process yields various useful products from isoeugenol and vanillin. To process biomass in the liquid phase at high temperatures, isomerization and oxidation are typically utilised with metal oxide catalysts. Catalytic oxidation of carbohydrate-derived feedstocks has been shown to generate a variety of products. Thus, understanding the chemistry foundations behind photocatalytic and photochemical oxidation processes is critical for the ongoing development of developing “green chemistry” technologies.

- **Photocatalytic Oxidation**

Photocatalysis can be used for a variety of processes such as oxidation, polymerization, and substitution. Photocatalysis combines advanced oxidation processes with solar and chemical energy to generate a highly reactive radical species. Heterogeneous photocatalysis occurs when the catalyst and reactant are in distinct phases, such as solid and liquid. Heterogeneous photocatalysis, which uses a semiconductor catalyst to excite an electron from the valence to conduction bands, boosts the rate of oxidation. Titanium dioxide (TiO<sub>2</sub>) is well-known as the "most extensively utilised semiconductor photocatalyst." Figure 1 depicts the titanium dioxide energy-band diagram, which contains the valence band and conduction band of the titanium dioxide photocatalyst. The band-gap energy of TiO<sub>2</sub> is 3.1 eV ( $\lambda = 400$  nm).



**Figure 1. Energy-band diagram of the photocatalyst, titanium dioxide (TiO<sub>2</sub>)**

When a semiconductor photocatalyst, such as TiO<sub>2</sub>, is exposed to light, the photon is absorbed by the photocatalyst if its energy is equal to or greater than the photocatalyst's band gap. Photoexcitation of an electron from the valence band to the conduction band occurs in the semiconductor photocatalyst TiO<sub>2</sub> upon photon absorption.

- **Photochemical Oxidation**

A photon of light and an oxidant in the form of oxygen, either from ambient air or pure O<sub>2</sub>, are involved in photochemical oxidation reactions. This photon provides the activation energy for

photochemical processes. The photon is directly absorbed by the reactant molecule, also known as the substrate, and photoexcitation of the reactant molecule occurs (22). A general scheme of a photochemical reaction is depicted in Figure 2: M represents the organic substrate that absorbs the photon, while M\* represents the photoexcited form of the substrate. M (typically, first excited singlet state S1), the oxidant might be a molecule of dissolved oxygen O<sub>2</sub>, and the products represent molecular products of photooxidation processes.

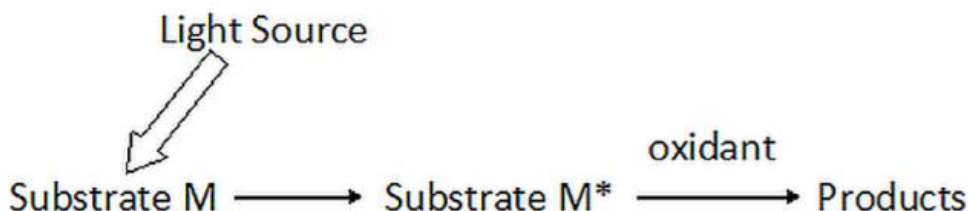
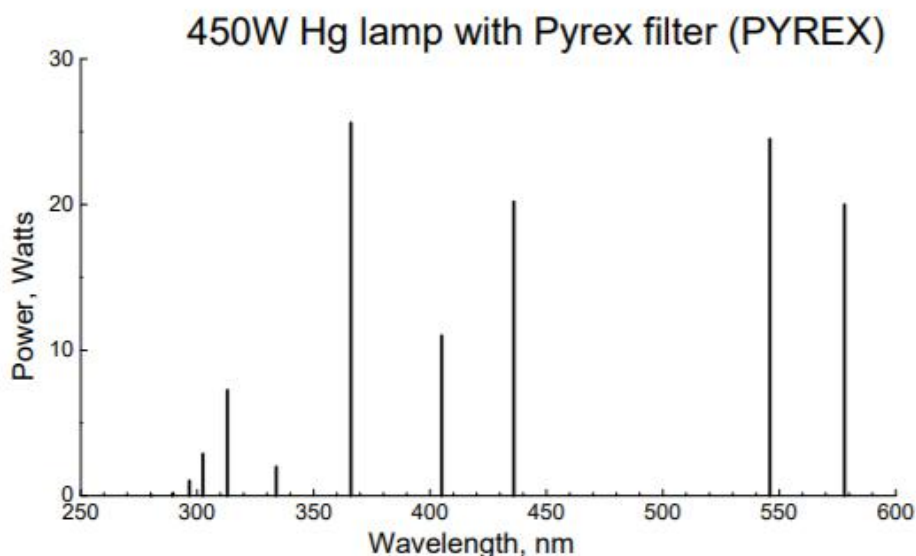
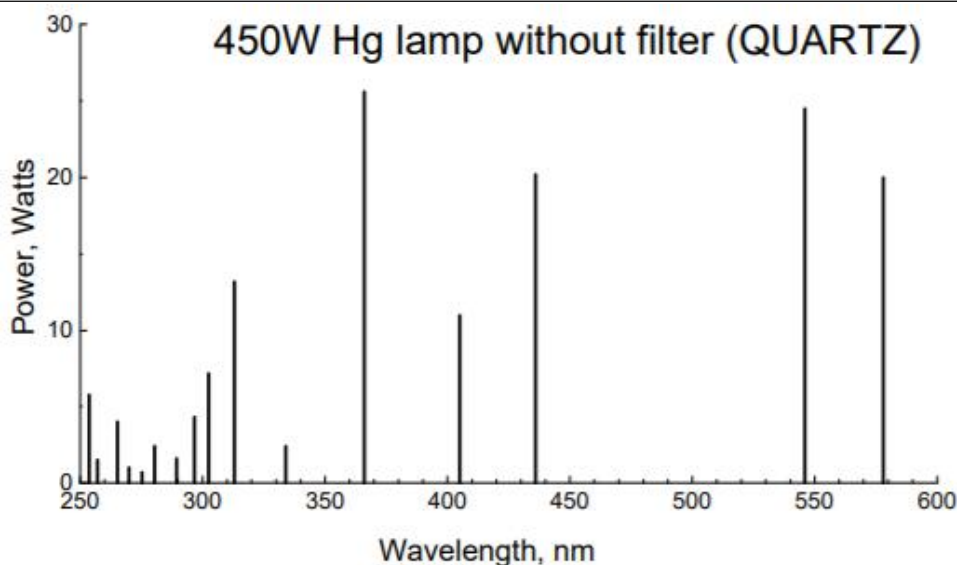


Figure 2. A general example of a photochemical reaction

### III. PHOTOCATALYTIC OXIDATION REACTIONS

A conventional mercury lamp emitting light of a specific spectrum was employed in photooxidation tests. The optical spectrum of light that penetrates the Pyrex reaction vessel (top) and the quartz reaction vessel (bottom) is depicted in Figure 3. (bottom). This is the light spectrum that is absorbed by the sample and causes a photocatalytic or photochemical reaction in the appropriate vessel. There are two prominent lines in the spectrum of light transmitted through the Pyrex vessel: a strong line at 366 nm and a weaker line at 313 nm. As a result, in photocatalytic tests conducted in Pyrex vessels, the reaction is expected to be caused by band gap excitation of TiO<sub>2</sub> with any of these wavelengths. If a quartz vessel is utilised, the radiation that penetrates the vessel will have the spectrum depicted in Figure 6. (bottom). Any wavelength, including and excluding 366 nm, is expected to generate a photocatalytic oxidation reaction due to absorption and photoexcitation of the TiO<sub>2</sub> photocatalyst, as shown in Figure 2. As a result, larger yields of the same reaction products or the production of new products might be expected when compared to a reaction in a Pyrex vessel.

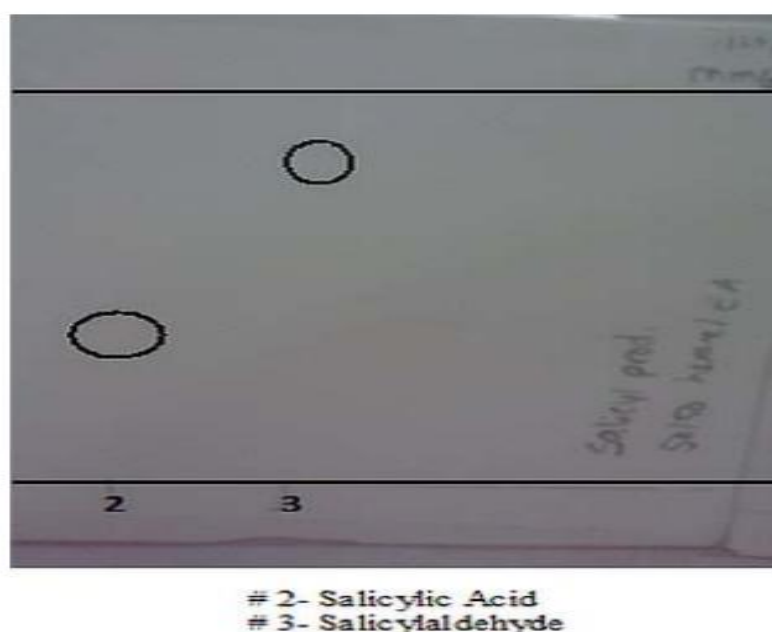




**Figure 3. Optical spectrum of light that penetrates the Pyrex reaction vessel (top) and the quartz vessel (bottom).**

### 3.1 Screening of Phenolic Compounds

In photocatalytic oxidation reactions, experiments began with phenolic chemicals typically present in bio-oil. After the initial photocatalytic oxidation processes, TLC was employed to screen the products. Phenolic substances that reacted by photocatalytic oxidation, such as isoeugenol and vanillin, have many spots on the TLC plate with a retention factor ( $R_f$ ) greater than zero. Salicylic acid and salicylaldehyde in Figure 4 show one area on the TLC plate with an  $R_f$  value larger than zero, indicating that they did not react under photocatalytic oxidation. Compounds that did not react were not studied further.



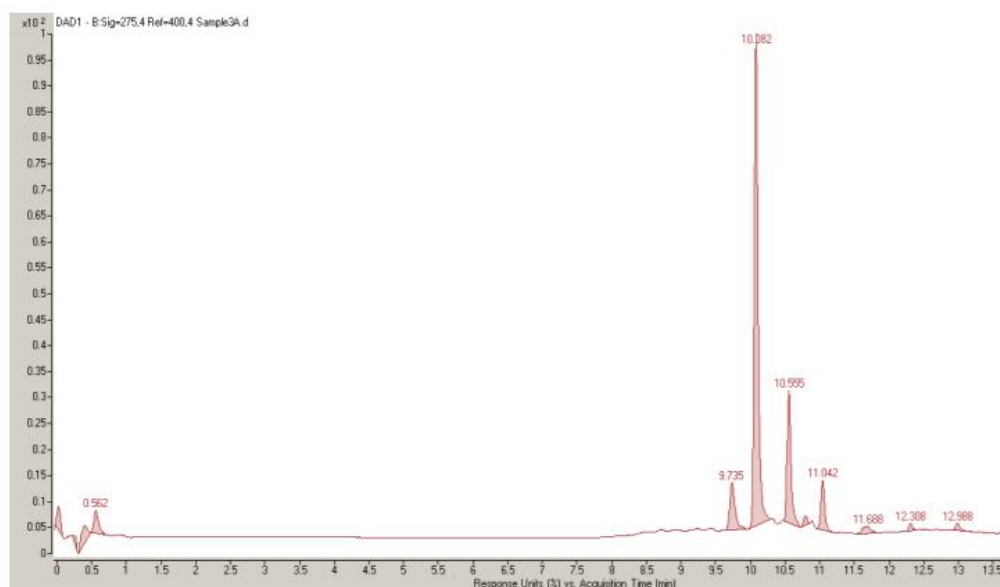
**Figure 4. TLC plate of phenolic compounds that do not react under photocatalytic oxidation.**

#### IV. SOLVENT DEPENDENCE FOR PHOTOOXIDATION OF ISOEUGENOL

Because it is abundant in bio-oil and hence inexpensive and feasible to use, isoeugenol was chosen to investigate the influence of photooxidation reactions on solvents. Isoeugenol originally generated DHDIE during photocatalytic oxidation in acetonitrile, hence it was chosen for future research into DHDIE production during both photocatalytic and photochemical oxidation. The first purpose was to see how the amount of DHDIE product produced by photocatalysis varied in different solvents. The second purpose was to see if different solvents produced different yields of DHDIE during photochemical oxidation. The solvents were chosen based on two criteria: 1) dipole moment and 2) position on the “green” solvent scale. Under both photocatalytic and photochemical oxidation conditions, the results varied for each solvent.

- **The Effect of the Solvent's Dipole Moment**

It was theorised that the larger the dipole moment, the higher the yield of DHDIE product. This theory was developed based on the assumption that in these studies, a highly polar reactive intermediate of isoeugenol was formed. Indeed, a radical-cation of isoeugenol (35) was reported to develop during flash photolysis in  $\text{CH}_3\text{CN}$  at an excitation wavelength of 308 nm. Because of its large dipole moment of 3.92 D, acetonitrile was chosen as the initial solvent of choice. Among the solvents studied,  $\text{CH}_3\text{CN}$  produced the highest DHDIE when utilised as the solvent in photocatalytic oxidation. Although dibutyl ether has a lower dipole moment (1.18 D), it was chosen since it is a “green” solvent. The product of photocatalytic oxidation of isoeugenol in dibutyl ether was examined using HPLC-UV and HPLCMS analysis, which revealed evidence of butyl group incorporation to generate the product shown in Figure 5, with  $m/z = 383$  amu: 326 amu (DHDIE) plus 57 amu ( $\text{C}_4\text{H}_9$ ).



**Figure 5. Chromatogram of “butyl substituted” DHDIE formed in dibutyl ether at a retention time of 10.56 minutes.**

Because of its high dipole moment of 3.86 D, dimethylformamide (DMF) was utilised. Following research, it was discovered that the yield of DHDIE produced under photocatalytic conditions was around 5% (yield is estimated on a molar basis). Because it possesses a zero-dipole moment, perfluorodecalin (PFD) was examined. Isoeugenol was only insoluble in PFD of all the solvents tested,

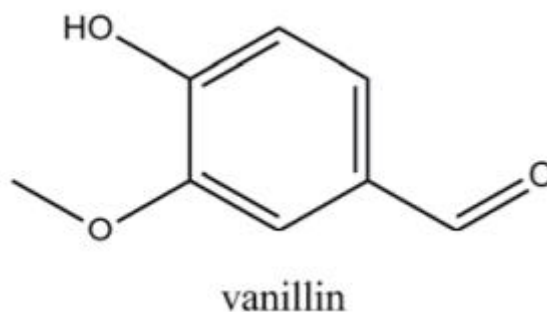
which is assumed to be why no substantial amount of product was identified in this solvent. Because of its high dipole moment, 3.96 D, dimethyl sulfoxide (DMSO) was chosen; however, no products were detected at a substantial yield under photocatalytic oxidation. Despite the fact that the dipole moments of the solvents are quite comparable, the amount of DHDIE generated in each solvent differed greatly. Under photocatalytic oxidation, the molar concentration of DHDIE was estimated for each solvent.

## 5. PHOTOCHEMICAL OXIDATION REACTIONS

Photochemical oxidation studies were carried out in a Pyrex tank using the light spectrum depicted in Figure 3. This is the light at 313 nm (Figure 3, top) that would photoexcite molecules with an optical band between 310 and 325 nm, such as isoeugenol.

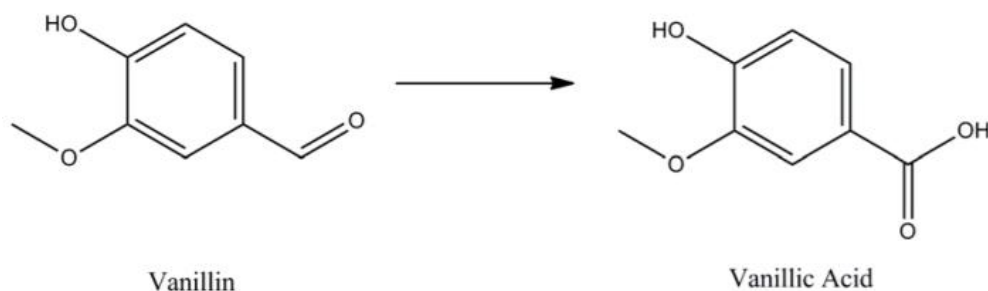
- **Chemical reactions involving the C=O bond**

A vanillin molecule (Figure 6) has an aromatic benzene ring with three distinct substituent groups surrounding it. As seen in Figure 6, the aldehyde group is in the para position to the hydroxyl group, whereas the methoxy group is in the meta position to the aldehyde group.



**Figure 6. Vanillin with a hydroxyl substituent group, methoxy substituent group, and aldehyde substituent group on the aromatic ring.**

Vanillic acid is a common byproduct of vanillin oxidation (11). Vanillin oxidised in a water solution after standing at room temperature in moist air for long periods of time, according to research. Others have used silver oxide to directly oxidise vanillin to vanillic acid. The liquid phase from the reaction vessel after photochemical oxidation with air was diluted with CH<sub>3</sub>CN and injected into the HPLC-UV-MS in this experiment. On the chromatogram, the product had a peak that eluted at 9 minutes. This product eluted at the same time and under the same conditions as the standard, vanillic acid. Figure 7 depicts the reaction of vanillin with vanillic acid (37). Because vanillin is photochemically reactive while salicylaldehyde, which lacks the methoxy group, is not (no peak for salicylic acid was detected on the chromatogram), it is hypothesised that the presence of the methoxy substituent on the ring plays a significant role in this molecule's reactivity.



**Figure 7. Photochemical oxidation of vanillin to vanillic acid.**

## V. CONCLUSION

The results of heterogeneous photocatalytic oxidation and photochemical oxidation of lignin-based phenolic compounds in non-water solvents have been demonstrated to be different. The reactivity of phenolic compounds with a C=C double bond in photocatalytic oxidation reactions strongly depends on the position of the C=C double bond in the substituent on the ring: the internal double bond is much more reactive than the terminal double bond. Photocatalytic oxidation reactions of phenolic compounds with a C=C double bond formed DHDIE as the major product through oxidative “dimerization.” It was also determined that photocatalytic oxidation of phenolic compounds with a C=C double bond yields more DHDIE under the short-wavelengths of UV light ( $\lambda \geq 254$  nm) than under the long-wavelengths of UV light ( $\lambda \geq 355$  nm). This could be due to an increased absorption of light by TiO<sub>2</sub> and the resulting yield increase due to the photocatalytic pathway, or due to an increased absorption of that light by the molecules of isoeugenol and the resulting yield increase due to the photochemical pathway.

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