

# Conversion of Sugar to Organic Acids using TiO<sub>2</sub> Photocatalysts Synthesized by Hydrothermal Process

Nuch Puttipat<sup>1</sup>, Jiraporn Payormhorm<sup>1</sup>, Siriluk Chiarakorn<sup>2</sup>, Navadol Laosiripojana<sup>1</sup> and SurawutChuangchote<sup>1+</sup>

<sup>1</sup> The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, 126 Prachauthit Rd., Bangmod, Tungkru, Bangkok 10140, Thailand

<sup>2</sup> School of Energy Environment and Materials, King Mongkut's University of Technology Thonburi, 126 Prachauthit Rd., Bangmod, Tungkru, Bangkok 10140, Thailand

**Abstract.** Photo-conversion of sugar into acidic compounds was carried out under UV light ( $\lambda_{\text{max}} = 365$  nm) with TiO<sub>2</sub> photocatalysts. The photocatalysts were synthesized by hydrothermal method with 4 h of hydrothermal time which showed a small particle size of anatase phase at 22.6 nm after the calcination at 500 °C. The anatase phase of crystal was also observed in XRD pattern of as-synthesized TiO<sub>2</sub>. Photocatalytic conversion of fructose (C6 sugar) (68.8%) was higher than that of xylose (C5 sugar) (49.8%) at 120 min of illumination time. Moreover, TiO<sub>2</sub> with small particle sizes of anatase crystal, which were synthesized with 4-h hydrothermal time were the good photocatalyst for conversion of sugar to acidic compounds. The generation of organic acid products was investigated by reduction of pH value.

**Keywords:** biomass, Sugar, Titanium dioxide, Hydrothermal, Photocatalysis.

## 1. Introduction

Biomass has been widely used as a potential source for several industrial purposes such as biofuel synthesis and production of high value bio-chemicals. Its main components are lignocelluloses (cellulose, hemicelluloses, and lignin) those are composed with sugar monomer such as glucose, xylose, fructose, and mannose, *etc.*, in their chemical structures [1]. Biomass can be converted into chemicals and fuels with a number of technologies that have been developed for synthesis of fuel and chemicals products such as fermentation, fast pyrolysis, steam gasification, and supercritical conversion. The main drawback of these processes is the high energy requirement. Therefore, the photocatalytic transformation of biomass is a new route for the production of chemicals or fuels, because it can convert biomass to several chemicals by sunlight and it can operate at room temperature [2]. The photoconversion of biomass into oxygenated hydrocarbons (*e.g.* CH<sub>3</sub>CHO, CH<sub>3</sub>CH<sub>2</sub>CHO, HCO<sub>2</sub>CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>) can be occurred with the presence of UV light and photocatalysts. Titanium dioxide (TiO<sub>2</sub>) is a well-known photocatalyst that it has been widely used in many applications. It has strong oxidizing abilities, chemical stability, non-toxicity, and low cost. The hydrothermal synthesis is the most important technique of TiO<sub>2</sub> fabrication and promising new catalyst synthesis method for nano-sized TiO<sub>2</sub> [3]. Therefore, this research focused on the effects of TiO<sub>2</sub> fabrication on their properties and photocatalytic activity via sugar conversion to high-value products (organic acids) that are used as the platforms or/and building blocks for food, pharmaceutical, and fuel industries. The xylose and fructose sugars were used as models of biomass for this research.

## 2. Experimental

### 2.1. Synthesis of TiO<sub>2</sub>

The 0.032 mol titanium (IV) butoxide (Ti(OBu)<sub>4</sub>, Fluka) used as a TiO<sub>2</sub> precursor was mixed with the same mole of acetylacetone (C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>, Sigma-Aldrich) to slow down the hydrolysis and condensation reaction

---

<sup>+</sup> Corresponding author. Tel.: +66 2 470 8310; fax: +66 2 872 6978.  
E-mail address: surawut\_c@jgsee.kmutt.ac.th

under continuous stirring. Afterwards, the distilled water was added into the mixture solution, and then 2-propanol (C<sub>3</sub>H<sub>8</sub>O, QR ǎC) was added into solution under continuously stirred at room temperature. The solution was poured into a Teflon-lined stainless steel autoclave and heated at 120 °C for 4, 8, and 12 h, with stirring condition.

After hydrothermal treatment, the solution was cooled at room temperature. Then, the synthesized TiO<sub>2</sub> particles were washed with distilled water and separated by centrifugation, followed by drying at 100 °C for overnight [4]. The synthesized TiO<sub>2</sub> was crashed into the small particles (designated as as-synthesized TiO<sub>2</sub>). Finally, as-synthesized TiO<sub>2</sub> was calcined at 500 °C for 2 h in a furnace.

## 2.2. Photocatalytic reaction

The photocatalytic activity of TiO<sub>2</sub> was investigated via the photocatalytic conversion of sugar (fructose and xylose). The 500 mL of sugar (1 g/L) in a mixture of Milli-Q water and acetonitrile (10:90 v/v) were placed in a borosilicate cylindrical double-walled photo-reactor that beside equipped with a 400-W UV lamp ( $\lambda_{\text{max}}=365$  nm). The photocatalyst system was circulated with water to maintain the temperature at 30 °C. The 1 g/L of calcined TiO<sub>2</sub> photocatalyst was put in the photo-reactor with continuous magnetic stirring under ambient air and dark condition for 30 min to reach completed adsorption equilibrium of sugar on the TiO<sub>2</sub> surface. The UV lamp was turned on to start the reaction, then liquid product was taken from the reactor at pre-specified periods of time to analysis and filtrated through a 0.45- $\mu\text{m}$  nylon filter. The photocatalytic conversion of sugar was monitored by a high-performance liquid chromatography (HPLC, Shimadzu), equipped with a refractive index detector (Shimadzu, RID-10A). Separation was performed on an Aminex HPX-87H column, 300 $\times$ 7.8 mm. The mobile phase was 5mM H<sub>2</sub>SO<sub>4</sub> at a flow rate of 0.5 mL/min. The injection volume was 20  $\mu\text{l}$ .

## 2.3. Characterizations of photocatalysts

The crystallite structures of synthesized TiO<sub>2</sub> were monitored by X-ray diffraction (XRD, X'Pert PRO MPD model pw 3040/60, PANalytical) with Cu K $\alpha$  irradiation at 40 kV and 30 mA. The size of crystal were calculated by the Scherrer equation (1);

$$D = K\lambda / \beta \cos\theta, \quad (1)$$

where D is the crystallite size,  $\lambda$  is wavelength of X-ray radiation (0.154 nm), K is coefficient (0.9),  $\beta$  is the full-width at half-maximum of peak, and  $\theta$  is the diffraction angle.

# 3. Results and Discussion

## 3.1. Photocatalyst characterizations

Fig. 1 shows XRD patterns of as-synthesized and calcined TiO<sub>2</sub> which were hydrothermally prepared for 4, 8, and 12 h under continuous stirring. The peaks of anatase phase at  $2\theta$  of about 25.2°, 37.9°, and 47.8°, were found in XRD patterns. However, the diffraction lines of anatase in case of as-synthesized TiO<sub>2</sub> are weak and broad compared with calcined TiO<sub>2</sub>. For crystallite size of anatase crystal as shown in Table 1, it was found that anatase crystals of as-synthesized TiO<sub>2</sub> (8-13 nm) were smaller than that of calcined TiO<sub>2</sub> (22-45 nm). This result can be explained that the thermal treatment significantly affected on a crystallite size of anatase. The phase composition of calcined TiO<sub>2</sub> showed only an appearance of anatase phase. Increase of heat treatment (calcination) temperature up to 500 °C could enhance phase transformation to anatase phase. In addition, hydrothermal time of TiO<sub>2</sub> fabrication at 12 h provides the smallest crystallite size of anatase (8.4 nm). This result indicated that long hydrothermal time under continuous stirring might inhibit the growing of crystalline. Unfortunately, small crystal size of anatase crystals was easy to agglomerate to form large crystallite size (45.2 nm) after calcinations at high temperatures.

## 3.2. Photocatalytic reactions

The photocatalytic activity of TiO<sub>2</sub> was proposed in photocatalytic conversion of sugars. Fructose and xylose were converted to be organic acids those were mentioned as sugar-derived platform molecules. Those organic acids were considered as high value chemicals [5]. The resulted conversions of fructose and xylose are presented in Fig. 2. The results found that conversion of sugar was increased with long illumination time. Interestingly, the conversion of fructose (C6 sugar) (see in Fig 2(a)) is higher than that of xylose (C5 sugar)

(see in Fig 2(b)). The conversions of fructose and xylose with 4-h hydrothermal time of synthesized TiO<sub>2</sub> after 120 min were 68.8 and 49.8%, respectively. It can be explained that the chemical structure of substrate might affect to photocatalytic oxidation on position of hydroxylated carbon atom in sugars. The OH• radicals that was obtained from photocatalytic reaction of water reacted with hydroxylated carbon atom in sugar leaded firstly to formation of a new carbonyl group [6]. Since, hydroxylated carbon atom at the end of fructose molecule might be easy oxidized to compare with xylose. To consider the effect of hydrothermal time, it was found that conversion of sugar obtained from photooxidation of TiO<sub>2</sub> synthesized at 120 °C with short hydrothermal time of 4 h was higher than that of synthesized TiO<sub>2</sub> at 12 h. This result might be influence of small crystallite size of synthesized TiO<sub>2</sub> at 4 h. Their small crystallite sizes related to formation of small particles and presence of high surface area of photocatalysts then enhanced the photocatalytic activity. Fig. 3 shows pH value of products in solution that were obtained from photocatalytic oxidation of fructose and xylose with synthesized TiO<sub>2</sub> at 4 h of hydrothermal time. The pH value of products in fructose and xylose solution reduced with increasing illumination time. Although, pH value of product solutions of fructose and xylose solutions were similar. This result indicated that the products were obtained from photocatalytic oxidation of sugar was organic acids.

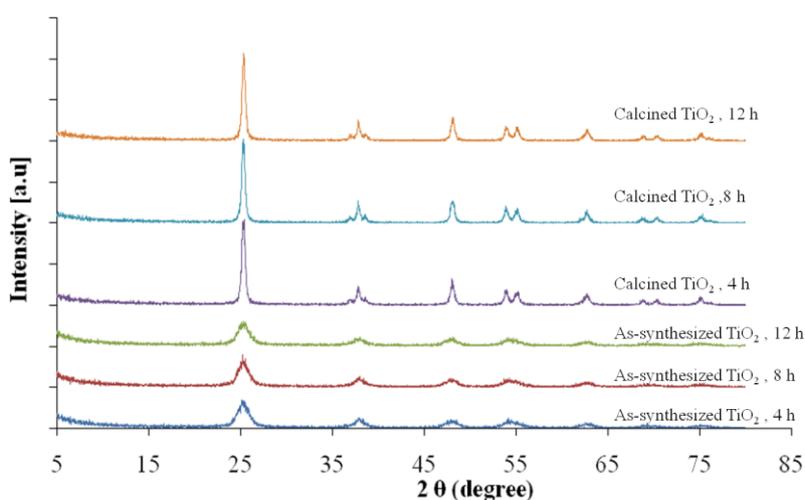


Fig.1: XRD patterns of the TiO<sub>2</sub> photocatalyst obtained from hydrothermal method at 120°C of aging temperature under continuous stirring for 4, 8 and 12 h.

#### 4. Conclusion

Photoconversion of sugar into acidic compounds was carried out under UV light with TiO<sub>2</sub> photocatalysts. TiO<sub>2</sub> particles which were synthesized by hydrothermal method with a short hydrothermal time provided the small crystallite size and high anatase crystalline. These small particles of TiO<sub>2</sub> resulted in high photocatalytic conversion of sugars to be organic acids. Lower temperature in hydrothermal process resulted in the presence of smaller anatase crystal size. The crystallite size of as-synthesized TiO<sub>2</sub> was growth after calcination at high temperature. The ability of photocatalytic conversion was also depended on functional group in chemical structure of sugars.

Table 1. Effect of hydrothermal treating time on physico-chemical properties of TiO<sub>2</sub>

Hydrothermal time (h)	TiO <sub>2</sub> photocatalyst	XRD	
		Crystallite size of anatase (nm)	Anatase over rutile ratio (A:R)
4	As-synthesized TiO <sub>2</sub>	12.7	-
	Calcined TiO <sub>2</sub>	22.6	-
8	As-synthesized TiO <sub>2</sub>	12.8	-
	Calcined TiO <sub>2</sub>	22.5	100 : 0
12	As-synthesized TiO <sub>2</sub>	8.4	100 : 0
	Calcined TiO <sub>2</sub>	45.2	100 : 0

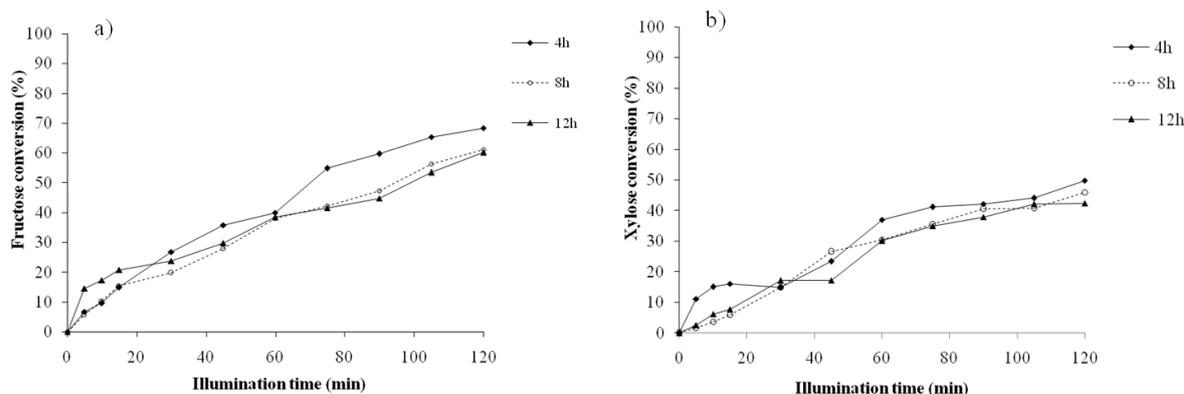


Fig. 2: Results obtained from catalytic photoconversion: (a) conversion of fructose and (b) conversion of xylose at different reaction times.

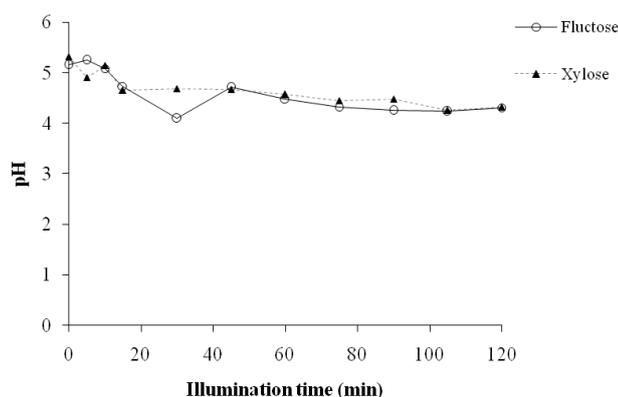


Fig. 3: pH changes during 120 min illumination of fructose and xylose solutions in the presence of synthesized  $\text{TiO}_2$  fabricated by hydrothermal method at  $120^\circ\text{C}$  for 4h.

## 5. Acknowledgements

The authors would like to acknowledge financial support for this research from the Joint Graduate School of Energy and Environment. The authors would like to thank for the research collaborations from Rajamangala University of Technology Thanyaburi and National Center for Genetic Engineering and Biotechnology (BIOTEC).

## 6. References

- [1] Lu, Liua, Y. X. Philip, A. R. Womaca, S. Sokhansanj. Variability of biomass chemical composition and rapid analysis using FT-NIR techniques. 2010, 81, 820–829.
- [2] J. C. Colmenares, R. Luque, J. M. Campelo, F. Colmenares, Z. Karpinski, A. A. Romero. Nanostructured photocatalysts and their applications in the photocatalytic transformation of lignocellulosic biomass. 2009, 2, 2228–2258.
- [3] J. Jitputti, T. Rattanavoravipa, S. Chuangchote, S. Pavasupree. Low temperature hydrothermal synthesis of mono dispersed flower-like titanate Nano sheets. 2009, 10, 378–382.
- [4] J. Jitputtia, S. Pavasupreea, Y. Suzukia, S. Yoshikawa. Synthesis and photocatalytic activity for water-splitting reaction of nanocry stallinemesoporoustitania prepared by hydrothermal method. 2007, 180, 1743–1749.
- [5] J. C. Colmenares, A. Magdziarz, A. Bielejewska. High-value chemicals obtained from selective photo-oxidation of glucose in the presence of nanostructured titanium photocatalysts. 2011, 102, 11254–11257.
- [6] W. Zmudzinski. Preliminary results of glucose oxidation by photocatalysis on titanium dioxide primary intermediates. 2010, 45, 141–151.