

# Synthesis of the $MVO_3$ (M= Li, Na, K) composite as a catalyst for transesterification to produce biodiesel

Yu-Chiao-Wang<sup>1</sup>(王昱喬), Jia-Hao-Lin<sup>1</sup>(林佳豪), Yong-Ming Dai<sup>2</sup>(戴永銘) and Chiing-Chang Chen<sup>1\*</sup>(陳錦章)

<sup>1</sup> Department of Science Education and Application, National Taichung University of Education, Taichung 403, Taiwan

<sup>2</sup> Department of Chemical and Materials Engineering, National Chin-Yi University of Technology, Taichung 411, Taiwan

\*Corresponding author, E-mail: ccchen@mail.ntcu.edu.tw; ccchen0516@gmail.com

## Abstract

Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable. We investigated the use of Vanadium trioxide and three alkali metals (Li, Na, and K) as  $MVO_3$  (M=Li, Na, K) composite as solid-base catalysts for biodiesel production.

$MVO_3$  catalysts were prepared using a simple solid-state reaction, mixing, and grinding vanadium trioxide with alkali metals calcined at 800 °C in air for 4 h. The synthesized  $MVO_3$  was analyzed by X-ray diffractometer (XRD), Field Emission-Scanning Electron Microscopy (FE-SEM), Field Emission-Transmission Electron Microscope-Energy Dispersive Spectroscopy (FE-TEM-EDS), High Resolution X-ray Photoelectron Spectroscopy (HR-XPS), Surface Area and Porosity Analyzer (BET) and other instruments to identify the product composition and compound structure and oxidation state information.

The optimal conditions contain the oil to methanol molar ratio 1:36, the catalyst amount 8wt%, the reaction temperature 180°C, the reaction time 4hr, and the conversion rate 97.6%. The physicochemical properties of the biodiesel were further studied and compared with the ASTM and the EN biodiesel specifications. The results showed that the properties of the biodiesel produced complied with the international standard specifications.

## Experimental Section



## Results and Discussion

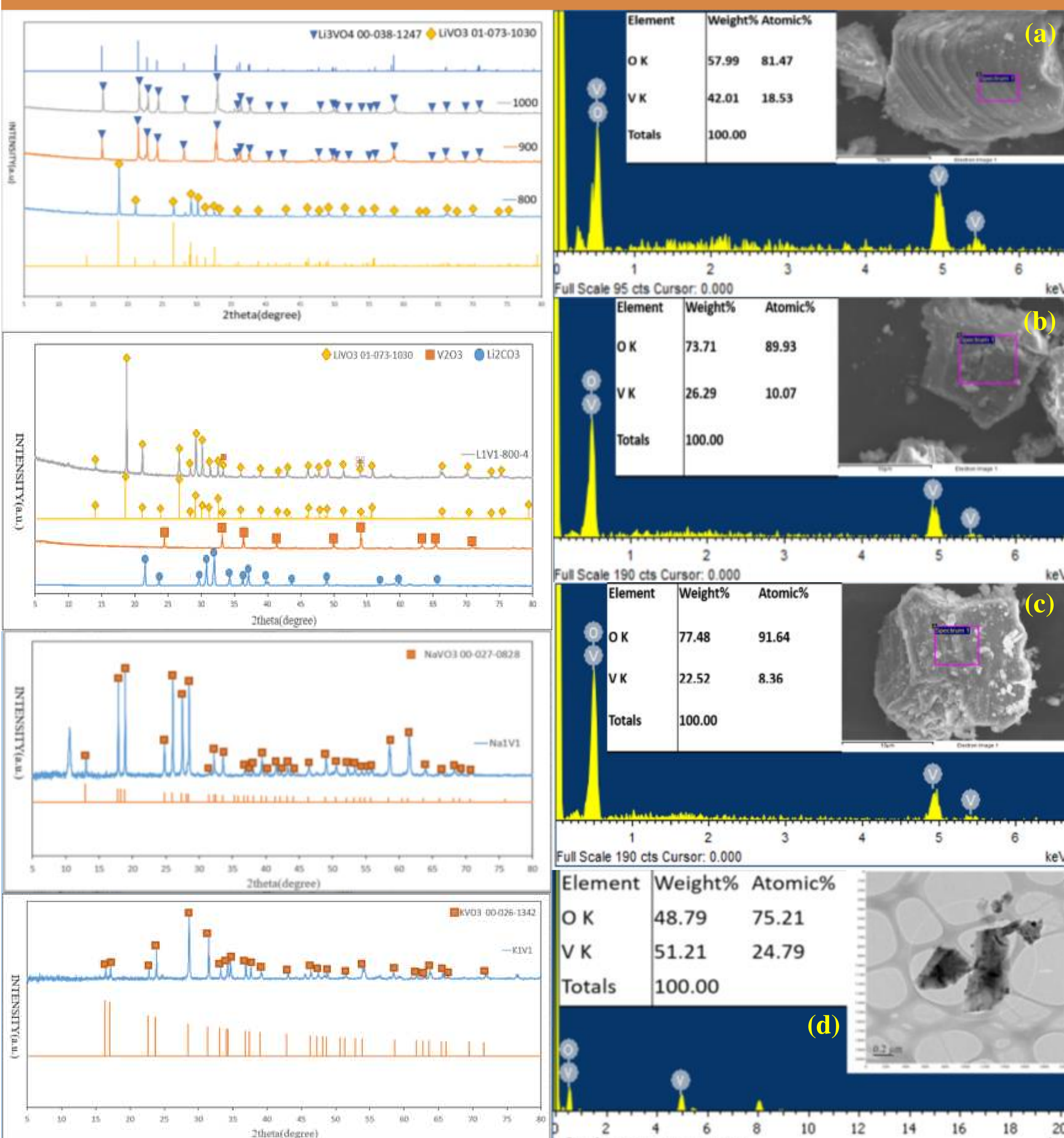


Fig.1 XRD patterns of  $MVO_3$  (M= Li, Na, K) +  $V_2O_3$  calcination in difference calcination temperature(°C)

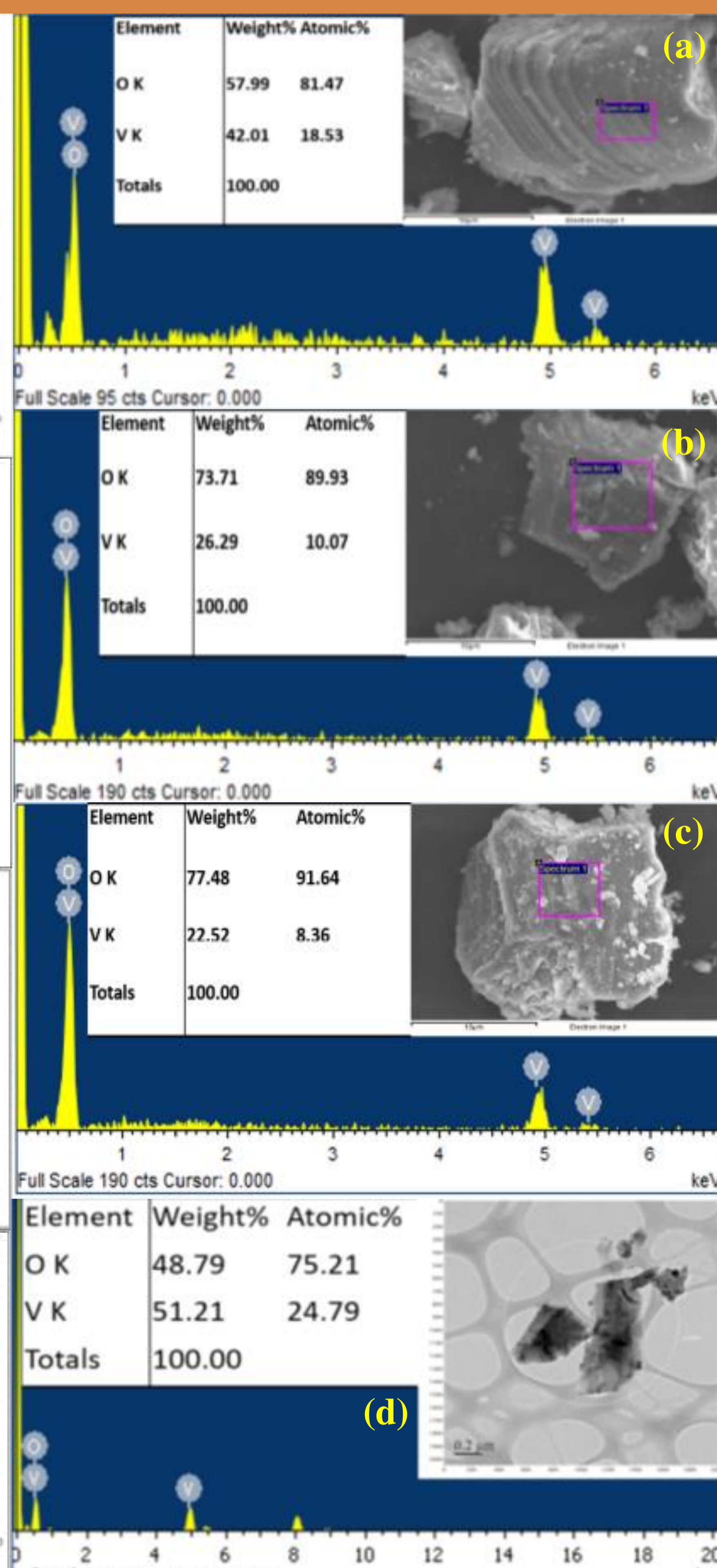


Fig.2 SEM photograph and EDS elemental analysis of calcination temperature(°C) (a)800 (b)900 (c)1000

Table.2 CNS standard form of the oil which use  $LiVO_3$  to product

Property	Range		Unit	Test-Method
	Measured value	Standard value		
Water content	363.28	<500	mg/kg	CNS-4446 ISO-12937
Viscosity at 40°C	4.46	3.50-5.00	mm <sup>2</sup> /s	CNS-3390
Density at 15°C	886.3	860-900	kg/m <sup>3</sup>	CNS-12017 CNS-14474 ISO-12185
Acid value	0.12	<0.50	mg KOH/g	CNS-14669 CNS-14906
Iodine value	123.2	≤ 120	g I <sub>2</sub> /100g	CNS-15060
Flash point	200	>120	°C	CNS-3574 CNS-14473 ISO-3679
Sulfur content	na	<10.0	mg/kg	CNS-13877 CNS-14505 CNS-15461 ISO-20846 ISO-20884
Alkal Metals (Na+K)	<0.7a	<5.0	mg/kg	CNS-15052
Alkal Metals (Mg+Ca)	<8.1	<5.0	mg/kg	CNS-15053
Phosphorus content	0	<4.0	mg/kg	CNS-15019
Cold filter plugging point	X	≤ 0	°C	CNS-15058 CNS-15061
Copper band corrosion (3 hours at 50 °C)	Class 1	Class 1	rating	CNS-1219
Monoglyceride content	0.16	<0.80	% (m/m)	ISO-15018
Diglyceride content	0.026	<0.20	% (m/m)	ISO-15018
Triglyceride content	0.102	<0.20	% (m/m)	ISO-15018
Free Glyceride content	0.002	<0.02	% (m/m)	ISO-15018
Total Glyceride content	0.06	<0.25	% (m/m)	ISO-15018

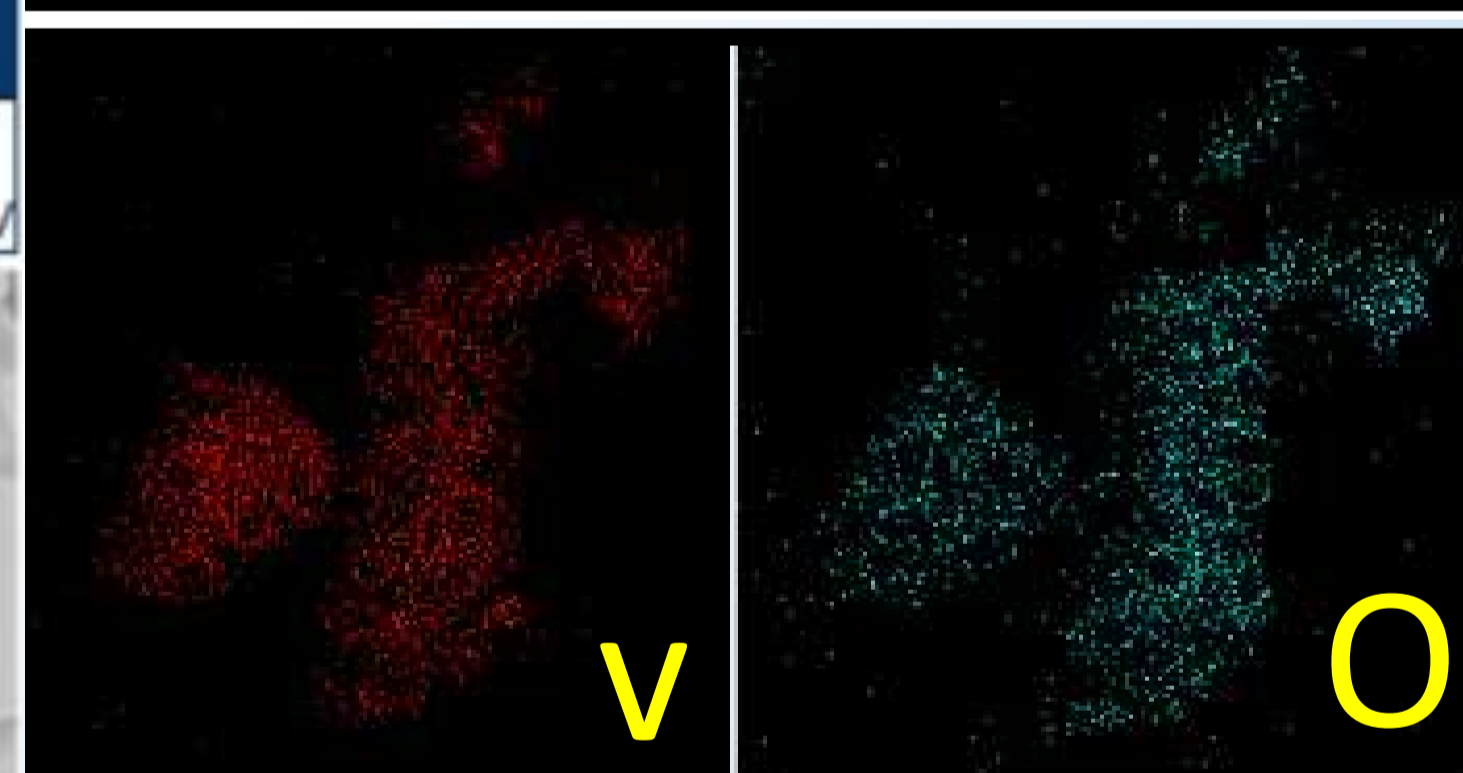


Fig.3 TEM photograph and elemental analysis of (d)LiV1-800-4

Table.1 BET information of the catalyst (H)

Catalyst	Specific surface area (m <sup>2</sup> /g)	Pore diameter (Å)	Pore volume (cm <sup>3</sup> /g)
LiV1-800-4	0.3589	1168.828	0.007218

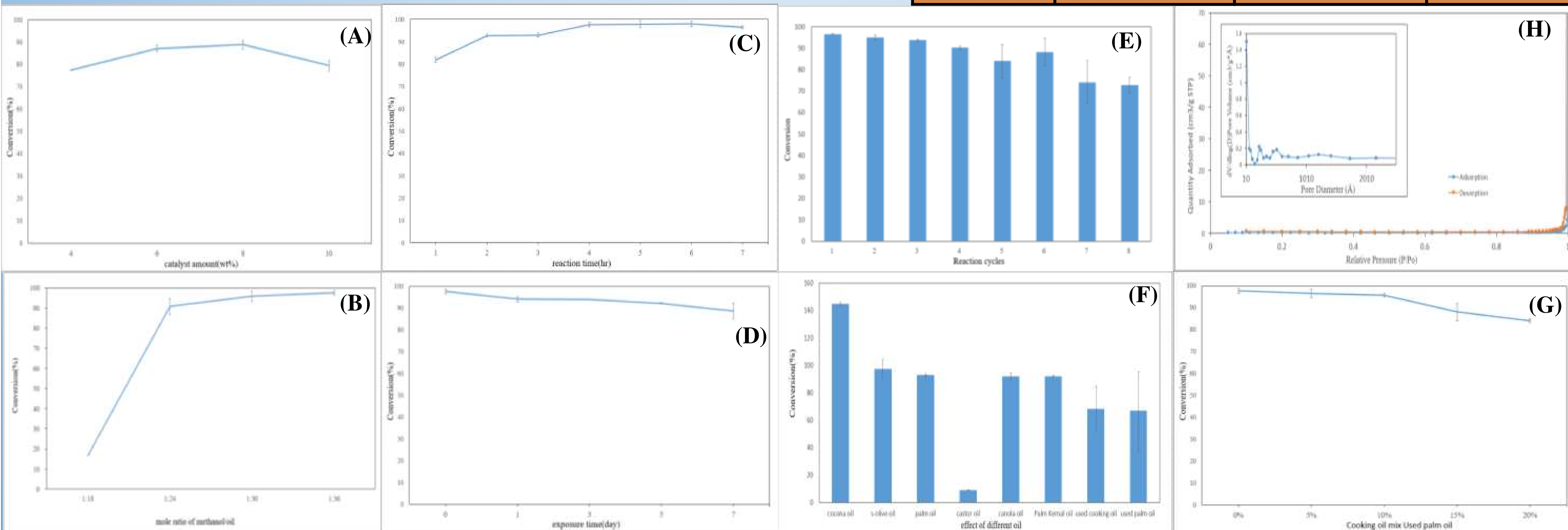


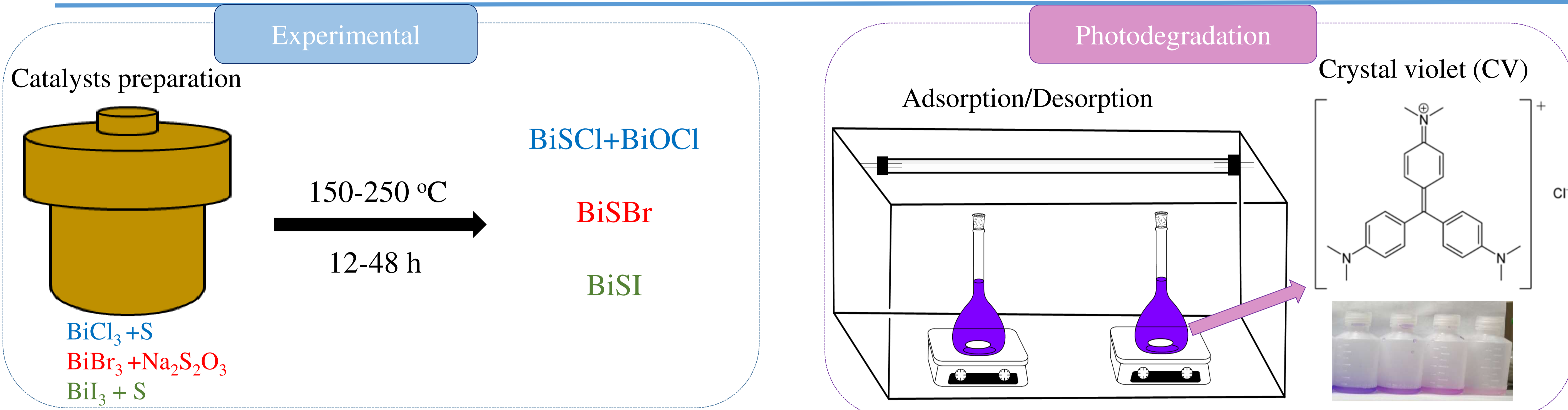
Fig.4 Influence of (A) Catalyst amount (wt%) (B) methanol/oil molar ratio (C) reaction time (hr)(D) exposure time(day) (E) recovery of the number of catalyst (F) different oil (G) mix cooking oil & used palm oil(wt%) on the conversion.

# BiSX (X = Cl, Br, I): Synthesis, Characterization, and Photocatalytic Activity for Crystal Violet Dye

科四甲 王道遠, 陳郁升, 黃楷雯  
指導教授 陳錦章 教授

## Abstract

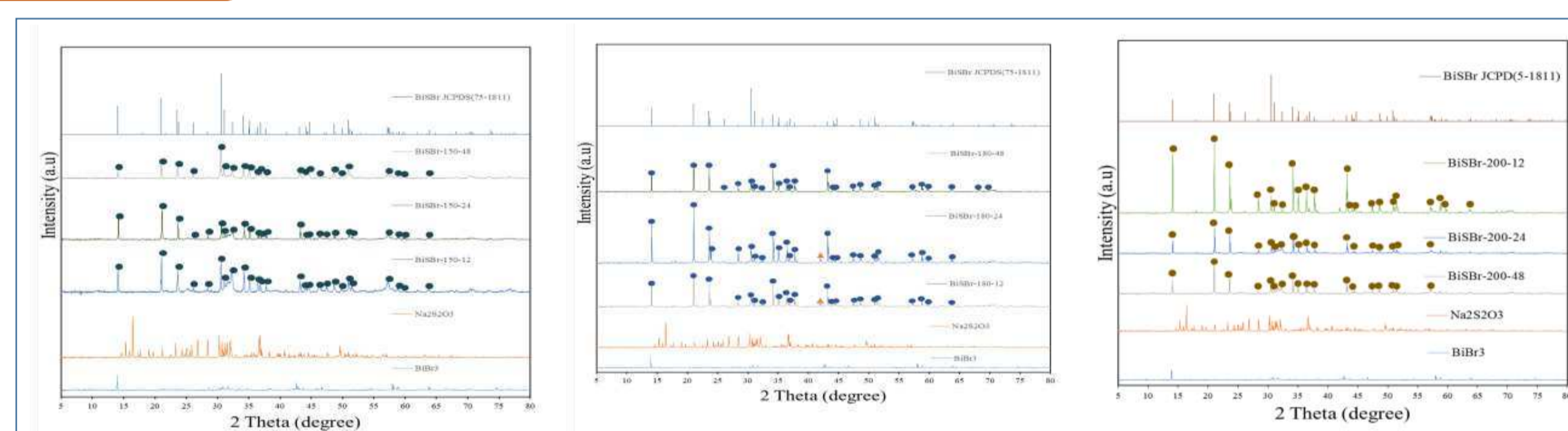
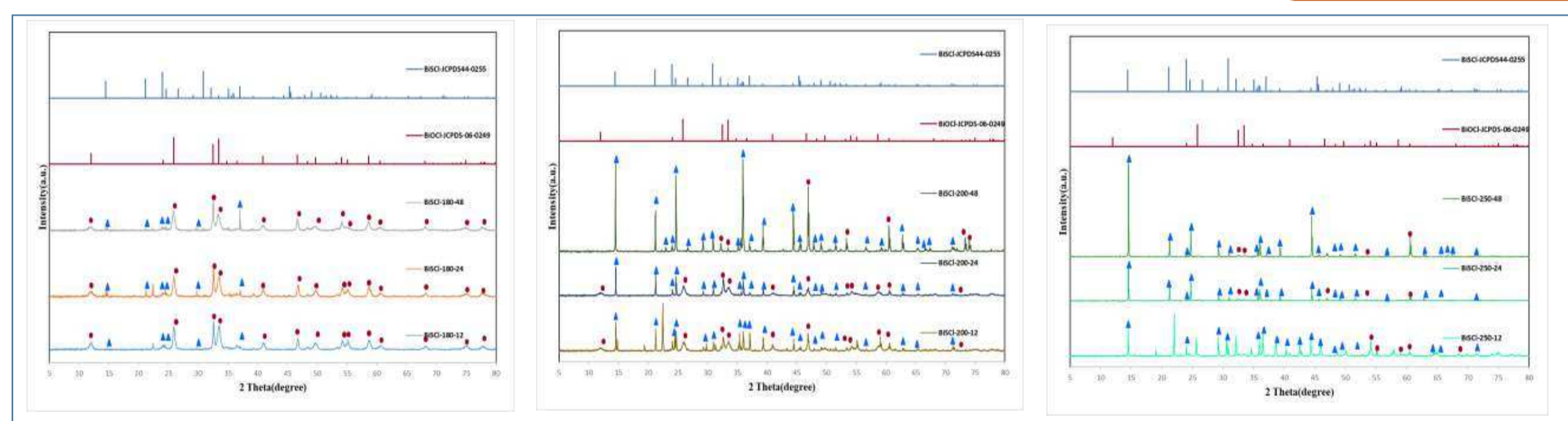
We successfully prepared a series of BiSX, including BiSbCl, BiSbBr and BiSbI were used a simple solution-based hydrothermal method. The characteristics of the samples were identified using various techniques, such as scanning electron microscopy–energy-dispersive X-ray spectroscopy, high-resolution transmission electron microscopy, Fourier-transform infrared spectroscopy, high-resolution X-ray photoelectron spectroscopy, diffuse reflectance ultraviolet–visible (UV–Vis) spectroscopy, X-ray diffraction, and Brunauer–Emmett–Teller analysis. The photocatalytic activity of a series of BiSX samples is further discussed by degrading crystal violet (CV) in aqueous solution under visible light irradiation. The photocatalytic activity of BiSbCl, BiSbBr and BiSbI composites reached a maximum rate constant of 0.0708 h<sup>-1</sup>, 0.1152 h<sup>-1</sup> and 0.0204 h<sup>-1</sup>. The photocatalytic degradation of the CV for future applications in environmental pollution and control.



XRD

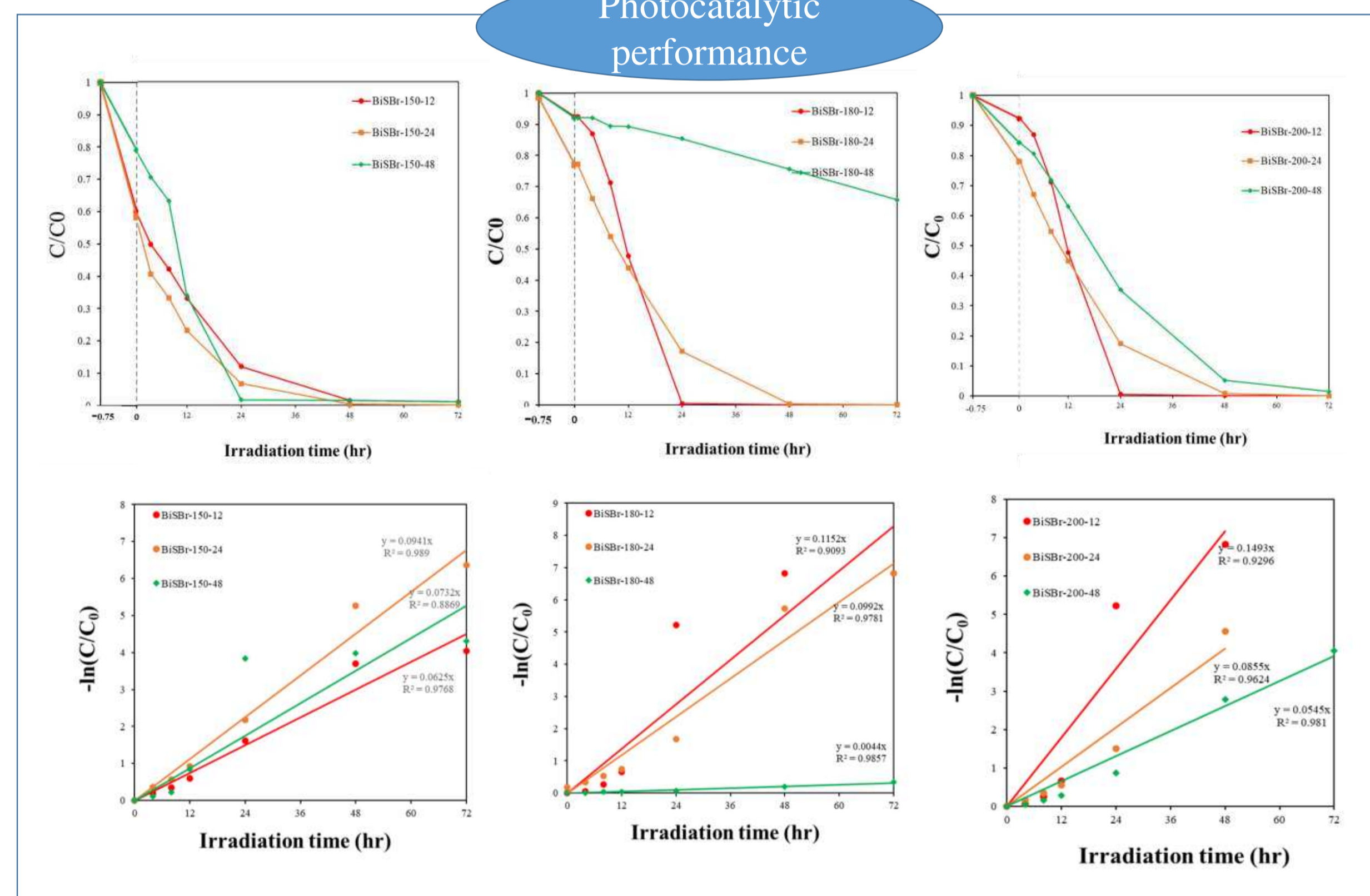
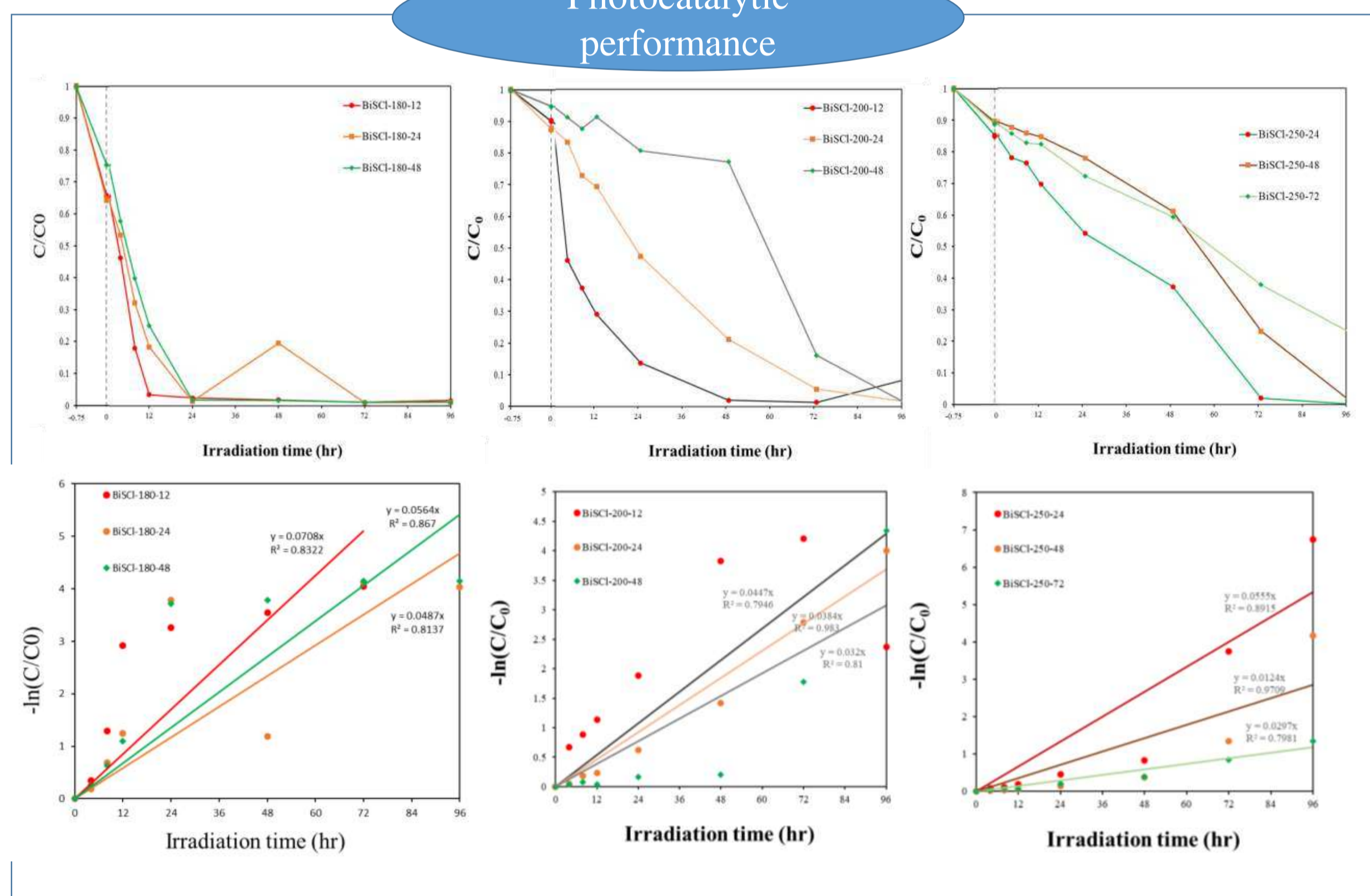
Result & discussion

XRD



Photocatalytic performance

Photocatalytic performance

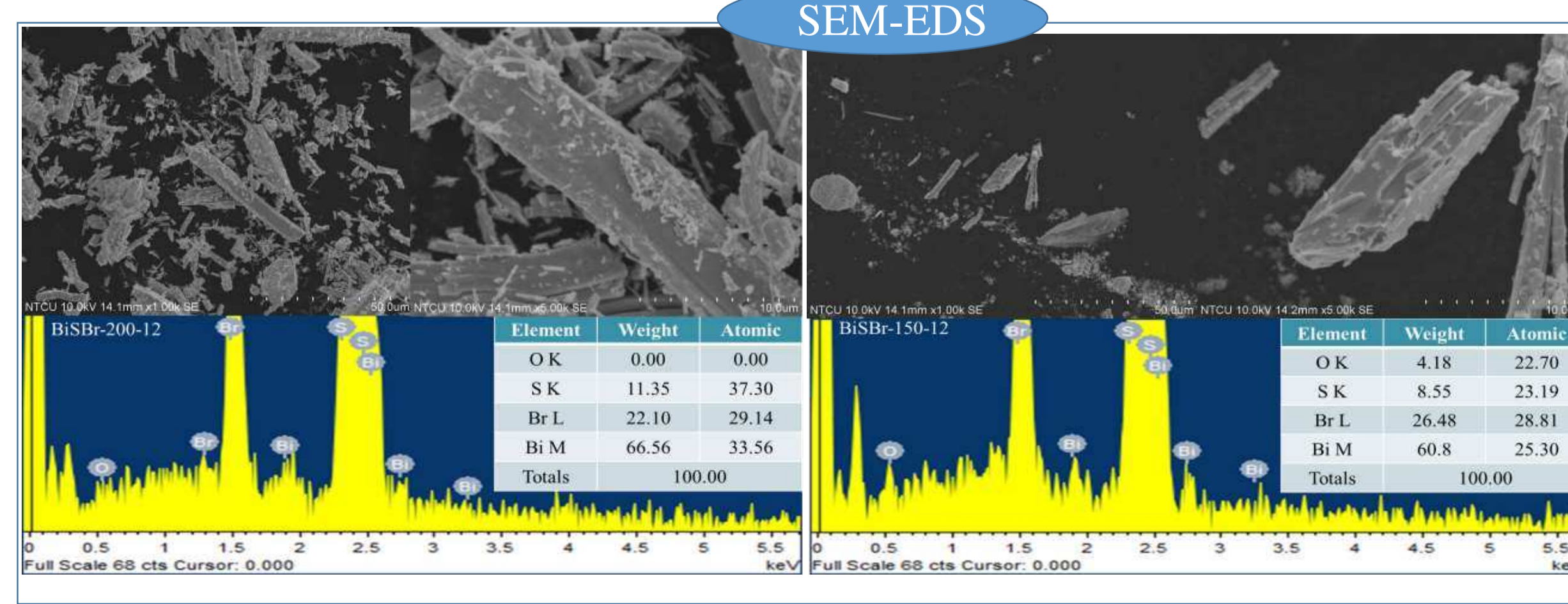
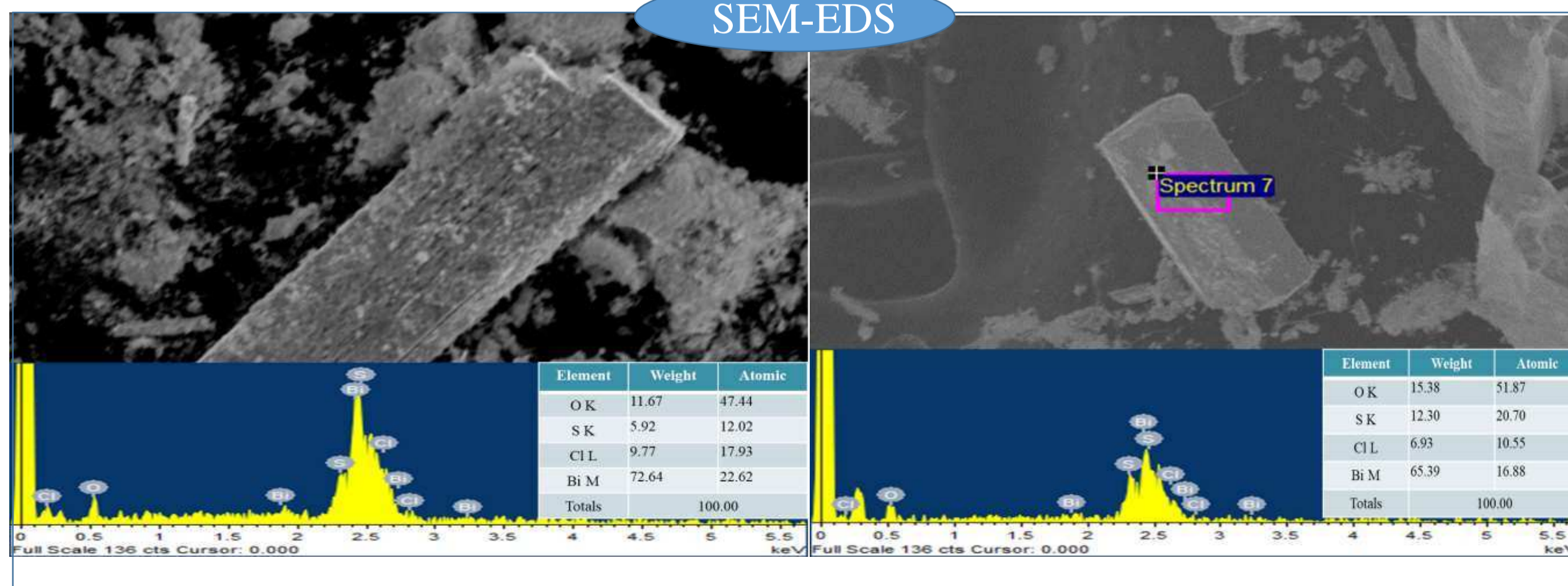


BiSbCl						
Time (hr)	Temp (°C)					
	180		200		250	
	K (h <sup>-1</sup> )	R <sup>2</sup>	K (h <sup>-1</sup> )	R <sup>2</sup>	K (h <sup>-1</sup> )	R <sup>2</sup>
12	0.0708	0.8322	0.0447	0.9222	0.017	0.6399
24	0.0487	0.8137	0.0384	0.983	0.0555	0.8436
48	0.0564	0.867	0.032	0.81	0.0124	0.9512

BiSbBr						
Time (hr)	Temp (°C)					
	150		180		200	
	K (h <sup>-1</sup> )	R <sup>2</sup>	K (h <sup>-1</sup> )	R <sup>2</sup>	K (h <sup>-1</sup> )	R <sup>2</sup>
12	0.0625	0.9768	0.1152	0.9093	0.1493	0.9296
24	0.0941	0.988	0.0922	0.9781	0.0855	0.9624
48	0.0732	0.8869	0.0044	0.9857	0.0545	0.981

SEM-EDS

SEM-EDS



# Production of glycerol triacetate through esterification of glycerol using Silicotungstic acid.

Wen-Ying Chen<sup>1</sup> (陳玟穎), Jia-Hao Lin<sup>1</sup> (林佳豪), Yong-Ming Dai<sup>2</sup> (戴永銘) and Chiing-Chang Chen<sup>1\*</sup> (陳錦章)

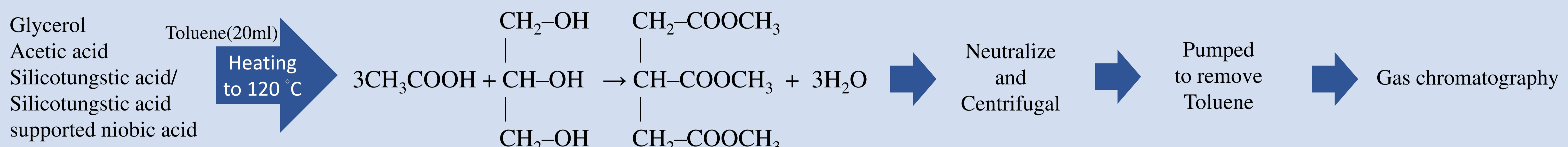
<sup>1</sup> Department of Science Education and Application, National Taichung University of Education

<sup>2</sup> Department of Chemical and Materials Engineering, National Chin-Yi University of Technology, Taichung 41170, Taiwan.

## Abstract

The rapid increase of biodiesel production has led to a wider availability of crude glycerol as a by-product in chemical industry. Esterification of glycerol can be a good alternative of glycerol produced by biodiesel. Glycerol triacetate (GTA) is an important chemical used in the production of foods and spices, and in printing and dyeing. The esterification of glycerol with acetic acid effectively takes place on acid catalysts, hence providing a promising way to transform glycerol into value added products. In this work, we study the esterification of glycerol with acetic acid over Silicotungstic acid (STA) and STA supported niobic acid (STA/Nb<sub>2</sub>O<sub>5</sub>). The optimum conditions for the process include STA and STA/Nb<sub>2</sub>O<sub>5</sub> catalysts amount 1.5g, acetic acid to glycerol molar ratio 6:1, and a reaction temperature of 120°C. The catalyst exhibits the best catalyst performance with the maximum esteriacetin yield of 99.07% and 77.07% respectively. The glycerol conversion is well correlated with the acidity of the catalysts. The selectivity during glycerol esterification not only depends on the nature of catalysts but also on acetic acid to glycerol molar ratio. Different reaction parameters are studied and the optimum reaction conditions are established.

## Experimental section



## Results and Discussion

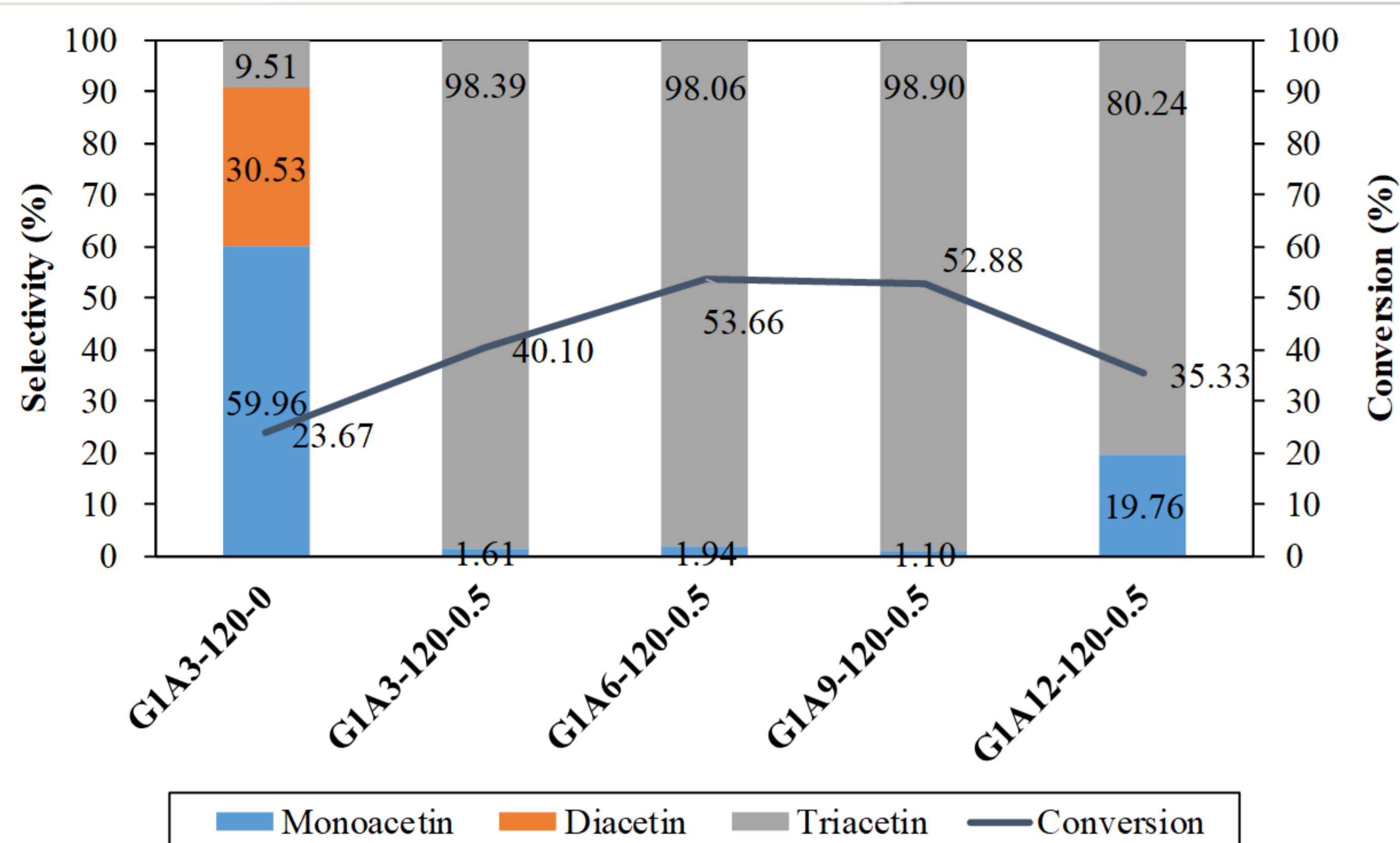


Fig. 1. Effect of acetic acid to glycerol mole ratio on selectivity and conversion rate during glycerol acetylation.

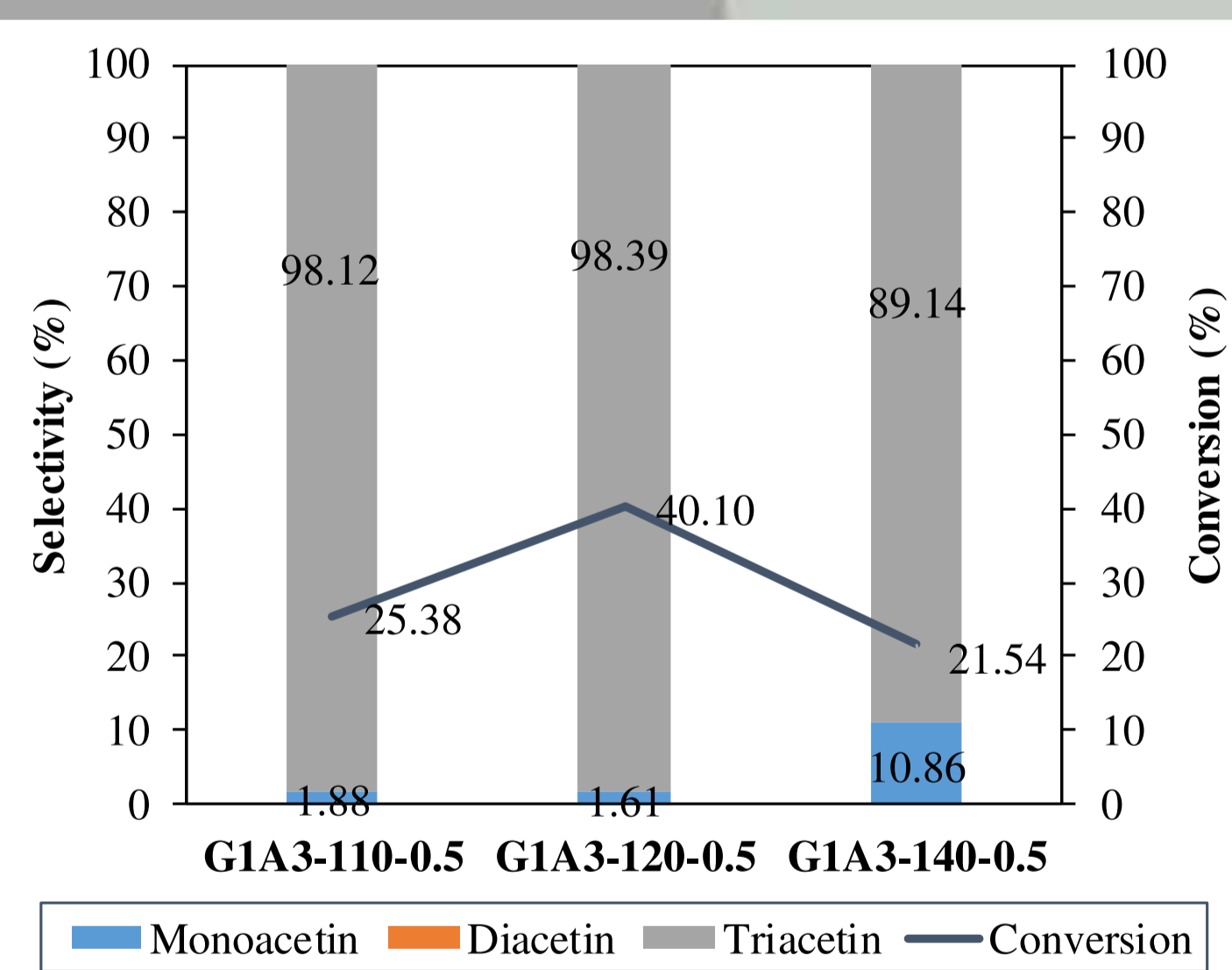


Fig. 2. Effect of reaction temperature on selectivity and conversion rate during glycerol acetylation. Reaction conditions: glycerol to acetic acid mole ratio: 1:3.

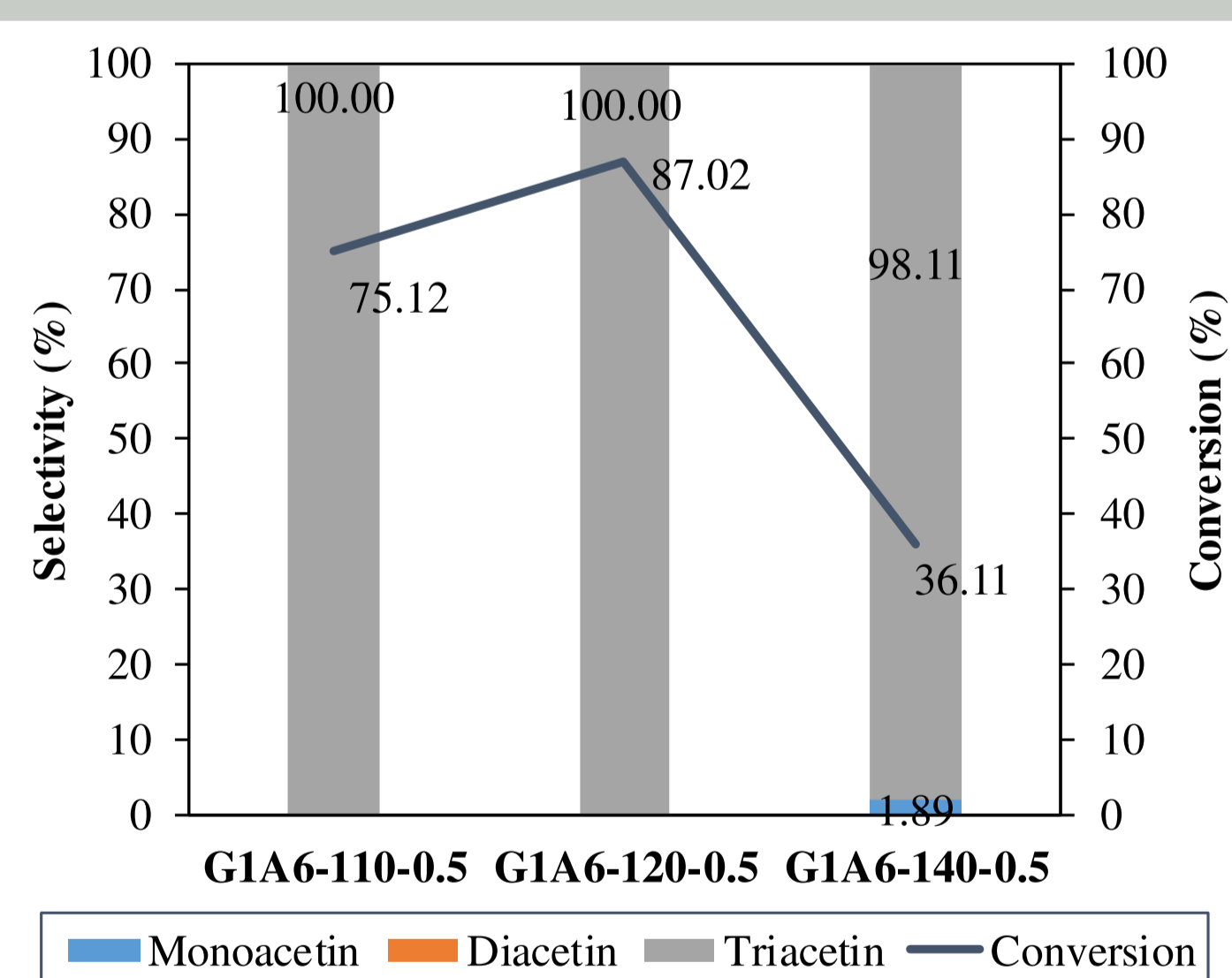


Fig. 3. Effect of reaction temperature on selectivity and conversion rate during glycerol acetylation. Reaction conditions: glycerol to acetic acid mole ratio: 1:6.

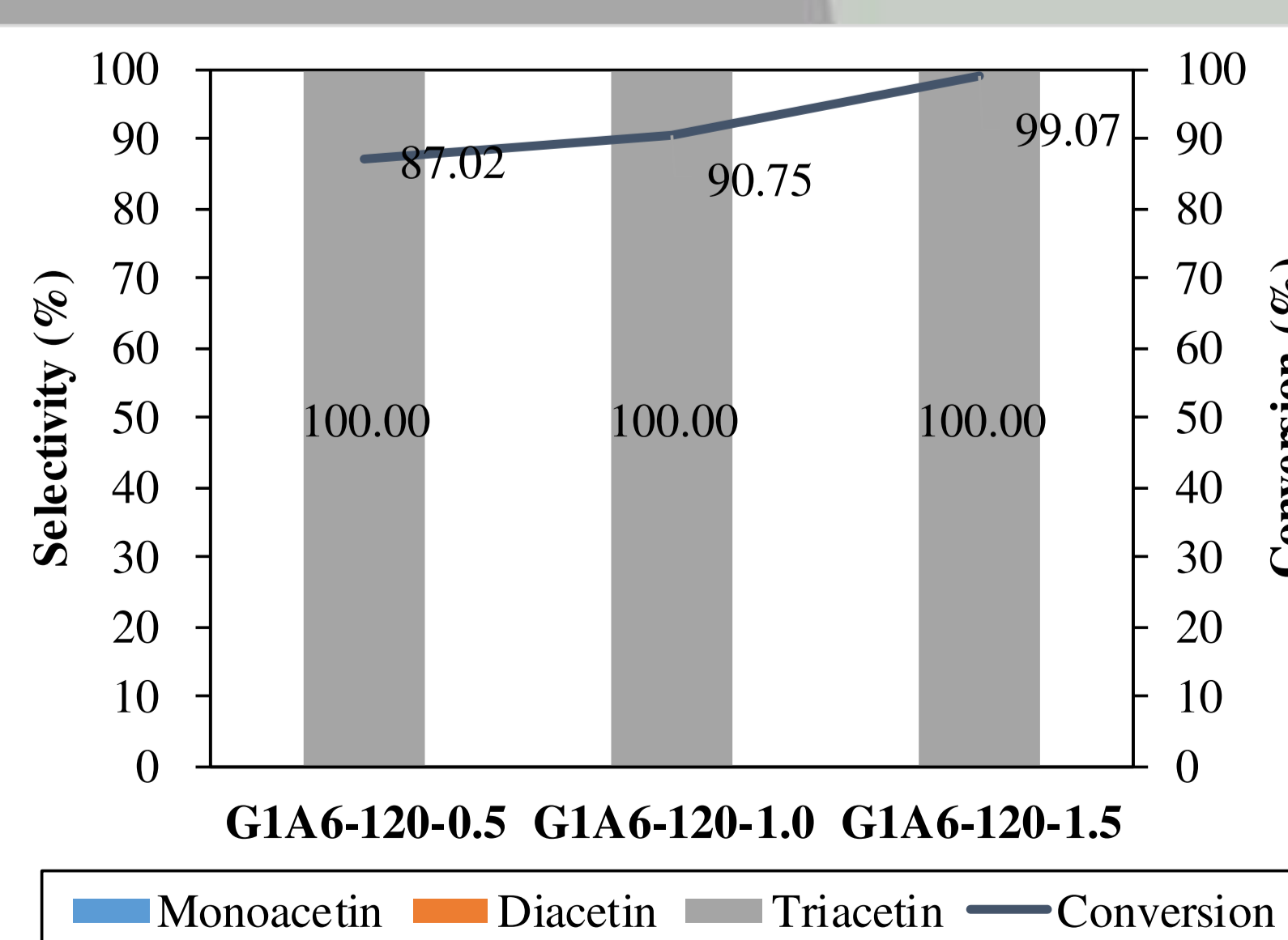


Fig. 4. Effect of silicotungstic acid catalyst amount on selectivity and conversion rate during glycerol acetylation.

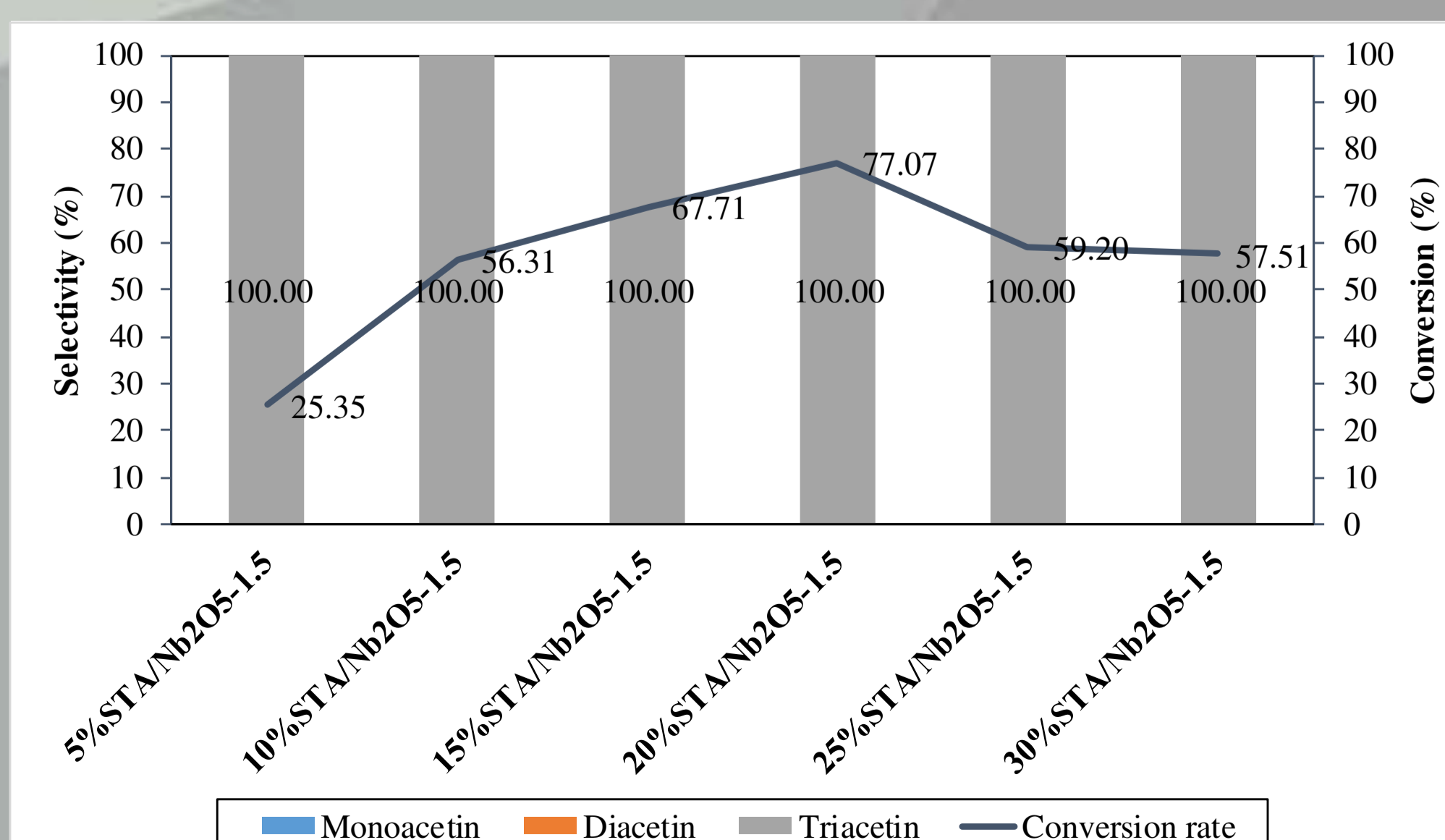


Fig. 5. Effect of STA content on selectivity during glycerol acetylation. Reaction conditions: reaction temperature: 120 °C; catalyst weight: 1.5g; glycerol to acetic acid mole ratio: 1:6.

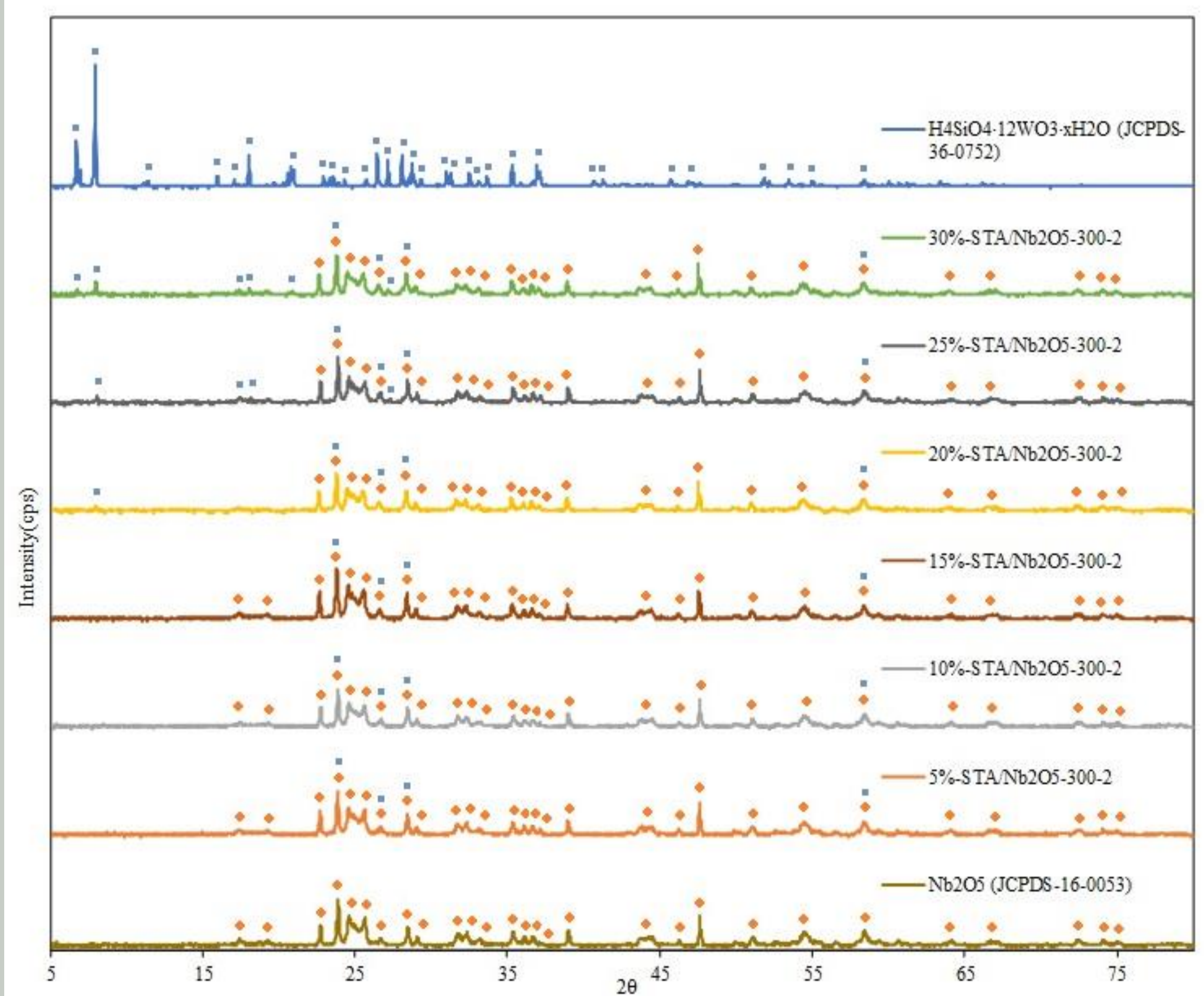


Fig. 6. XRD diffraction patterns of STA/Nb<sub>2</sub>O<sub>5</sub> in different STA content.

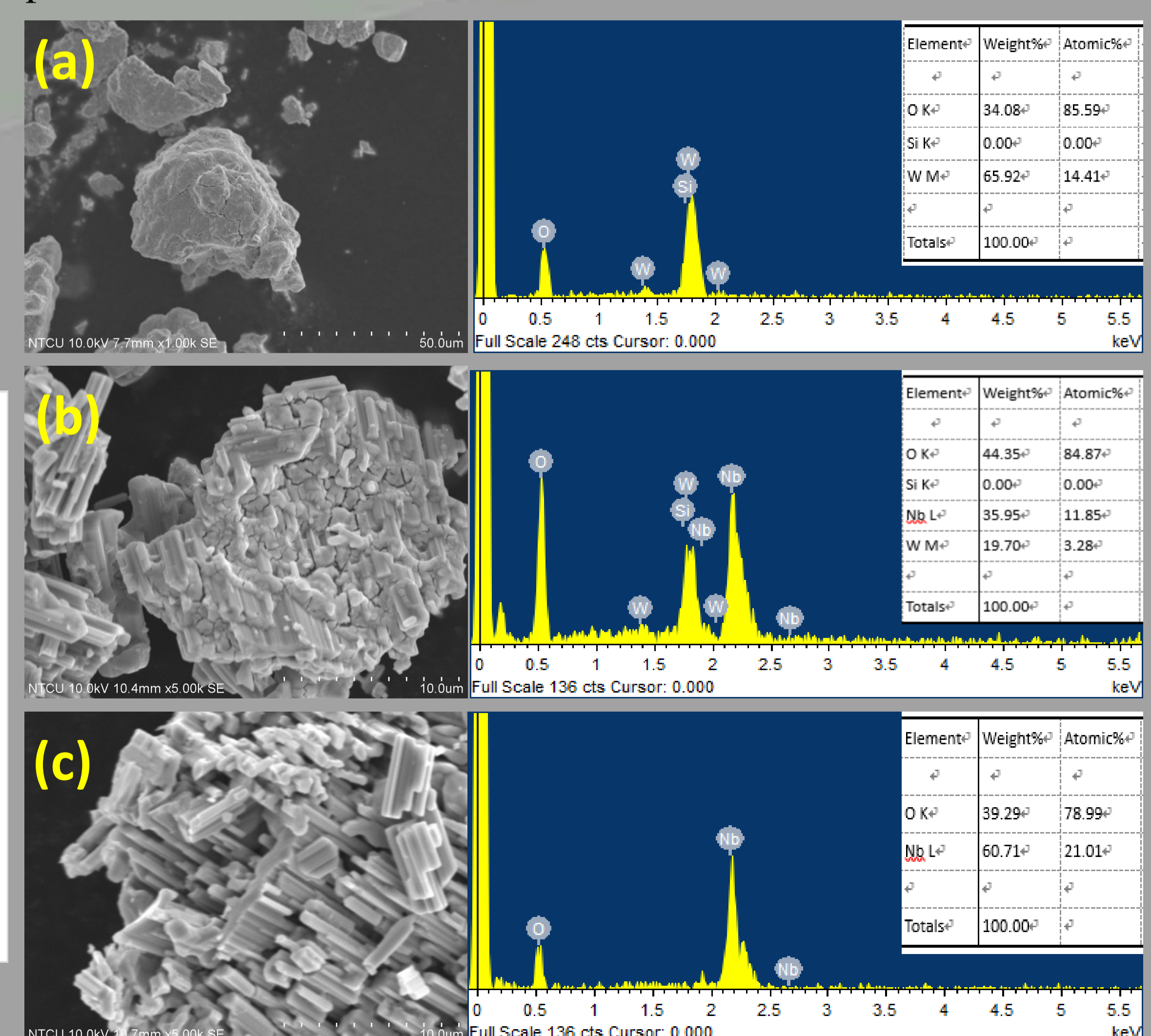


Fig. 7. SEM photograph and EDS elemental analysis of (a) STA (b) STA supported niobic acid (c) Niobic acid catalysts.

# Production of glycerol triacetate through esterification of glycerol using tungstophosphoric acid.

Cheng-Jhe Tsai<sup>1</sup>(蔡承哲), Jia-Hao Lin<sup>1</sup>(林佳豪), Yong-Ming Dai<sup>2</sup>(戴永銘) and Chiing-Chang Chen<sup>1\*</sup>(陳錦章)

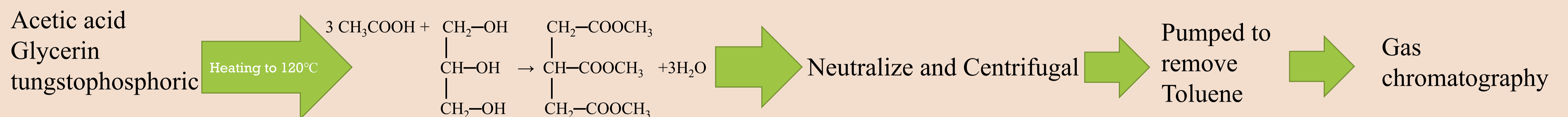
<sup>1</sup>Department of Science Education and Application, National Taichung University of Education

<sup>2</sup>Department of Chemical and Materials Engineering, National Chin-Yi University of Technology, Taichung 41170, Taiwan; ccchen@mail.ntcu.edu.tw\*

## Abstract

The rapid increase of biodiesel production has led to a wider availability of crude glycerol as a by-product in chemical industry. Esterification of glycerol can be a good alternative of glycerol produced by biodiesel. Glycerol triacetate (GTA) is an important chemical used in the production of foods and spices, and in printing and dyeing. The esterification of glycerol with acetic acid effectively takes place on acid catalysts, hence providing a promising way to transform glycerol into value added products. In this work, we study the esterification of glycerol with acetic acid over tungstophosphoric acid. The optimum conditions for the process include catalysts amount 0.5g, acetic acid to glycerol molar ratio 6:1, a reaction temperature of 120°C, and a reaction time at 1.5h. The catalyst exhibits the best catalyst performance with the maximum esteriacetin yield of 66.3%. The glycerol conversion is well correlated with the acidity of the catalysts. The selectivity during glycerol esterification not only depends on the nature of catalysts but also on reaction time. Different reaction parameters are studied and the optimum reaction conditions are established.

## Experimental section



## Results and Discussion

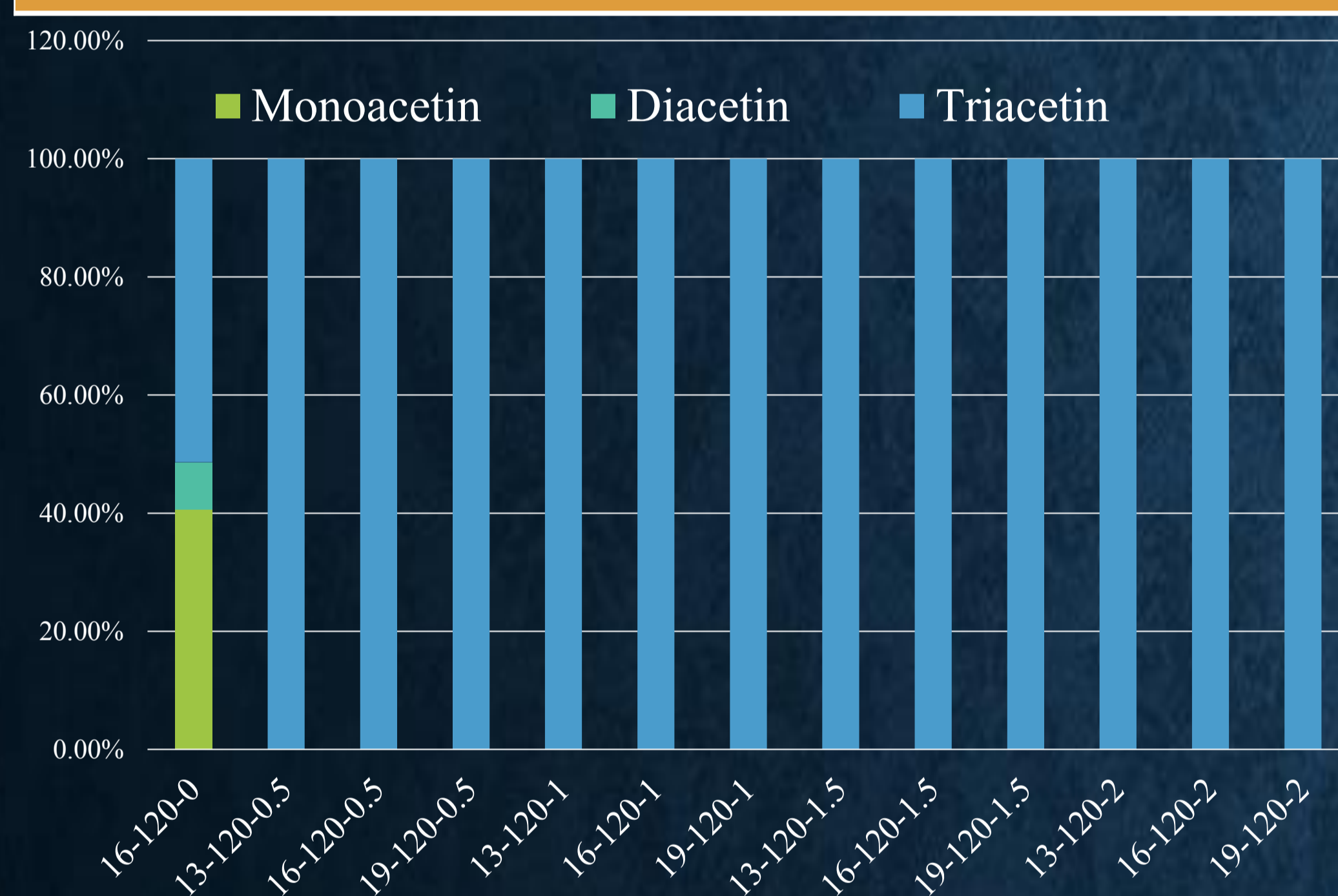


Fig.1 Proportional distribution diagram of products with different qualities of tungstophosphoric acid as catalyst

	Conversion rate		Conversion rate
16-120-0	19.06%	13-120-1.5	66.27%
13-120-0.5	20.25%	16-120-1.5	57.84%
16-120-0.5	47.86%	19-120-1.5	50.83%
19-120-0.5	48.67%	13-120-2	48.68%
13-120-1	35.91%	16-120-2	51.36%
16-120-1	42.93%	19-120-2	33.39%
19-120-1	46.97%		

Table.1 Conversion rate with different quality of tungstophosphoric acid as catalyst

	Conversion rate
13-100-0.5	30%
13-120-0.5	20.25%
13-150-0.5	29.43%

Table.2 Conversion rate at different temperatures

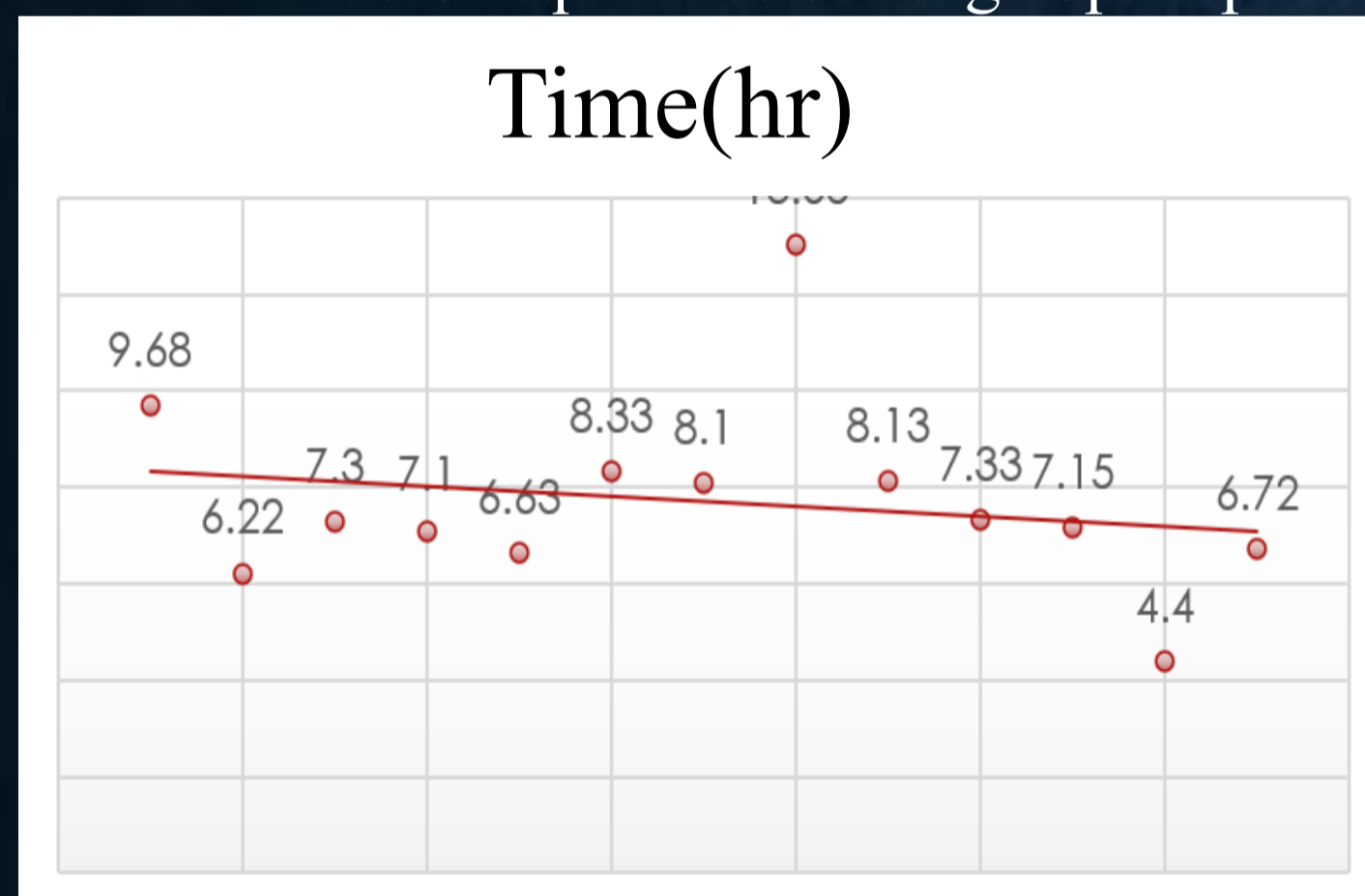


Fig.2 Reaction time

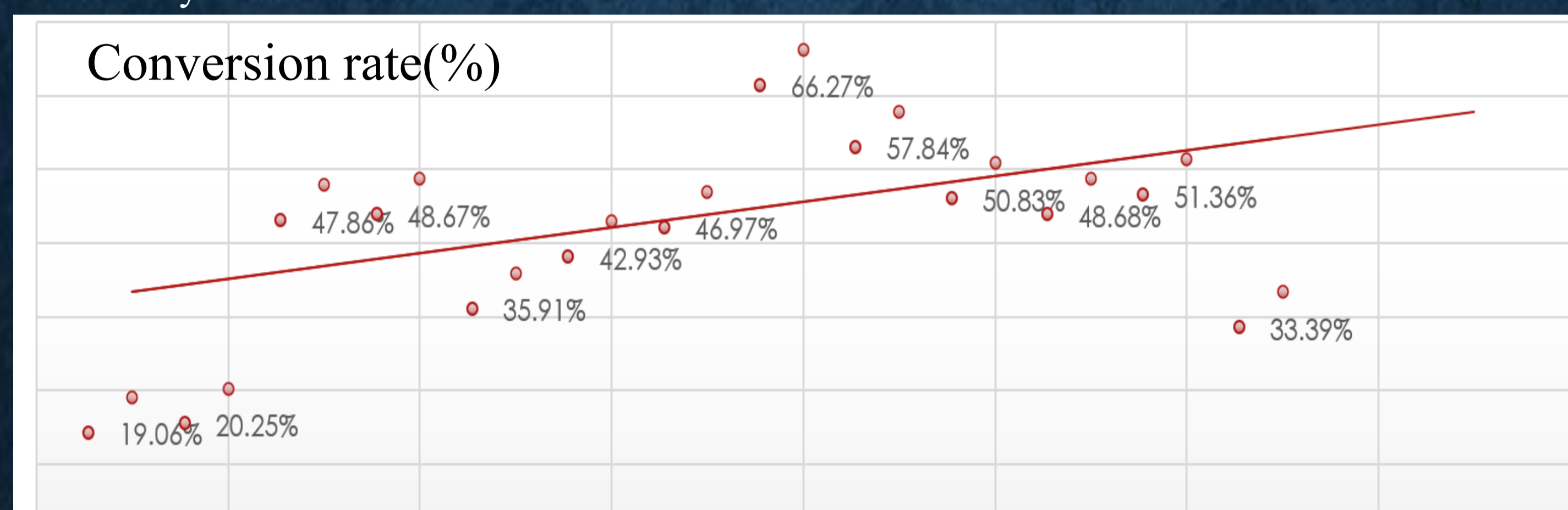


Fig.3 Conversion rate trend graph

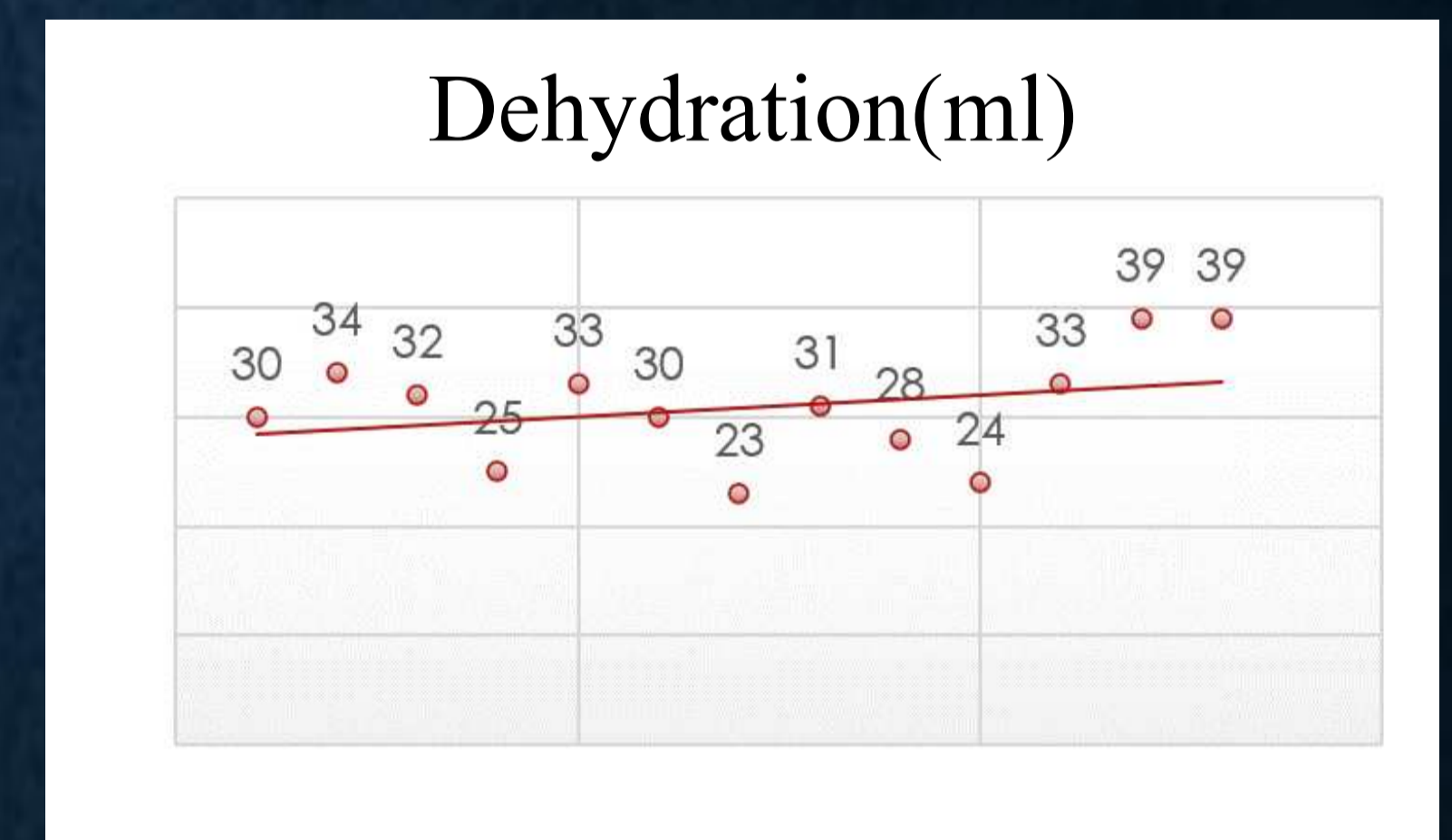


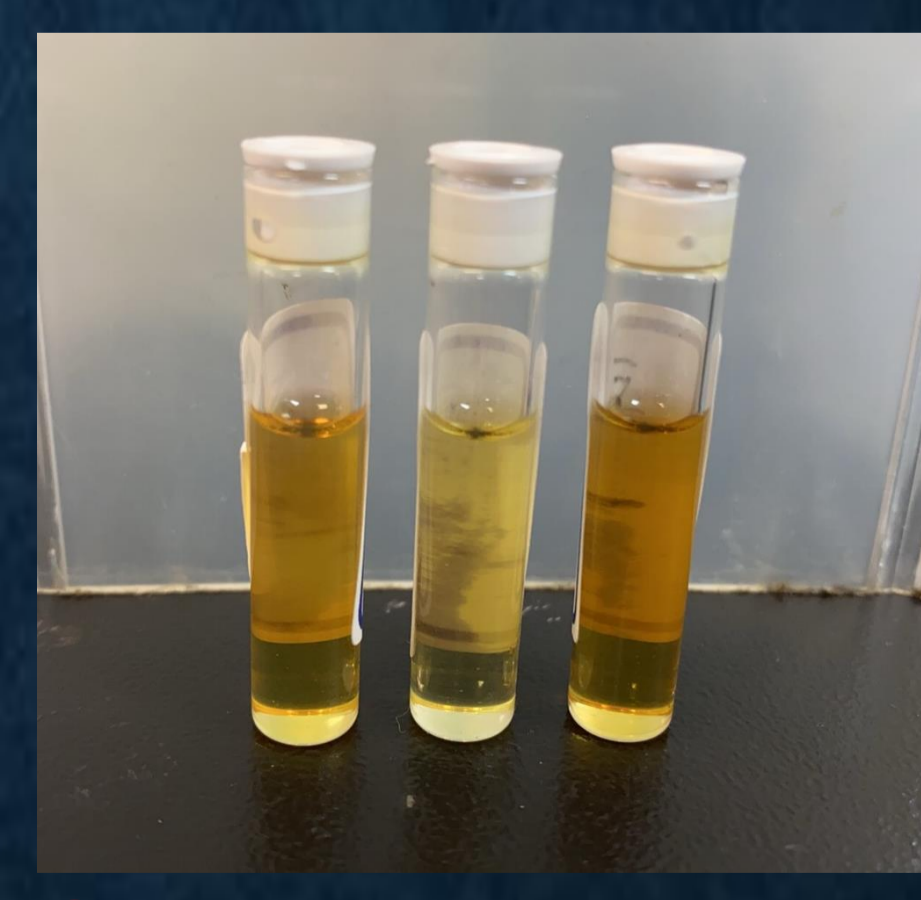
Fig.4 Amount of dehydration



Pic.1 120°C · 0.5g tungstophosphoric acid  
The ratios from left to right are 1:3, 1:6, 1:9



Pic.2 100°C · 0.5g tungstophosphoric acid  
And 150°C · 0.5g tungstophosphoric acid



Pic.3 120°C · 2g tungstophosphoric acid  
The ratios from left to right are 1:3, 1:6, 1:9



Pic.4 120°C · no added tungstophosphoric acid

## Conclusion

When tungstophosphoric acid is used as a catalyst for the reaction, the product selectivity can only be triacetin. When tungstophosphoric acid is added more, the reaction time tends to be short, and the conversion rate tends to increase. The ratio of glycerol to acetic acid is 1-3, and 1.5 g of tungstophosphoric acid has the highest conversion rate 66.27%. The blank reagent products without any tungstophosphoric acid are 40.64% Monoacetate, Diacetin 7.99% and Triacetin 51.37%.