Esterification of Acetic Acid and Ethanol for Ethyl Acetate Production by Vanadium Catalyst on Biochar Support

Viputthawat Suwannaphan[*] and Bunjerd Jongsomjit

Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Thailand

ABSTRACT

Ethyl acetate can be synthesized by Fisher esterification reaction using acetic acid and ethanol for raw materials with acid catalysts. In this study, we firstly developed the solid acid catalyst of V_2O_5 supported on biochars for this reaction. The use of biochar as support is very interesting since it is renewable. Experimentally, the vanadium (V) catalyst was prepared by the incipient wetness impregnation method with various V contents from 3, 6, and 9 wt%. The supports used were biochars derived from two sources including bamboo and palm. After calcination, all catalysts were characterized using various techniques SEM-EDX, FTIR, XRD, ammonia-TPD, and N_2 physisorption to determine the physicochemical properties. To perform esterification, the liquid phase reaction of ethanol and acetic acid was conducted in the batch reactor using ethanol: acetic acid molar ratio of 1.5:1 with a total volume of 50 ml and 1 wt% of solid catalyst based on weight of acetic acid. The reaction occurred at 80 ºC for 40 minutes. The product distribution was analyzed by gas chromatography to determine acetic acid conversion and ethyl acetate selectivity. It was found that 9 wt% V_2O_5/biochar catalyst exhibited the highest activity having acetic acid conversion of 72% with ethyl acetate selectivity of 45%. It revealed that metal leaching occurred during the reaction. However, this study shows the new insight that biochars can be used for support for V catalyst with promising results in the esterification.

Keyword: Esterification/ Biochar/ Chemical Engineering/ Ethyl acetate/ Vanadium catalytic

1. INTRODUCTION

Ethyl acetate is an important chemical reactant and solvent which is the key volatile organic compound (VOC)[1]. Ester has a structure consisting of R-COOR$^/$, where R and R$^/$ are both alkyl and allyl groups. Ester is generally prepared by heating carboxylic acids R-COOH and alcohol R$^/$-OH until water is extracted[2]. Fischer esterification is a main process in the industry for the synthesis of ethyl acetate, this reaction starts using ethanol and acetic acid by a homogeneous acid catalyst. In commercial is interesting vanadium pentoxide V_2O_5; oxovanadium catalytic chemistry which utilized for the oxidation of organic compounds ex alcohols, ketones, aldehydes, organohalides, and carboxylic acids. It uses molecular oxygen form oxidizing agent[3] which has good dispersion and catalytic activity[4]. In addition, the biochars, pyrolysis supports, have begun to be developed because a pore structure mechanism is created based on physicochemical properties and porosity properties, and is used as support for the catalyst in chemical reactions and reducing agents in metallurgy[5]. For Initiation, the metal was embedded into the carbon structure by using a wet impregnation and calcination process for generate catalyst. Then analyzing their various properties; functional groups, surface area, pore volume, pore diameter, and adsorption/desorption isotherms. Analysis of structure, crystallinity, physical properties, morphology of catalysts, elements of catalysts, and gas chromatography also were analyzed [6] [7] [8] [9]. The advantage of using a heterogeneous catalytic in an esterification reaction is that the product can be easily separated and reused [10]

----
*Corresponding Author: Viputthawat Suwannaphan
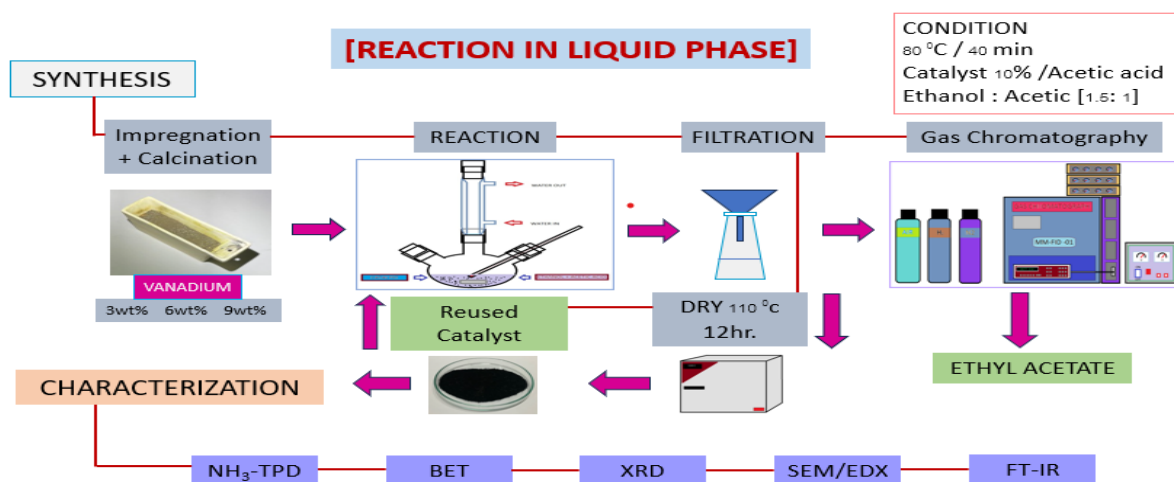E-mail address: 6470080221@student.chula.ac.th

Figure 1. methodology for ethyl acetate reaction by vanadium biochar support

2. METHODOLOGY

2.1 Preparation of catalyst

Pyrolysis biochar from bamboo and palm were used as precursors for metal catalytic supporters. The materials were treated by the Pyrolysis Method with nitrogen purge gas. The first impregnation method was applied to the precursor, ammonium metavanadate. Synthesized vanadium catalysts on bamboo biochar pyrolysis support by grinding biochars for powder. Prepare vanadium metal using 3wt% 6wt% and 9wt% of ammonium (1.4205 g. 2.9317 g. and 4.5426 g.) dissolved in water by stirring with a magnetic stirrer for 20 min. The suitable weight supports of bamboo and palm pyrolysis biochar were 19.3814 g. 18.7234 g. and 18.0220 g according to 3%, 6% and 9% then ammonium metavanadate solution was add into biochar, mix well, and bring it into the oven at 110°C overnight. Then the metal impregnation for fixing catalyst on the supports and calcination with condition 550°C. 5 hr and keep the catalyst away from moisture.

2.2 Catalytic Characterization

Catalysts were characterized by the actual amount of the metal on the support and also catalyst components before and after the reaction. Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM-EDX) scanned the formation of vanadium on the surface and the percent of metal loading. Crystallization of samples in which vanadium catalyst synthesis was detected by powder X-ray Diffraction (XRD). The nitrogen adsorption-desorption isotherm measured the specific surface area of vanadium impregnation on support biochar by the BET method which analyzed pore volume and pore diameter together according to analysis nitrogen adsorption isotherm. The acid strength was characterized by Ammonium Temperature-Programmed Desorption (NH₃-TPD chemisorption) and Fourier Transform Infrared Spectroscopy (FTIR) of numerous peaks suggesting the multifunctional structure.

2.3. Reaction

The esterification reaction was conducted in a batch reflux system. A 50 ml glass round bottom flask, with acetic acid and alcohol molar ratio for each reaction (1:1.5). The addition of synthetic catalysts (10wt%/acetic acid %wt) were added in reaction was stirred at 80°C for 40 min. Finally liquid samples after removing the catalyst by centrifugation and filtration. The ethyl acetate and remained substance were analyzed by gas chromatography.

$$\text{Conversion (\%)} = \left(\frac{\text{Ethanol in} - \text{Ethanol out}}{\text{Ethanol in}} \right) \times 100 \text{ or } \left(\frac{\text{Acetic Acid in} - \text{Acetic Acid out}}{\text{Acetic Acid in}} \right) \times 100$$

----
*Corresponding Author: Viputthawat Suwannaphan
E-mail address: 6470080221@student.chula.ac.th

$$\text{Selectivity (\%)} = \frac{\text{Ethyl acetate} \times 100}{\text{All Product}}$$

$$\text{Yield of Ethyl acetate (\%)} = \frac{\text{Molar Ethyl acetate produced} \times 100}{\text{Molar Acetic Acid in}}$$

3. RESULTS AND DISCUSSION

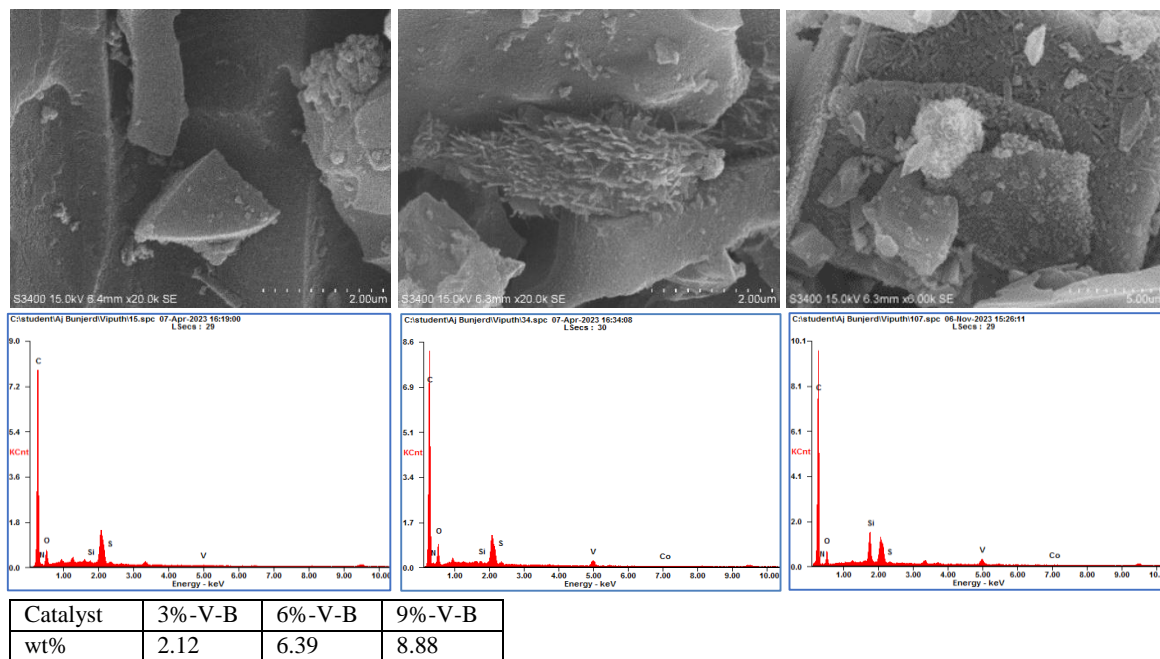### *3.1 Scanning electron microscope (SEM) and Energy dispersive X-ray spectroscopy (EDX)*

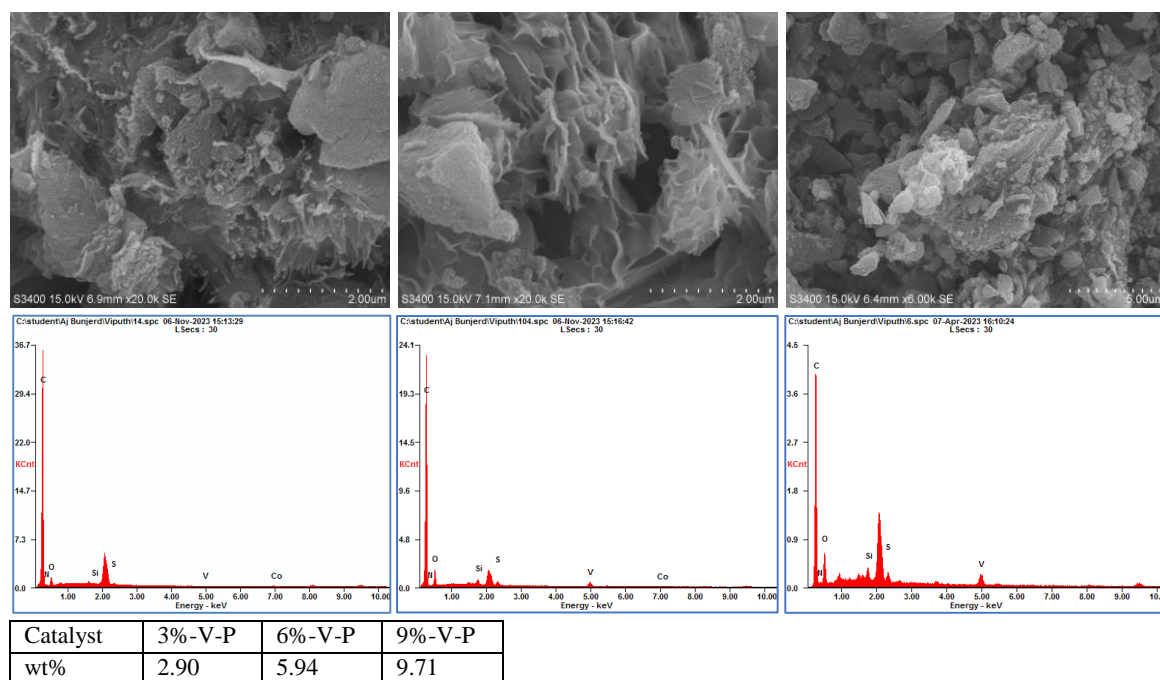| Catalyst	3%-V-B	6%-V-B	9%-V-B
wt%	2.12	6.39	8.88

Figure 2. (SEM EDX) of 3%-V-B, 6%-V-B and 9%-V-B

Catalyst	3%-V-P	6%-V-P	9%-V-P
wt%	2.90	5.94	9.71

Figure 3. (SEM EDX) of 3%-V-P, 6%-V-P and 9%-V-P

----

*Corresponding Author: Viputthawat Suwannaphan
E-mail address: 6470080221@student.chula.ac.th

Metal distribution on the support from the analysis of SEM-EDX images, it was found that the vanadium on the surface and in the pores from the impregnation process and crystal sintering caused the oxygen bonding of vanadium metal and O vacancy [V=O]. Both biochar roughness surface position were raised by the dispersing formation of vanadium metal, which was very important and related to the vacancy position on both biochar surfaces. The crystal lattice by metal loading and calcination at 550°C was prepared for a reaction. In Figures 2 and 3 the characterization of the covering metal found the impregnated crystalline on the surface. The dispersion crystal plane caused increases in the surface area on the support by SEM image which was not to determine metal scattering because the disorder occurs the agglomeration which vanadium cluster was discovered that arrangement depended on many factors such as the preparation step, O vacancy catalyst properties, metal cluster, metal-support co-binding surface vacancies, temperature, and percent metal loading distribution by the EDX method according to the experiment.
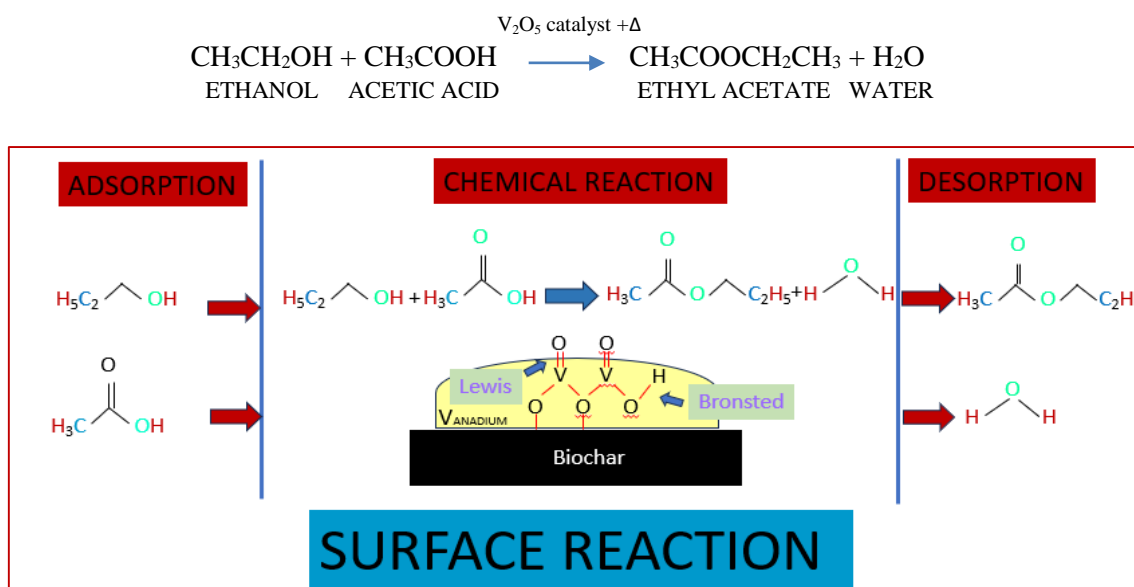
$$CH_3CH_2OH + CH_3COOH \xrightarrow{V_2O_5 \text{ catalyst} +\Delta} CH_3COOCH_2CH_3 + H_2O$$

ETHANOL   ACETIC ACID   ETHYL ACETATE   WATER

Figure 4. Vanadium catalyst on surface reaction for ethyl acetate production by esterification

3.2 Conversion and Yield of Ethyl Acetate

Table 1. Result Conversion and Yield of Fresh Catalyst and Reused Catalyst.

CATALYST	ETHYL ACETATE	ACETIC CONVERSION	SELECTIVITY	YIELD ETHYL ACETATE
FRESH	(g)	%	%	%
3%-V-B	3.43	31	6.9	10.83
6%-V-B	6.36	55	12.7	20.05
9%-V-B	10.43	72	20.9	32.89
3%-V-P	3.71	48	7.4	10.68
6%-V-P	6.51	39	13.0	20.51
9%-V-P	10.20	51	20.4	32.17
REUSED	(g)	%	%	%
3%-V-B	2.97	79	5.9	8.55
6%-V-B	4.66	61	9.3	13.43
9%-V-B	6.51	44	13.0	18.76
3%-V-P	2.79	88	5.4	7.80
6%-V-P	5.85	50	11.7	16.85
9%-V-P	6.34	42	12.7	18.26

_%-V-B ; percent loading Vanadium on Bamboo support.

_%-V-P ; percent loading Vanadium on Palm support.

----

*Corresponding Author: Viputthawat Suwannaphan
E-mail address: 6470080221@student.chula.ac.th

The result of esterification with gas chromatography (Table 1). This presents the efficiency of acetic acid conversion to ethyl acetate reached 72% and the product yield 32.89% (10.43 g.). By reaction conditions, the result of using the reused catalyst showed that percent acetic acid substance conversion was increased while ethyl acetate yield was decreased with volume of 44% effect to yield remained 18.76% (6.51g. ethyl acetate) respectively. So the activity of vanadium can be recovered and reused 1 time as a catalyst in a new reaction, but it was not possible to avoided the leaching effect of the metal.

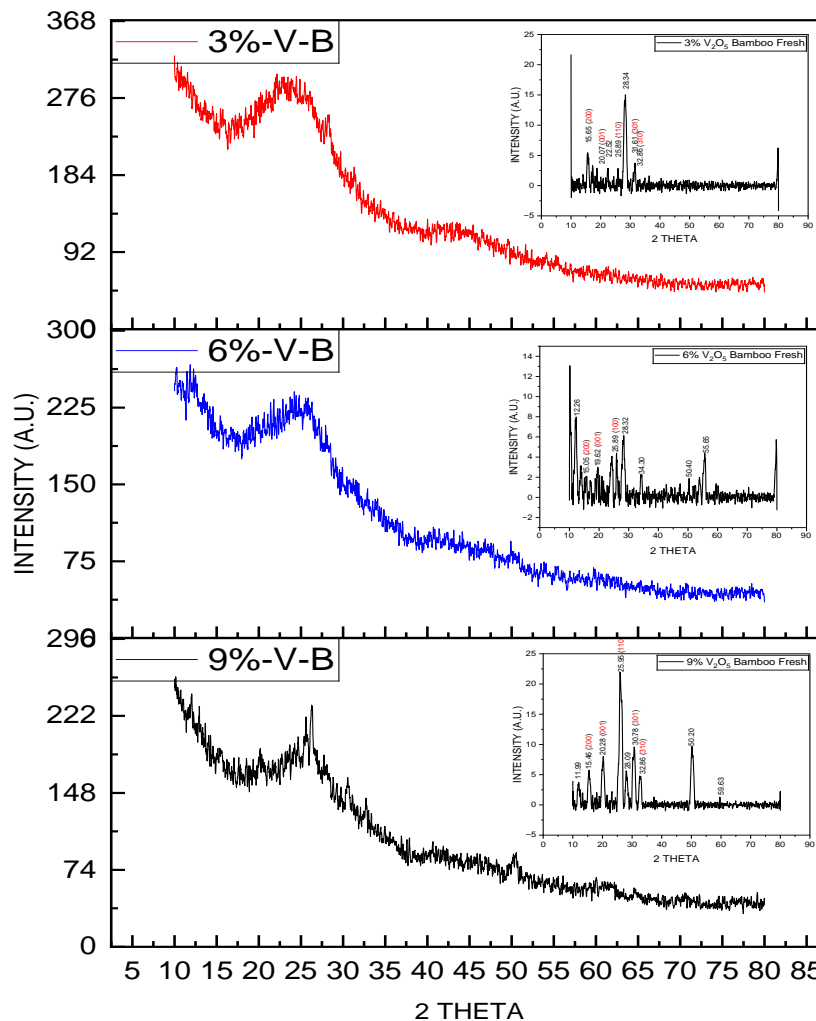### 3.3 X-ray diffraction (XRD) pattern of Catalyst

Figure 5. XRD Pattern of 3%-V-B, 6%-V-B and 9%-V-B

XRD results from calcination 550^0C method, diffraction of V_2O_5 peak $2\theta = 15.46^0$, 20.28^0, 23.16^0, 26.95^0, 30.78^0, 32.86^0 of [9%-V-B] is crystallization for high conversion in this method and diffraction of V_2O_5 peak $2\theta = 20.75^0$, 26.49^0, 31.81^0 and 49.85^0 of [9%-V-P]. The metal shape related to the lattice plane of the crystals is as follows $15^0(200)$, $20^0(001)$, $26^0(110)$, $31^0(400)$, $32^0(011)$, $34^0(311)$, $41^0(002)$, $45^0(411)$, $47^0(600)$[11]. The results of the V_2O_5 phase crystallinity on bamboo present the various plane shapes of three-dimensional space. The major plane observed by x-ray founded a lattices V_2O_5 parameter was orthorhombic species with lattices constants ($a = 11.484$ A˚ $b = 3.556$ A˚ $c = 4.357$ A˚) which referred by JCPDS card no. 41-1426 the peaks $2\theta = 15.49$, 20.35, 26.23 and 31.09 correspond to (200), (001), (101), (110) [12] formed formation and chemical interaction between vacancy groups on the biochar surface with V=O functionals. Thus the plane and arrangement of crystals on the biochar surface 20^0 (001) were investigated as not outstanding peaks from any metal loading on bamboo support and (6%-V-P and 9%-V-P) but were found obvious in 3%-V-P. The lattice $26^0(110)$ originates from a silica oxide[13]

---
*Corresponding Author: Viputthawat Suwannaphan
E-mail address: 6470080221@student.chula.ac.th

compound in material that was found in both biochar supports vanadium loading. Another result $41^0(002)$ lattice of graphite[14] was not occur in this catalyst. From observation the curve of 2-theta without smoothness may be caused by different chemical structures on the heterogeneous surface and vacancy of both biochar supports may affect XRD analysis.
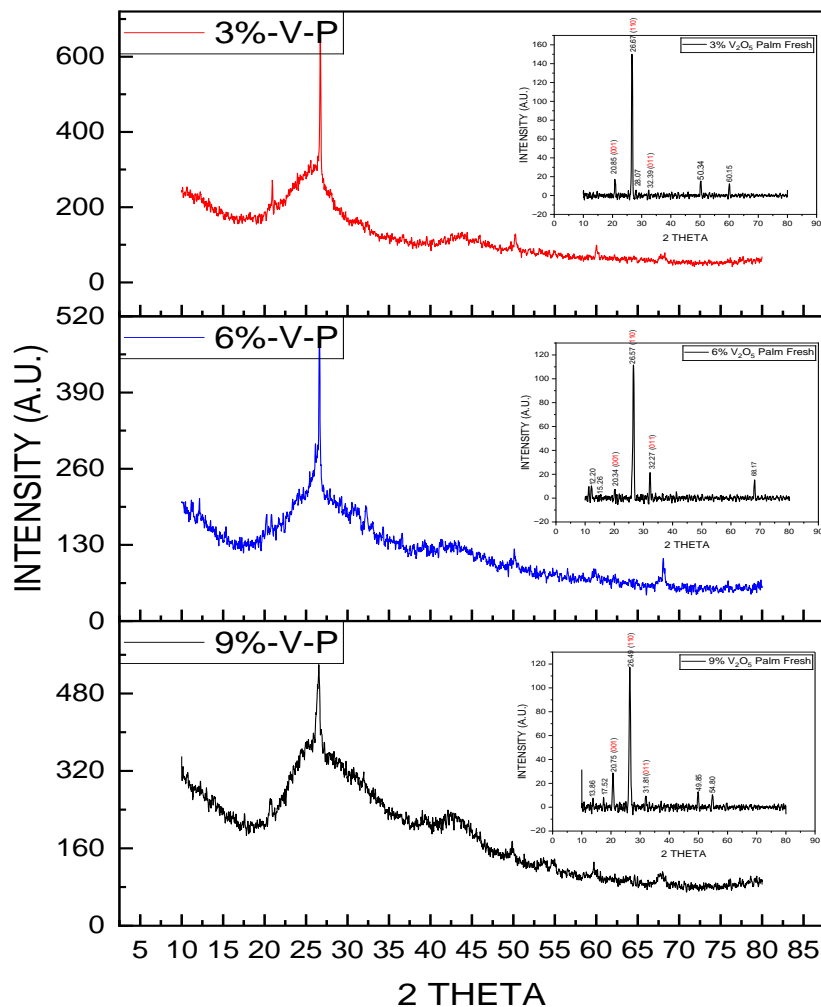

Figure 6. XRD Pattern of 3%-V-P, 6%-V-P and 9%-V-P
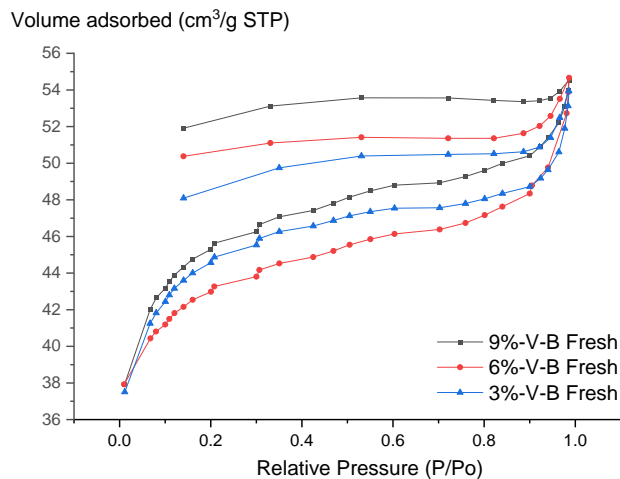
3.4 N_2 Physisorption (BET) pattern of Catalyst

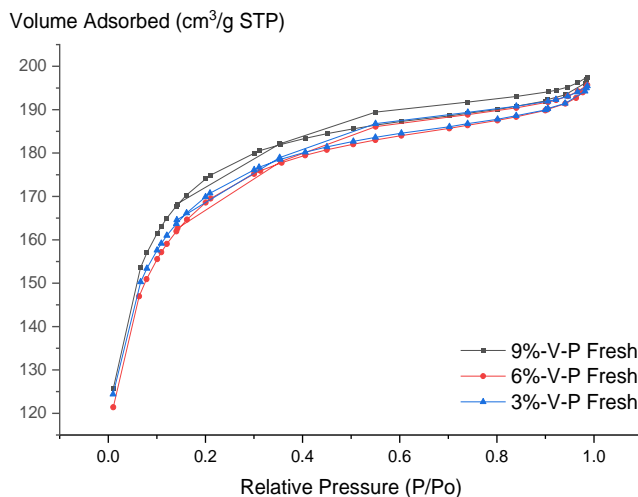

Figure 7. BET Fresh Catalyst 3%-V-B, 6%-V-B and 9%-V-B

----
*Corresponding Author: Viputthawat Suwannaphan
E-mail address: 6470080221@student.chula.ac.th

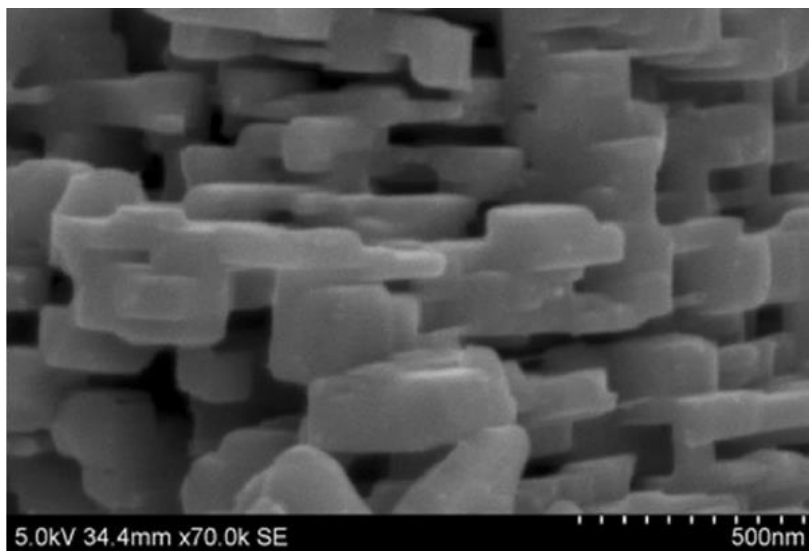**Figure 8.** BET Fresh Catalyst 3%-V-P, 6%-V-P and 9%-V-P

Figure 9. FESEM Image lattice of 1 g. V_2O_5 nanostructure grown by 550 C decomposition and agglomerate structure. [16]

Table 2. Result Physical Adsorption Fresh Catalyst

CATALYST	BET m^2/g	Pore volume cm^3/g	Pore diameter A
Fresh Catalyst			
3%-V-B	70.26	0.0413	24.07
6%-V-B	157.69	0.0835	21.70
9%-V-B	179.65	0.0947	21.10
3%-V-P	524.07	0.2717	20.72
6%-V-P	584.60	0.3007	20.65
9%-V-P	605.61	0.3046	20.24

----
*Corresponding Author: Viputthawat Suwannaphan
E-mail address: 6470080221@student.chula.ac.th

Table 3. Result Physical Adsorption Reaction 1 Catalyst

CATALYST	BET m^2/g	Pore volume cm^3/g	Pore diameter A
Reused 1 Catalyst			
3%-V-B	17.32	0.0199	46.00
6%-V-B	53.32	0.0376	28.22
9%-V-B	77.35	0.5476	28.31
3%-V-P	423.73	0.2244	21.18
6%-V-P	503.75	0.2687	21.33
9%-V-P	546.74	0.2879	21.03

BET Analysis is according to the surface area of 9% vanadium on bamboo was 179.65 m^2/g. Pore volume 0.0947 cm^3/g. Pore diameter by adsorption isotherm 21.1 A˚ was present hysteresis loop type IV isotherm of mesoporousity was excellent in size between 2-50 nm. Results found that the different surfaces of the support materials did not affect the conversion, and different loading of vanadium metal on bamboo and palm support when going through the pyrolysis process creates pore volume. Results from BET analysis, surface area values, found that palm is higher than bamboo which went through the pyrolysis process, it has a surface area of less than 100 m^2/g. while the palm is put through a process of increasing porosity, palm biochar has a high surface area in the range of 100-500 m^2/g. The area present increased by increase metal loading which the crystalline bonding together, are more bonding support. Refer to Figure 8. The lattice of V$_2$O$_5$ was decomposition and agglomeration after impregnation and used a temperature 550 C. The formation of nanorods increased the area on the surface and pore volume [16]. So 9%-V-B and 9%-V-P metal loading had BET (m^2/g) and pore volume more than other conditions. This reaction causes the leaching of metal from the supports. As a result, found the surface area decreases when recycled catalyst. Then the ethyl acetate decreased productivity. However, the utilization metal-biochar is more advantageous because it is less poisonous than strong acid chemicals. A pore diameter is the micropore range. The surface area of palm is rougher than the surface area of bamboo so palm biochar has more surface area than bamboo. The vacancies of biochars are interactions between metals which increasing loading of vanadium may affect the surface roughness and the plane crystalizes.

3.4 Ammonium Temperature-Programmed Desorption (NH$_3$-TPD) pattern of Catalyst

The strength of the acid sites of vanadium/biochar from peak shows the peak result of a strong acid by NH$_3$-TPD profiles was 400-700 °C. Acidity increases when added percent vanadium metal. Acid sites were important on the surface of the catalyst because the surface reaction was the main step for the conversion of a substance to a product. Bronsted site was a chemical species that was able to donate hydrogen cation H$^+$ to carboxylic acid to cause in the next step nucleophilic addition when an electron from alcohol was added to the center carbon. Hydrogen and electron transfer were important to activate esterification when the bronsted site increases. There is a tendency to increase the reaction forward due to the rate of protonation being related to the acidity of the protonation species that result from NH$_3$-TPD profiles curve from the experiment showing vanadium metal capacity in the high range of strong acid correlation with a high rate of protronation. Oxovanadium was related to the Lewis acid site which had a high electronegativity number. It had a strong acid by addition O functional which calculated by Equation pK$_a$ = - log K$_a$ when K$_a$ = acidity constant.
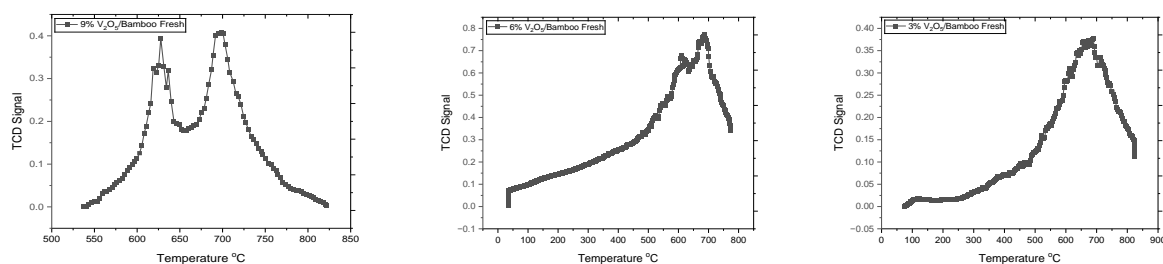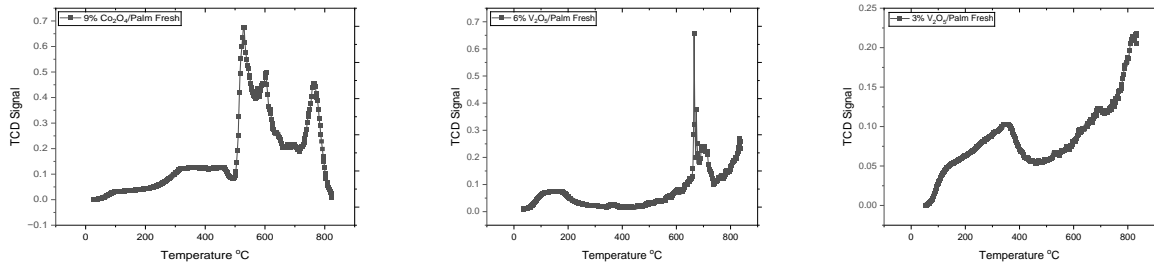

Figure 10. TPX 3%-V-B, 6%-V-B and 9%-V-B

----
*Corresponding Author: Viputthawat Suwannaphan
E-mail address: 6470080221@student.chula.ac.th

Figure 11. TPX 3%-V-P, 6%-V-P and 9%-V-P

3.5 *Fourier Transform Infrared Spectroscopy method*
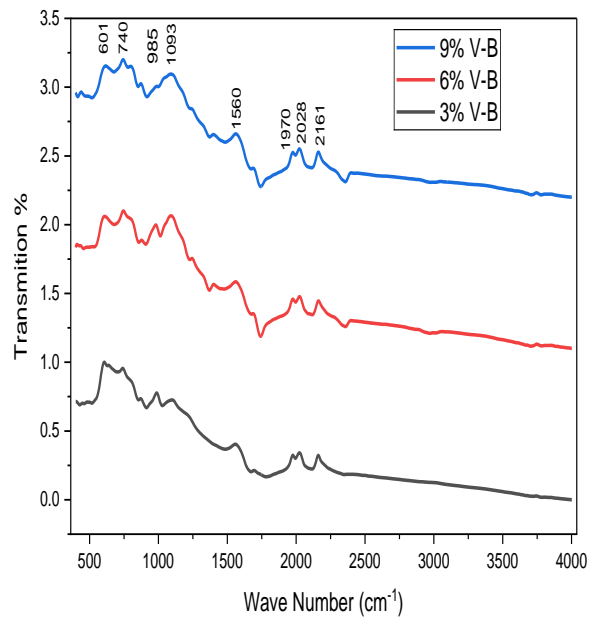
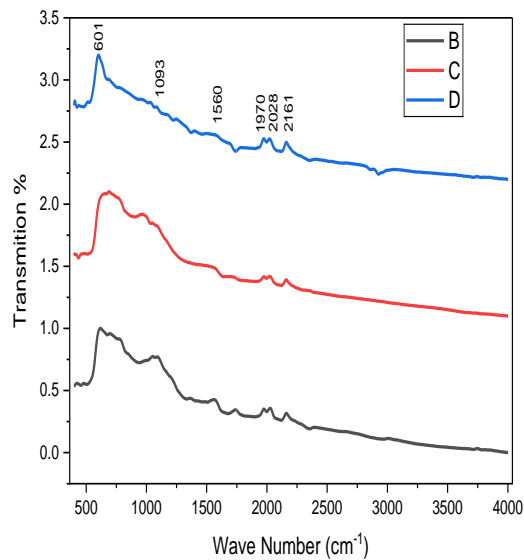**Figure 12.** FT–IR study of 3%-V-B, 6%-V-B and 9%-V-B

Figure 13. FT–IR study of 3%-V-P, 6%-V-P and 9%-V-P

----
*Corresponding Author: Viputthawat Suwannaphan
E-mail address: 6470080221@student.chula.ac.th

Adsorption of metal on the support surface using Fourier Transform Infrared Spectroscopy for studies vanadium catalyst structure on the biochar supports and surface organic functional groups. The stretching vibrations vanadium oxide (V_2O_5) were observed in the spectrum of peak region at position V=O (985 and 1093 cm^{-1}). FTIR spectrum of pure vanadium oxide showed a sharp band at 1020 cm^{-1} due to the V=O stretching vibration in vanadium oxide (1100-850 cm^{-1})[15]. While the stretching vibrations of (bridge oxygen) V–O–V (1038 cm^{-1}) [16]. Chemisorption by the oxide of vanadium [V=O] in order to vacancy region reacted with the vacancy position (result Table 4) on biochar surface together by impregnation and calcination method. his bonding was an important reused catalyst by mechanism of metal to hold up from unpredictable leaching conditions resulting in decreased vacancy region [V=O] on surface reaction.

Table 4. Biochar surface functional groups [14]

Vibration	Absorption band	Functional
O–H	2,900 cm^{-1}	phenolic groups
C=C	1,564 cm^{-1}	aromatic structure
O–H bending or C–O	1,425 cm^{-1}	phenol
C–H bending	1,384–1,402cm^{-1}	alkanes/alkyl
–C–OH bending	1,063 cm^{-1}	polysaccharides
C–H bending	874 cm^{-1}	*B*-glucosidic linkage
O–Si–O	461 cm^{-1} /800 cm^{-1}	silica

4. CONCLUSIONS

1. Based on study for vanadium supported by bamboo biochar used for esterification reaction was found that 9 wt% V_2O_5/biochar catalyst exhibited the highest activity having an acetic acid conversion of 72% with ethyl acetate selectivity of 45% by liquid phase reaction

2. The results of catalyst synthesis by impregnation and calcination method found the vanadium crystalline on surface biochar which detected the by catalytic characterization and found the activity of vanadium can be recovered and reused as a catalyst in a new reaction, but occurred leaching effect of the metal from catalyst.

3. The catalyze in a heterogeneous reaction of vanadium-biochar was propered for produce ethyl acetate because it can be easily separated and nontoxic also reduced pollution virtual green chemical and renewable.

Acknowledgement

References

[1] M. A. Cliff, G. J. Pickering. (2006). Journal of Wine Research, 17(1), 45-52.

[2] Hangx G., Kwant G., Maessen H., Markusse P., and Urseanu I. (2010) Kinetic Study of Esterification Reaction. Al-Khwarizmi Engineering Journal, 6(2), 33-42.

[3] Ryan R Langeslay , David M Kaphan. (2001) Christopher L Marshall 1, Peter C Stair 1, Alfred P Sattelberger , Massimiliano Delferro. (2019) Catalytic Applications of Vanadium: A Mechanistic Perspective. Chem Rev, 119(4), 2128-2191.

[4] Xie Z, Yan B, Kattel S, Lee JH, Yao S, Wu Q. (2018) . Dry reforming of methane over CeO2- supported Pt-Co catalysts with enhanced activity. Applied Catalyst B, 236, 280–293.

[5] Gohr, M.S.; Abd-Elhamid, A.; El-Shanshory, A.A.; Soliman, H.M. (2021) Adsorption of cationic dyes onto chemically modified activated carbon: Kinetics and thermodynamic study. J. Mol. Liq, 346(3), 118227.

[6] H. Liu, C. Ye, Y. Xu and Q. Wang. (2022) Effect of Activation condition and iron loading content on the catalytic cracking of toluene by biochar. Energy Journal, 247, 123409.

[7] Bijay N. Pattanaik, Hiren C. Mandalia. (2011) ETHYL ACETATE: PROPERTIES, PRODUCTION PROCESSES AND APPLICATIONS - A REVIEW. IJCRR, 3(12), 23-40.

----

*Corresponding Author: Viputthawat Suwannaphan
E-mail address: 6470080221@student.chula.ac.th

[8]   Sheng Li, Guojie Zhang , Jiming Wang , Jun Liu, Yongkang Lv. (2021) Enhanced activity of Co catalysts supported on tungsten carbide-activated carbon for CO2 reforming of CH4 to produce syngas. International Journal of Hydrogen Energy, 56, 28613-28625.

[9]   Beata Krzyżyńska, Anna Malaika, Karolina Ptaszyńska, Agnieszka Tolińska, Piotr Kirszensztejn, Mieczysław Kozłowski. (2020) Modified activated carbons for esterification of acetic acid with ethanol. Diamond & Related Materials, 101, 107608.

[10]   Lehmann, J. and Joseph, S. (2012) Biochar for environmental management: an introduction in Biochar for Environmental Management. Science and Technology, 183–205.

[11]   K. M. Shafeeq, V. P. Athira1, C. H. Raj Kishor, P. M. Aneesh. (2020) Structural and optical properties of V_2O_5 nanostructures grown by thermal decomposition technique, 126(586), 1-6.

[12]   Yinlu Sun, Zhiping Xieb and Yanwei L. (2018). Enhanced lithium storage performance of V2O5 with oxygen vacancy. RSC Adv, 69, 39222 – 39786.

[13]   Hisashi Miyata, Kozo Fujii, Takehiko Ono and Yutaka Kubokawa. (1989) Fourier-transform Infrared Investigation of Structures of Vanadium Oxide on Various Supports. Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 12, 3901 – 4366.

[14]   Yali Liu, Xiurong Zhao, Jianli Li, Dan Ma, Runping Han. (2012). Characterization of bio-char from pyrolysis of wheat straw and its evaluation on methylene blue adsorption. J. Desalination and Water Treatment, 46, 115–123.

[15]   Balaga Viswanadham. (2023) Facile Synthesis of Ethyl Acetate over ZrO2.TiO2 Mixed Oxide. Journal of Chemistry, 1-9.

[16]   A. Venkatesan, N. Krishna Chandar, S. Arjunan, K.N. Marimuthu,R, Mohan Kumar and R. Jayavel. (2013) Structural, morphological and optical properties of highly monodispersed PEG capped V2O5 nanoparticles synthesized through a non-aqueous route. Materials Letters, 91, 228-231.

----
*Corresponding Author: Viputthawat Suwannaphan
E-mail address: 6470080221@student.chula.ac.th