

The authors thank the Reviewers for excellent comments on the manuscript. The itemized response to each comment is given below and the manuscript is modified accordingly. These modifications helped to improve the quality of the manuscript. The discussion added to the manuscript are based on the Reviewers' comments and are highlighted in the rebuttals below. Also, please note that the title of the manuscript is slightly shortened.

Reviewer #2

1. The novelty and the advantages of this manuscript did not express cleared. Great efforts must be made to explain the novelty of your study, especially in introduction.

Our response: We thank the Reviewer for this comment. Based on this input, new information is added to the revised manuscript (please see lines 81-84 on page 2) as follows:

To our knowledge, no study has explored the potential of MAP as a support material for immobilized HPW and for its application in biodiesel production. Besides, a novel and simple hydrothermal method was used for synthesis of MAS, which has not been investigated before.

2. The English writing is good, but there are some errors need to correct.

Our response: We thank the Reviewer for this comment. Based on the comments, the manuscript is modified to make it free from errors.

3. In the part of "Results and Discussion", more correlation of catalyst structure and its performance could be established.

Our response: This input has helped to improve the quality of the manuscript. New information is added to the revised manuscript (Please see lines 202-205, 239-243, and 349-351 on pages 5, 8, and 16, respectively), which are given as follows:

The BET data confirm the suitability of these support materials due to their high surface area and appropriate porosity for HPW immobilization, which are important physical properties for enhancing catalytic activity.

The suitable incorporation of Keggin anion on the surface of support materials verified by XRD, can be attributed to the difference in the pore size of the support materials (γ -Al₂O₃= 7.5 nm, MAP= 4.7 nm, and MAS= 5 nm) and Keggin anion (1.2 nm). This can facilitate the uniform dispersion of HPW on the surface of support materials preventing agglomeration of HPW.

As HPW supported catalysts are not sensitive to water, the formation of water during the reaction has no adverse effect on their catalytic activity, which can be maintained during the process.

4. In the methodology, no information has not been provided regarding the lower p/p₀ range from which the measurement starts. The pore size distribution provided in Figure 2 starts from approx. 2.5 nm, although the pores relevant for the accessible SSA for the supercapacitors starts from c.a. 1 nm, so the assessment does not include them due to application of the too-high p/p₀ initial point.

Selection of the too high value of the initial p/p_0 point leads to an artificial shift of the pore size distribution, hence not reliable as well as information obtained from it. Was that considered during the selection of the pressure range for the N_2 adsorption assessment? Also, was the CO_2 adsorption considered as the micropore assessment method?

Our response: The initial point of p/p_0 , in which the measurement started, was around 0.05 for all the materials. The primary objective of this work was to use inorganic mesoporous catalysts for esterification and transesterification reactions. Because of the nature of our reactants, microporous materials introduce diffusion limitations in the catalyst and therefore are avoided. The theory which best explains pore structure in the mesopore range (2-50 nm) is the Barrett–Joyner–Halenda (BJH) model. The BJH method is based on the Kelvin equation and corrected for multilayer adsorption. However, due to the quadrupolar moment in nitrogen, any pores smaller than 1 nm cannot be accurately characterized by this model.

CO adsorption technique is most reliable for carbon-based materials like activated carbon or multiwalled carbon nano-tubes and was therefore not considered for this study.

5. To determine the BET surface area, the amount of the material used for the experiment is affecting the surface area calculations. Can the authors disclose the exact amount of each material for BET analysis?

Our response: For each BET measurement, 0.2 g of catalyst sample was used (Please see lines 153 on page 4 in modified manuscript).

6. BET results: why the surface area of HPW/MAP is quite decreased compared to MAP, but the average pore size is increased? The author needs to pay attention in this result.

Our response: We thank the Reviewer for this comment.

Larger average pore size of HPW/MAP compared to that of MAP could be due to the occupation or blockage of the mesopores of the support with HPW anions. Similar finding is reported for TPA anchored to two mesoporous aluminosilicate (MAS-7, MAS-9) in the literature [30]. Please see lines 184-187 on page 5.

30. A. Kurhade, J. Zhu, Y. Hu, and A. K. Dalai, "Surface Investigation of Tungstophosphoric Acid Supported on Ordered Mesoporous Aluminosilicates for Biodiesel Synthesis," *ACS Omega*, vol. 3, pp. 14064–14075, 2018.

7. Considering on the Figure 1b, the full isotherm of HPW/MAP is weird compared to others impregnated samples. It looks like this material has collapsed on its structure rather than pore blocking by HPW.

Our response: Our response is explained in the manuscript for all the HPW support materials (Please see lines 196-200 on page 5).

After impregnation of HPW on MAP, the general shape of HPW supported MAP isotherm was considerably alike with MAP and hysteresis loops remained in the same region of relative pressure

similar to other impregnated samples. This shows that the loading of HPW on MAP does not affect its mesoporous structure.

8. The pore size distribution in Figure 2b and 2c is weird, this is due to the point for full isotherm is not appropriated. The authors need to check the point.

Our response: The initial point of p/p_0 , in which the measurement was made, is around 0.05 for all the materials.

9. What kind of isotherms that the author uses for calculation in this manuscript?

Our response: This is explained in the manuscript (Please see lines 190-191 on page 5) as follows:

All samples indicate IV type of isotherms based on IUPAC classification that shows the mesoporous structure of these catalysts [31].

31. W. Roschat, T. Siritanon, B. Yoosuk, T. Sudyoardsuk, and V. Promarak, "Rubber seed oil as potential non-edible feedstock for biodiesel production using heterogeneous catalyst in Thailand," *Renew. Energy*, vol. 101, pp. 937–944, 201.

10. The condition and amount of material used for the experiment are affecting the total acidity. Can the authors disclose the exact amount of each material for this analysis?

Our response: For each TPD experiment, 0.04 g of catalyst sample was used (Please see 164 on page 4).

11. The baseline is also important. How does the authors calculate the total acidity? The authors could also provide the information for calculation because the total amount is very unusual.

Our response: For this work, according to the cited article as follow; the total acidity of the materials was calculated by integrating the curve from TPD data and comparing the data with those of standard samples in temperature range from 100 °C to 700 °C. This is added in lines 263-265 on page 10 in the revised manuscript.

12. The type of acid needs to analyze in deep detail and could provide in this manuscript. The acidity of bare HPW could also provide for comparison.

Our response: We thank the Reviewer for this comment. New explanations on the types of acids and Pyridine FTIR analysis are added to the manuscript (Please see lines 306-315, and 217-229 on page 13, and 8, respectively).

The existence of both Lewis and Bronsted acid sites on the solid acid catalysts are essential in developing simultaneous esterification and transesterification reactions for biodiesel production. Lewis acid catalyst is favorable to ease the transesterification reaction, while for facilitating esterification reaction, Bronsted acidic sites play a significant role. Regarding the HPW supported catalysts used in this research study, alumina and the synthesized support materials provide Lewis acid sites, and HPW provides the Bronsted acidic sites. Therefore, immobilization of HPW on

these support materials that possess both Bronsted and Lewis acidic sites is favorable for biodiesel production through simultaneous esterification and transesterification reactions [16, 40].

16. A. Gaurav, S. Dumas, C. T. Q. Mai, and F. T. T. Ng, "A kinetic model for a single step biodiesel production from a high free fatty acid (FFA) biodiesel feedstock over a solid heteropolyacid catalyst," *Green Energy Environ.*, vol. 4, no. 3, pp. 328–341, 2019.
40. J. Gupta, M. Agarwal, and A. K. Dalai, "An overview on the recent advancements of sustainable heterogeneous catalysts and prominent continuous reactor for biodiesel production," *J. Ind. Eng. Chem.*, 2020.

Pyridine FTIR was carried out to identify the type of acid sites (Bronsted and Lewis acids) in synthesized HPW/MAS, HPW/MAP, and HPW/ γ -Al₂O₃ catalysts. As illustrated in Fig., five characteristic peaks at 1446, 1487, 1537, 1600, and 1634 cm⁻¹ were observed in all supported HPW catalysts. The band at 1446 cm⁻¹ is related to the hydrogen bonded pyridine which correlates to Lewis acid sites. The band at 1487 is attributed to the presence of both Bronsted and Lewis acid sites. The characteristic peaks at around 1537 and 1634 correspond to Bronsted acid sites, while the peak at approximately 1600 can be attributed to the bond formed between pyridine and Al³⁺ Lewis acid sites of all the catalysts. The obtained results confirm the presence of both types of acid sites in the synthesized catalysts [30, 33].

30. A. Kurhade, J. Zhu, Y. Hu, and A. K. Dalai, "Surface Investigation of Tungstophosphoric Acid Supported on Ordered Mesoporous Aluminosilicates for Biodiesel Synthesis," *ACS Omega*, vol. 3, pp. 14064–14075, 2018.
33. A. Kurhade, J. Zhu, A. K. Dalai, J. Zhu, Y. Hu, and A. K. Dalai, "Meso-Structured HPW-MAS - 7 and HPW-MAS - 9 Composite Catalysts for Biodiesel Synthesis from Unrefined Green Seed Canola Oil," *Fuel Process. Technol.*, vol. 3, no. August, pp. 14064–14075, 2018.

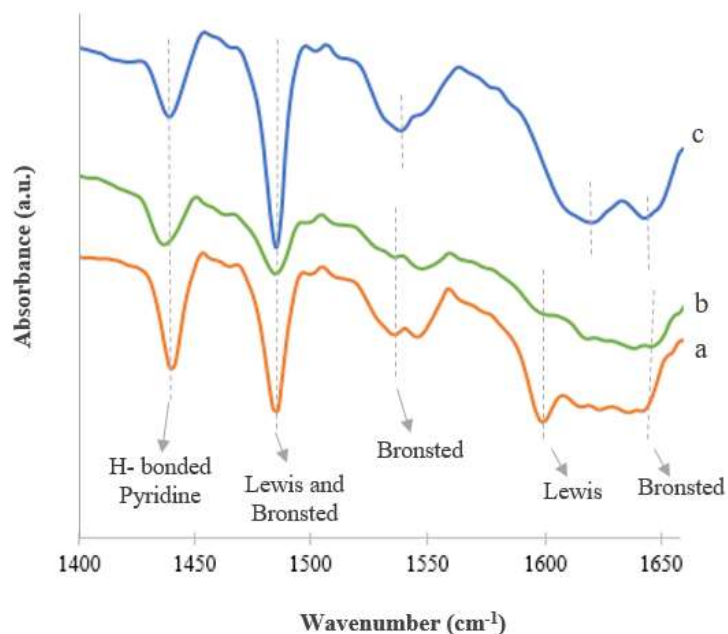


Figure 3. FTIR spectra after pyridine desorption of (a) HPW/MAS, (b) HPW/MAP, and (c) HPW/ γ -Al₂O₃.

13. XRD results: it is interesting provide the low angle XRD data for confirm the characteristic of mesoporous types.

Our response: We thank the Reviewer for the suggestion. We consider providing low angle XRD data for our future works.

14. What is the active species on the surface of each catalyst? The author must identify and provide (may be used XPS for analysis) because this work is focused to study the enhancement of catalysts after by HPW.

Our response: The presence of HPW on support material was verified successfully by XRD results. Besides, TEM images confirm the suitable dispersion of HPW on the support materials. Furthermore, ICP-OES characterization technique was added to identify the metal concentration in all the HPW supported catalysts and the information was added to the manuscript and Table 2 (Please see lines 175-177 on page 4). This is also given below:

The textural features of support materials and HPW supported catalysts obtained from BET analysis and the concentration of tungsten (W) in HPW supported catalysts obtained from ICP-OES technique are represented in Table. 2.

Table 2. Textural features and metal concentration in catalysts.

Catalyst	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore size (nm)	ICP-OES W (wt. %)
γ -Al ₂ O ₃	297	0.82	7.5	-
HPW/ γ -Al ₂ O ₃	195	0.50	7.2	23.2
MAP	581	0.14	4.7	-
HPW/MAP	111	0.08	5.1	22.5
MAS	703 ± 9	0.99 ± 0.03	5.0 ± 0.7	-
HPW/MAS	504	0.68	4.4	22.8

15. To improve the quality of the manuscript, the comparison in HPW immobilization on the MAS and MAP need to include

Our response: The comparison between the performances of HPW/MAS and HPW/MAP is explained based on the characterizations provided in this manuscript. Accordingly, more information is added in conclusions (lines 371-375 on page 17) as follows:

Both synthesized support materials of MAP and MAS provide high surface area and suitable porosity for immobilization of HPW, however, according to the results obtained, using HPW/MAS led to a better biodiesel yield (82.3%) compared to HPW/MAP (78.3%), which can be attributed to the higher surface area and acidity of HPW/MAS with 504.3 m²/g and 1111 μ mol/g, respectively.

16. It is not clear in Table 2 and 3, why some sample the author provides some error but not all for those samples?

Our response: In this research, same instrument is used for all the materials, so the error is likely to be close for all of them. Therefore, only a few samples were examined several times to obtain the error.

17. The comparison of the results obtained in this paper should be compared with similar work already published. What is the conclusion and originality of this work compared with already published one?

Our response: The information on the similar works is added both in the introduction (lines 70-79 on page 2) and also in catalytic activity section (lines 333-336 and Table 4 on pages 14 and 15, respectively). This is also given below.

Various support materials were employed for immobilization of heteropoly acids for different applications. Srilatha et al. [26] studied the esterification reaction of palmitic acid using TPA supported on ZrO_2 catalysts. This resulted in ~95% conversion of palmitic acid to biodiesel with better reusability confirming strong interaction between TPA and ZrO_2 . Kumbar et al. [27] reported the use of TiO_2 supported TPA as a suitable solid acid catalyst in alkylation process. It is reported that titanium oxide improved the catalytic activity, which attributed to the strong attachment between TiO_2 and the active phase. $\text{H}_4\text{SiW}_{12}\text{O}_{40}\text{-SiO}_2$, synthesized by one-step method, was used for biodiesel production [28]. $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ was successfully loaded inside the mesoporous channels of -SiO_2 which enhanced reusability and diffusion of reactants.

26. K. Srilatha, N. Lingaiah, P. S. Sai Prasad, B. L. A. Prabhavathi Devi, and R. B. N. Prasad, "Kinetics of the esterification of palmitic acid with methanol catalyzed by 12-tungstophosphoric acid supported on ZrO_2 ," *React. Kinet. Mech. Catal.*, vol. 104, no. 1, pp. 211–226, 2011.
27. S. M. Kumbar, G. V. Shanbhag, F. Lefebvre, and S. B. Halligudi, "Heteropoly acid supported on titania as solid acid catalyst in alkylation of p-cresol with tert-butanol," *J. Mol. Catal. A Chem.*, vol. 256, no. 1–2, pp. 324–334, 2006.
28. K. Yan, G. Wu, J. Wen, and A. Chen, "One-step synthesis of mesoporous $\text{H}_4\text{SiW}_{12}\text{O}_{40}\text{-SiO}_2$ catalysts for the production of methyl and ethyl levulinate biodiesel," *Catal. Commun.*, vol. 34, pp. 58–63, 2013.

Table 4 shows the reaction conditions of some similar work that used HPW supported catalysts for biodiesel production. Accordingly, the amount of catalyst used in this study is less than that in most of the other studies, which can have a significant impact on the cost of production.

Table 4. Tungstophosphoric supported catalysts for biodiesel production.

Catalyst	Reaction conditions	Conversion or yield (wt. %)	Ref.
HPA/MK700	Temperature= 200 °C, reaction time= 2 h, alcohol to oil molar ratio = 10, catalyst loading= 10 wt. %	Conversion= 83.0	[29]
$\text{H}_4\text{SiW}_{12}\text{O}_{40}\text{-SiO}_2$	Temperature= 65 °C, reaction time= 6 h, catalyst loading= 20 wt. %	Yield= 73.0	[28]
TPA/SBA-15	Temperature= 65 °C, reaction time= 8 h, alcohol to oil molar ratio= 8, catalyst loading= 0.3 g	Conversion= 86.0	[41]

TPA/zeolite H β	Temperature= 60 °C, reaction time= 6 h, alcohol to oil molar ratio= 20, catalyst loading= 30 wt. %	Conversion= 84.0	[42]
TPA/SnO ₂	Temperature= 65 °C, reaction time= 200 min, alcohol to oil molar ratio= 14, catalyst loading= 1 g	Conversion= 81.2	[43]
HPW/ γ -Al ₂ O ₃	Temperature= 200 °C, reaction time= 7 h, alcohol to oil molar ratio= 20, catalyst loading= 3 wt. %	Yield= 64.2	This study
HPW/ MAP	Temperature= 200 °C, reaction time= 7 h, alcohol to oil molar ratio= 20, catalyst loading= 3 wt. %	Yield= 78.3	This study
HPW/ MAS	Temperature= 200 °C, reaction time= 7 h, alcohol to oil molar ratio= 20, catalyst loading= 3 wt. %	Yield= 82.3	This study

29. K. Yan, G. Wu, J. Wen, and A. Chen, "One-step synthesis of mesoporous H₄SiW₁₂O₄₀-SiO₂ catalysts for the production of methyl and ethyl levulinate biodiesel," *Catal. Commun.*, vol. 34, pp. 58–63, 2013.
28. L. H. O. Pires et al., "Esterification of a waste produced from the palm oil industry over 12-tungstophosphoric acid supported on kaolin waste and mesoporous materials," *Appl. Catal. B Environ.*, vol. 160–161, no. 1, pp. 122–128, 2014.
41. N. Narkhede, V. Brahmkhatri, and A. Patel, "Efficient synthesis of biodiesel from waste cooking oil using solid acid catalyst comprising 12-tungstosilicic acid and SBA-15," *Fuel*, vol. 135, pp. 253–261, 2014.
42. A. Patel and N. Narkhede, "12-tungstophosphoric acid anchored to zeolite H β : Synthesis, characterization, and biodiesel production by esterification of oleic acid with methanol," *Energy and Fuels*, vol. 26, no. 9, pp. 6025–6032, 2012.
43. K. Srilatha, C. Ramesh Kumar, B. L. A. Prabhavathi Devi, R. B. N. Prasad, P. S. Sai Prasad, and N. Lingaiah, "Efficient solid acid catalysts for esterification of free fatty acids with methanol for the production of biodiesel," *Catal. Sci. Technol.*, vol. 1, no. 4, pp. 662–668, 2011.

Furthermore, the novelty of this work compared to the other studies is highlighted in the introduction (Please see lines 81-84 on page 2). Please see the text earlier to edit the following lines.

To our knowledge, no study has explored the potential of MAP as a support material for HPW immobilization and its application for biodiesel production. Besides, the employment of HPW/MAS for biodiesel production in which a novel hydrothermal synthesis method was used for MAS synthesis, has not been investigated before.