

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 Comments:

Reviewer #3

The authors studied the esterification and transesterification of unrefined green seed canola oil over HPW/MAP, HPW/MAS, and HPW/ γ -Al₂O₃ catalysts in a 100 mL Parr reactor at 200 °C with 600 rpm for 7 h under 4 MPa. The authors characterized synthesized catalysts by BET, XRD, NH₃-TPD, TGA, and TEM analyses. The highest biodiesel yield (82.3%) was achieved over the HPW/MAS catalyst, which possessed the highest acidity and surface area. I think that the topic of this investigation is in the scope of MDPI Catalysts and can be interesting for the journal audience. At the same time, I have found some weaknesses in the manuscript body. In my opinion, this work can be considered for publication in MDPI Catalysts only after major revision. Please find my comments below.

Our response: We thank the Reviewer for the comments. Based on the comments, the manuscript is modified.

1. The title must be corrected/improved. The authors did not mention the HPW/ γ -Al₂O₃ Moreover, I recommend the authors decrypt or exclude abbreviations in the title.

Our response: The title was changed to “Comparative catalytic performance study of 12-tungstophosphoric heteropoly acid supported on mesoporous supports for biodiesel production from unrefined green seed canola oil”

2. The authors must mention in the abstract obtained product (biodiesel).

Our response: Thanks to the Reviewer for this comment. The “biodiesel” product is added in the abstract of the revised manuscript

3. Did the authors analyze the real catalyst composition? I think this information should be provided in Table 2. ICP-OES or XRF analyses can be useful.

Our response: We thank the Reviewer for this comment. 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 \pm 9	0.99 \pm 0.03	5.0 \pm 0.7	-
HPW/MAS	504	0.68	4.4	22.8

4. How the authors can explain the average pore size increasing for the HPW/MAP catalyst compared to MAP (Table 2), while for the other HPW catalysts it was observed opposite effect?

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 kinds of 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.

5. How the pore size distribution curves were built? Based on adsorption or desorption volume? This information must be presented in the manuscript.

Our response: The information is added to the manuscript (Please see lines 209-210 on page 6) as follows.

Pore size distribution curves (Fig. 2) is derived using BJH technique based on adsorption volume data.

6. The carbon and/or mass balance must be provided.

Our response: Since the objective of this study is to obtain the maximum yield of biodiesel, the amount of unreacted materials and by-products were not calculated. However, to response to the Reviewer's comments, regarding simultaneous esterification and transesterification reactions using HPW/MAS as the best catalyst, the amounts of unrefined green seed canola oil and methanol used as reactants were 35 g, and 25.6, respectively. The obtained amount of methyl ester (biodiesel) was 28.8 g (yield: 82.3%). Therefore the remaining amount which is 31.8 g contain the unreacted reactants (methanol and oil), and by products (water and glycerol).

7. The authors should decrypt the type of percent for the obtained product yield.

Our response: The wt. percentage of biodiesel yield was obtained based on the weight of methyl ester over weight of oil phase multiplied by 100. Please see lines 147-148 on page 4 as follows:

$$\text{Ester yield (\%)} = (\text{weight of methyl ester} / \text{weight of oil phase}) \times 100$$

8. I recommend the authors compare their achieved catalytic results with well-known literature data in a table format and include it in the Results and Discussion section.

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.

9. How the authors can explain decreasing of total acidity (Table 3) over the HPW/Al₂O₃ catalyst while other HPW supported catalysts showed reverse results?

Our response: The difference between the acidity of γ -Al₂O₃ compared to HPW/ γ -Al₂O₃ is less than one percent. After HPW immobilization, the total acidity does not have any significant change for HPW/MAS and HPW/MAP, but for all of them the weak acidity increased to moderate acidity as shown in Table 3, indicating the higher acidity for all the HPW supported catalysts in the range of 300- 500 °C compared to their related bare support material.

10. How the authors can make a statement about Bronsted acidity based on NH₃-TPD? For these conclusions, the authors should utilize a Pyridine-DRIFTS technique.

Our response: Thanks to the Reviewer for mentioning this point. Based on TPD ammonia, only the acidity of the catalysts can be determined and we have removed the statement of Bronsted acidity, which was an error. Pyridine FTIR analysis was added to the manuscript (Please see lines 217-229 on page 8) to show the types of active sites (Bronsted and Lewis acid) as follow:

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.

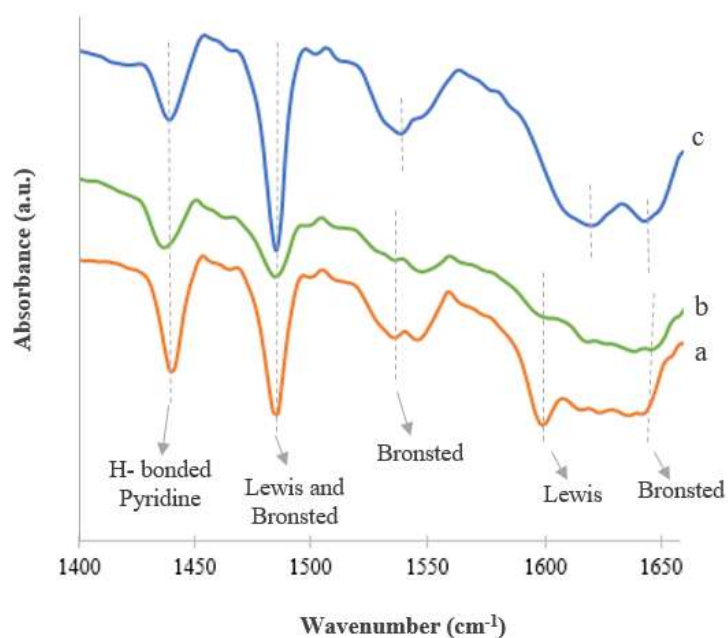


Figure 3. FTIR spectra after pyridine desorption of (a) HPW/MAS, (b) HPW/MAP, and (c) HPW/ γ -Al₂O₃.

11. What about the Lewis acid sites (LAS)? Why did the authors exclude LAS from the discussion? This must be explained. Moreover, the authors mentioned Lewis site in the proposed mechanism of HPW immobilization on MAS.

Our response: More information are added about Lewis acid sites and its application in our study. Also, Pyridine FTIR analysis is added to the manuscript (Please see lines 306-315 on page 13) as follows:

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 the 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.

12. The authors said: "According to them, the intensity of peaks in the range of 100-300 °C, which is related to the mild Bronsted acidity". What about the weak acid sites in this temperature range? Why did not the authors discuss it? This needs to be elucidated.

Our response: Following explanation is added to the manuscript (Please see lines 258-265 on page 10).

Three temperature intervals of 100-300 °C , 300-500 °C , and 500-700 °C were used for this analysis in Table 3, which can be categorized into mild acidic sites, medium and strong acidic sites, respectively. The acidity strengths of all HPW supported catalysts were related mainly to the range of 150 to 500 °C representing medium acidic sites. However, there is presence of weak acidic sites (in the range of 100 to 150 °C) for all the catalysts.