A MINERAL ACID CATALYZED ACETALIZATION OF FURFURAL TO ACETALS AS A BIO-RENEWABLE FUEL ADDITIVES

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ABSTRACT
Furfuraldehyde is a renewable and promising platform chemical, which is originated form lignocellulosic biomass that can be converted into value added chemicals such as biochemicals and biofuel additives. As the structural formula of furfural belongs a very important and reactive functionality (C=O) carbonyl group. Which can oxidize, reduced, condensed and many more functional group interconversions for generation of value-added chemicals. So, in present work we have synthesized derivatives of acetals from furfural and higher alcohols in presence of 2-3 drop of mineral acid.(Alcohols: 1-methanol,1-ethanol,1-propanol,1-butanol,1-pentanol,1-hexanol,1-heptanol and 1-octanol). And the synthesized products were confirmed by ^{1}HNMR and GCMS analysis.

Keywords: Acetalization, Mineral acid, Higher Alcohols, Biofuel additives, Acetals

INTRODUCTION
The regular consumption of petroleum resources and the world energy sources, so according to web chain of demand and supply the biomass valorization is one of the important tools to renew the resources via organic transformation of different process like oxidation, reduction esterification, acetalization of biomass derived compounds. So, these are the alternative protocols for the generation biofuel additives from biomass [1-4] the various application of renewable resources and biomass derived stuffs which is non-edible, non-consumable or partially consumables so it can be utilized for regeneration of resources that does not compete with commercial food production [5-8]. There is another resource like crude oil consist of fatty acids is utilized for the esterification [9]. So as per the literature studies the main key process like biomass valorization chemistry involves the selective removal of water (dehydration) from the simple carbohydrates and converted into the platform chemicals such as levulinic acid, furfuryl alcohol, furfural and hydroxymethyl furfurals [10-14]. which can be utilized for the conversion into the value-added chemicals (VAC). which act as a biofuel additive and it can be blend into the petrol as well as diesel as per their physio-chemical properties [15-18].
Furfuraldehyde is an important biomass-derived chemical, which is predictable as one of the top 30 platform compounds [19]. Furfuraldehyde has a high-valued feasible product, which explored for the generation of fuel additive's levulinic acid and levulinate esters, hydrocarbon fuels [20]. The motive of this study is to expand the alternative ways for the conversion of furfuraldehyde to value-added compounds (VAC).
In organic synthesis, acetalization of carbonyl compounds an important tool for generation of acetals via protecting the carbonyl group.Predictably, the reaction was taking place in presence of acid catalyst such as mineral acid hydrochloric acid, sulfuric acid and there is also some acid acetalization reactions produce vital cosmetics,drugs, solvents and food additivesin other synthetic reactions. Furthermore, the

furfural acetals are significant biofuel component that increase the cetane number of diesel fuel and diminish poisonous exhaust emissions with substantial antiknock qualities [21]. There are some other properties of furfural generated compounds act as adhesives, furan resins, and dyes are also achieved from furfural derivatives; subsequently, the furfuraldehyde is the promising and consisting biomass derived compound which can be utilized for the production of fine chemicals and fuels.

To achieve the successful organic transformation. There are so many acid catalysts have been used for the acetalization of furfural with lower to higher alcohols. The main objective of this work is to formed the different acetals of furfural with the series of lower alcohols to higher alcohols by very simple and easy work up method as a green approach to separate out the furfural acetals.

In present work, we have used biomass derived furfuraldehyde and alcohols (from lower to higher) by adding few drops of mineral acid (H_2SO_4) under reaction conditions. After completion of reaction the product separation was done by simple extraction method. Here we have used the extracting solvent as ethyl acetate with the similar ratio with water. If excess mineral acid is present in reaction mixture will removed easily while extracting with water and brine solution. So, in this work, we have explored the simple reaction pathway for the synthesis of furfural acetals as a biofuel additive.

EXPERIMENTAL SECTION

MATERIALS

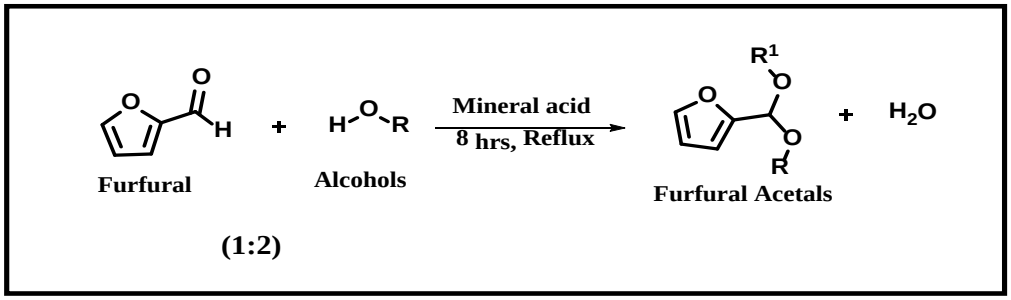
Methanol (99.5 %), Ethanol (99.9%) ,1-propanol (98%), 1-butanol (97%), 1-pentanol (98%), 1- hexanol (97%), 1-heptanol (99.9%), 1-octanol (97%) and furfural (98%) were purchased from SD Fine-Chem Ltd. ethyl acetate (98%) were procured from Avra chemical Pvt. Ltd. Sodium chloride Were acquired from Sisco Research Laboratories Pvt. Ltd.

CHARACTERIZATION TECHNIQUE

The Chemical structure of synthesized compounds was confirmed by spectral data. ^{1}H-NMR spectra were recorded onBRUKER AVANCE NEO 500 MHz spectrometer using DMSO and $CDCl_3$ solvent and TMS as internal standards at SAIF, Punjab University, Chandigarh (India). Chemical shifts are expressed in ppm. Mass spectrums were recorded onThermo Scientific TSQ 8000 Gas Chromatograph

GENERAL REACTION OF ACETALIZATION

The synthesis of various furfural acetals from furfural was developed by referring the literature [11]. To a 50 mL round bottom flask furfuraldehyde was added with few drops of (mineral acid) H_2SO_4 and stirred for 10 minutes and addition of primary alcohol (1:2) ratio of (mmol) and refluxed for 8 hr. Then after completion of reaction, the reaction mixture was taken in separating funnel and added the equimolar quantity of extracting solvent (ethyl acetate) and water with brine solution. And shake the separating funnel with 2-3 times properly for which the products can be easily separable. And then allow to stand the separating funnel for few minutes. We can saw the two layers one is organic layer (the product with ethyl acetate) and other later with water (if excess sulphuric acid is present). Drained out the water layer and collect the organic layer and kept it with 14 hr. with sodium sulphate for the absorption of excess moisture or water in organic layer. lastly evaporate the organic layer by rotatory evaporator to get desired product furfural acetals. And its structural analysis was confirmed by ^{1}H NMR and molecular weight was confirmed by GCMS analysis.



Scheme 1. Synthesis of Acetals

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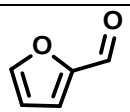
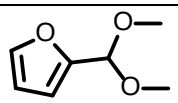
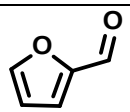
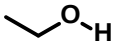
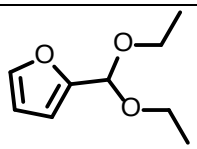
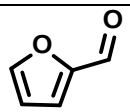
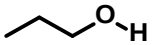
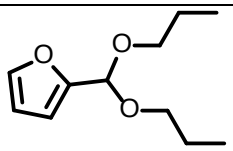
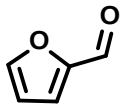
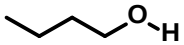
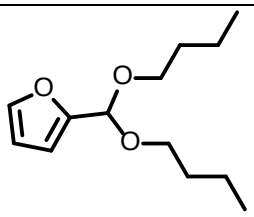
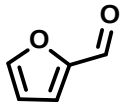
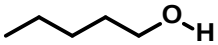
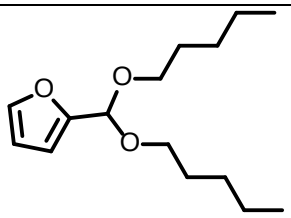
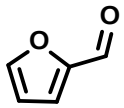
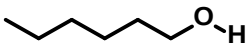
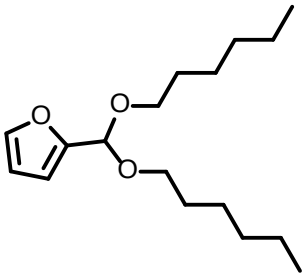
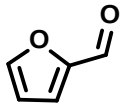
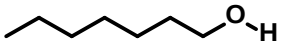
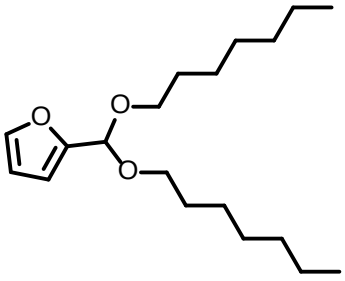
Here, we have used furfural and different aliphatic alcohols (1:2) ratio adding few drops of H_2SO_4 as a catalyst for 6-8 hrs. at reflux condition.

Table 1. Scope of furfural with different alcohols

Sr. No	Substrate	Reagent	Product	Time in Hrs.	Yield
1				8	81
2				8	79
3				8	83
4				8	86
5				8	78
6				8	82
7				8	74

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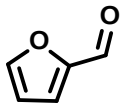
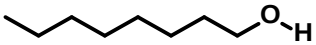
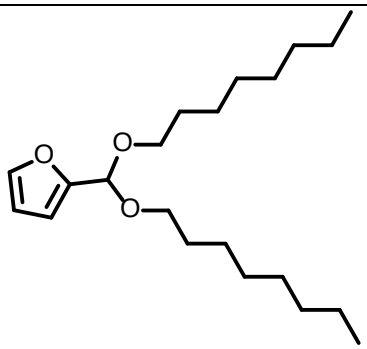
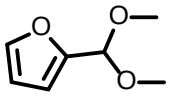
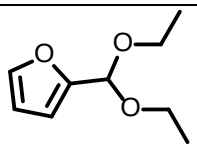
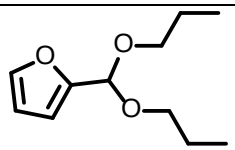
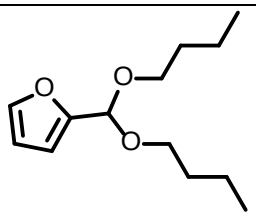
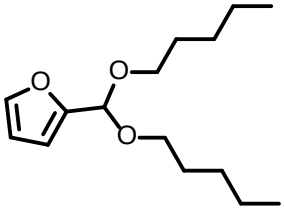
8				8	76

Table 2. Structural analysis of acetals

Sr. No	Structure of Products	Structural analysis by ^{1}HNMR and GCMS
1		**^{1}HNMR(500MHz,$CDCl_3$)**:δ7.58(d, 1H),6.61(s,1H),6.42(d,1H),6.40(d,1 H),3.30(s,6H) **GCMS:** Cal m/z: 142.06, Found m/z: 142.16
2		**^{1}HNMR(500MHz,$CDCl_3$):**δ7.59(d, 1H),6.61(s,1H),6.42(d,1H),6.40(d,1 H),3.35(q,4H)1.18(t,6H) **GCMS: Cal m/z:** 170.09, Found m/z: 170.20
3		**^{1}HNMR(500MHz,$CDCl_3$):**δ7.57(d, 1H),6.61(s,1H),6.42(d,1H),6.40(d,1 H),3.35(q,4H)1.49(m,4H),0.99(t,6) **GCMS:** Cal m/z: 198.13, Found m/z: 199.02
4		**^{1}HNMR(500MHz,$CDCl_3$)**:δ7.56(d, 1H),6.61(s,1H),6.42(d,1H),6.40(d,1 H),3.35(q,4H)1.461.50(m,8H),0.96(t,6H) **GCMS:** Cal m/z: 226.13, Found m/z: 226.20
5		**^{1}HNMR(500MHz,$CDCl_3$)**:δ7.59(d, 1H),6.61(s,1H),6.42(d,1H),6.40(d,1 H),3.35(q,4H)1.391.50(m,12H),0.90 (t,6H) **GCMS:** Cal m/z: 254.19, Found m/z: 254.30

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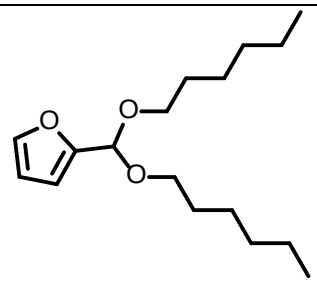
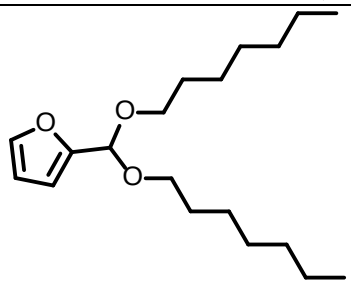
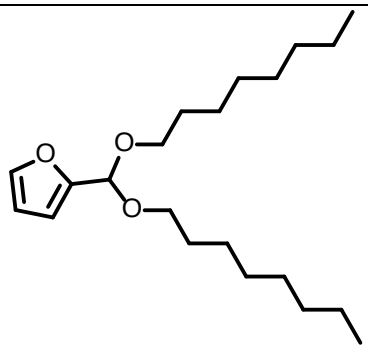
6		**^{1}HNMR(500MHz,$CDCl_3$)**:δ7.59(d, 1H),6.61(s,1H),6.42(d,1H),6.40(d,1 H),3.35(q,4H),1.371.50(m,16H),0.8 8(t,6H) **GCMS:** Cal m/z: 282.42 Found m/z: 282.38
7		**^{1}HNMR(500MHz,$CDCl_3$):**δ7.56(d, 1H),6.61(s,1H),6.42(d,1H),6.40(d,1 H),3.35(q,4H),1.431.50(m,8H),1.26 (m,12H),0.87(t,6H) **GCMS:** Cal m/z: 310.12 Found m/z: 310.24
8		**^{1}HNMR(500MHz,$CDCl_3$)**:δ7.58(d, 1H),6.61(s,1H),6.42(d,1H),6.40(d,1 H),3.35(q,4H),1.431.50(m,8H),1.26 -1.30(m,16H),0.86(t,6H) **GCMS:** Cal m/z: 338.28 Found m/z: 338.16

CONCLUSION

In summary, we have confirmed the acetalization of furfural-to-furfural acetals by reaction with methyl alcohol, ethyl alcohol, 1-propanol,1-butanol,1-pentanol,1-hexanol and 1-octanol the acetals can used as biofuel component and its miscible in neat diesel with (6-8%). In synthetic path the separation of product was done by simple extraction process with two solvent and brine solutions. Here we have used ethyl acetate (Ester extracting solvent) and water to remove the excess mineral acid. This acetalization reaction of biomass derived furfural is promising and efficient protocol to synthesize the different acetals from higher to lower alcohols. Which is having wide application in many other fields.

REFERENCES

1] Talebian-Kiakalaieh, A., Amin, N. A. S., Najaafi, N., &Tarighi, S. (2018). A review on the catalytic acetalization of bio-renewable glycerol to fuel additives. *Frontiers in Chemistry*, *6*, 573.

2] Natsir, T. A., & Shimazu, S. (2020). Fuels and fuel additives from furfural derivatives via etherification and formation of methylfurans. *Fuel Processing Technology*, *200*, 106308.

3] Akinnawo, C. A., Mosia, L., Alimi, O. A., Oseghale, C. O., Fapojuwo, D. P., Bingwa, N., &Meijboom, R. (2021). Eco-friendly synthesis of valuable fuel bio-additives from glycerol. *Catalysis Communications*, *152*, 106287.

4] Smirnov, A. A., Selishcheva, S. A., & Yakovlev, V. A. (2018). Acetalization catalysts for synthesis of valuable oxygenated fuel additives from glycerol. *Catalysts*, *8*(12), 595.

5] Raut, S. U., & Bhagat, P. R. (2021). Efficient photocatalytic acetalization of furfural to biofuel components using carboxyl-functionalized porphyrin photocatalyst, under visible light irradiations. *Biomass Conversion and Biorefinery*, 1-18.

6] Ravi, K., &Biradar, A. V. (2022). Highly active and scalable SO_3H functionalized carbon catalyst synthesized from bagasse for transformation of bio-based platform chemicals

into fuel precursors and its in-depth characterization studies. *Fuel*, *321*, 124008.

7] Zhang, H., Li, H., Hu, Y., Rao, K. T. V., Xu, C. C., & Yang, S. (2019). Advances in production of bio-based ester fuels with heterogeneous bifunctional catalysts. *Renewable and Sustainable Energy Reviews*, *114*, 109296.

8] Zahid, I., Ayoub, M., Abdullah, B. B., Nazir, M. H., Ameen, M., Zulqarnain, ... & Danish, M. (2020). Production of fuel additive solketal via catalytic conversion of biodiesel-derived glycerol. *Industrial & Engineering Chemistry Research*, *59*(48), 20961-20978.

9] Manimaran, S., Pandurangan, A., &Govindasamy, G. (2023). Green synthesis of spherical mesoporous SBA-16 and its supported Fe_2O_3-ZrO_2 catalyst for selective acetalization of glycerol to dioxolane as biofuel additive. *Journal of Environmental Chemical Engineering*, *11*(2), 109476.

10] Long, J., Xu, Y., Zhao, W., Li, H., & Yang, S. (2019). Heterogeneous catalytic upgrading of biofuranic aldehydes to alcohols. *Frontiers in Chemistry*, *7*, 529.

11] Deshmukh, S. A., Mataghare, B. C., Patil, V. S., Raut, S. U., Bhuse, D. V., Khajone, V. B., & Bhagat, P. R. (2023). Melamine-based porphyrin photosensitizer comprising sulphonic acid moieties for efficient aerobic oxidative acetalization of furfuryl alcohol: An access to octane booster under visible light. *Fuel*, *353*, 129209.

11] Barik, M., Mishra, J., Dabas, S., Chinnaraja, E., Subramanian, S., & Subramanian, P. S. (2022). Modified boehmite: a choice of catalyst for the selective conversion of glycerol to five-membered dioxolane. *New Journal of Chemistry*, *46*(2), 695-703.

12] Antunes, M. M., Silva, A. F., Bernardino, C. D., Fernandes, A., Ribeiro, F., & Valente, A. A. (2021). Catalytic transfer hydrogenation and acid reactions of furfural and 5-(hydroxymethyl) furfural over Hf-TUD-1 type catalysts. *Molecules*, *26*(23), 7203.

13] Doukeh, R., Râpă, M., Matei, E., Prodan, D., Győrgy, R., Trifoi, A., & Banu, I. (2023). An evaluation of glycerol acetalization with benzaldehyde over a ferromagnetic heteropolyacid catalyst. *Catalysts*, *13*(4), 782.

14] Isikgor, F. H., &Becer, C. R. (2015). Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. *Polymer chemistry*, *6*(25), 4497-4559.

15] Zhou, S., Wu, L., Bai, J., Liu, X., Lei, M., Long, M., & Huang, K. (2022). Titanate nanotubes-based heterogeneous catalyst for efficient production of biomass derived chemicals. *Frontiers in Chemistry*, *10*, 939289.

16] Islam, M. J., Mesa, M. G., Osatiashtiani, A., Taylor, M. J., Manayil, J. C., Parlett, C. M., &Kyriakou, G. (2020). The effect of metal precursor on copper phase dispersion and nanoparticle formation for the catalytic transformations of furfural. *Applied Catalysis B: Environmental*, *273*, 119062.

17] Yadav, N., Yadav, G., &Ahmaruzzaman, M. (2024). Camellia sinensis leaf-assisted green synthesis of SO_3H-functionalized ZnS/biochar nanocatalyst for highly selective solketal production and improved reusability in methylene blue dye adsorption. *Renewable Energy*, 120176.

18] Oton, L. F., Oliveira, A. C., Tehuacanero-Cuapa, S., Saraiva, G. D., de Sousa, F. F., Campos, A., &Bezerra, J. R. (2020). Catalytic acetalization of glycerol to biofuel additives over NiO and Co_3O_4 supported oxide catalysts: experimental results and theoretical calculations. *Molecular Catalysis*, *496*, 111186.

19] Fiorani, G., Perosa, A., & Selva, M. (2023). Sustainable valorisation of renewables through dialkyl carbonates and isopropenyl esters. *Green Chemistry*, *25*(13), 4878-4911.

20] Checa, M., Nogales-Delgado, S., Montes, V., &Encinar, J. M. (2020). Recent advances in glycerol catalytic valorization: A review. *Catalysts*, *10*(11), 1279.

21] Martín-Gómez, J., Pérez-Losada, M., López-Tenllado, F. J., Hidalgo-Carrillo, J., Herrera-Beurnio, M. C., Estévez, R., ... &Urbano, F. J. (2024). Insight into the reaction mechanism of photocatalytic production of solketal. *Catalysis Today*, 114506.