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Novel strategies for glucose production from biomass using heteropoly acid catalyst

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ABSTRACT

Bioethanol and direct glucose fuel cells pledged clean energy to the world. Cellulose depolymerization for glucose production has been a successful approach in bioethanol production. Heteropoly acids (HPAs) are strong Brønsted solid acid catalysts for biomass hydrolysis. Keggin type HPAs, namely, Silicotungstic acid (HSiW), Phosphotungstic acid (HPW), and Phosphomolybdic acid (HPMo), were used for the hydrolysis of lignocellulosic biomass to glucose. Five different biomass feedstocks, namely, miscanthus, sugarcane leaves, switchgrass, sunflower seeds, and bamboo leaves, were examined for the feasibility of total reducing sugar (TRS) yield through the composition analysis and catalytic biomass hydrolysis. Sunflower seeds contained the maximum holocellulose with 90.6%, and switchgrass contained the least i.e., 77.63%. Among the five biomass tested, switchgrass resulted in the highest TRS (5.77 wt/dry wt. %) with HPMo catalyst at a catalyst to biomass ratio of 30:100 (wt./wt. %), a reaction temperature of 120 °C for 3 h. The reaction parameters for depolymerization were optimized for all three HPAs, and the optimized conditions were 3 h and 120 °C. HPMo showed maximum TRS yield (5.77 wt/dry wt.%) among the three HPAs at 30:100 catalyst to biomass ratio. However, a catalyst to biomass ratio of 20:100 (wt./wt.%) was economical (5.25 wt/dry wt.%) for commercial application.

1. Introduction

The accelerated growth of the human population increased per capita energy consumption, and the growing demand for fuel has led to the exploration of alternate fuel sources. Global consumption of petrol is estimated to be 5–6 million barrels/day. At this rate, the petroleum reserves are expected to last just over five decades. Fuel price tends to increase because of high demand and low supply. This energy crisis is a long-term problem and a challenge to scientists around the world. The focus must shift towards alternative and renewable energy sources.

Possible alternatives are solar energy, wind energy, and biofuels (biodiesel, bioethanol, jet fuels). Poor battery technology and wind direction change, limit the use of solar and wind energies. Biodiesel burns like petroleum diesel producing soot. Bioethanol, a renewable fuel, burns clean with only water and carbon dioxide as products, appears to be a viable alternative to fossil fuels. Use of bioethanol as fuel is carbon neutral and hence a greener alternative for fossil fuels [1,2]. Even with some of the challenges of usage, bioethanol stand out to be the best alternative. Bioethanol in the form of blended fuel has been successfully introduced in countries like the USA, Brazil and the EU with bioethanol content as high as 85% [3]. Neat bioethanol is also being used as fuel with minor modifications in existing fuel dispensation infrastructure.

Every year billions of tonnes of crop residues and weed are wasted either by burning or dumping. The process of burning unwanted plants like weed and the residue not only pollutes air but has also been responsible for smog in some parts of India, on the other hand, dumping has just increased the amount of organic waste. While these plant matter could be put into use by producing energy, mishandling of major cellulose source which includes crop remains and unwanted plants like switchgrass was practiced. Heteropoly acids (HPAs) are promising solid acid catalyst for biomass conversion to biochemicals like glucose [4,5] and levulinic acid [6]. HPAs have well-defined structure at the molecular level with tunable chemical composition, as well as acid and redox properties. Inherent presence of water molecules and highly acidic protons in the crystal structure of HPAs makes these materials very promising acid catalysts for biomass hydrolysis reaction [7]. Solid

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acid catalysts like functionalized carbon materials [8–12], modified zeolites (Ir/zeolite HY) [13], simple metal oxides (MoO_3–CuO) [14] and complex metal oxides (heteropoly acids) [15–17], and polymeric materials [18–20] were developed for the hydrolysis of biomass (cellulose, cellobiose, glycogen, rice straw, wheat straw, eucalyptus chips, jute, cassava mash and corn stover) to glucose and total reducing sugars (TRS) in high yield as summarized in Table s1. Huang and Fu reviewed the key factors, namely, acid strength, acid site density, adsorption, microporosity, that contribute to the effective cellulose hydrolysis by solid acid catalysts (sulfonated carbons, polymer based acids and magnetics solid acids). Methods like pretreatment reduced crystallinity while use of ionic liquids and microwave irradiation enhanced the hydrolysis rate [21]. Hu et al., reviewed the use of solid acid catalysts (acid resins, metal oxides, H-form of zeolites, heteropoly acids, functionalized silica, supported metals, immobilized ionic liquids, carbonaceous acids and magnetic acids) as substitute to mineral acid and enzymatic catalysts for the hydrolysis of cellulose to glucose [22].

HPAs can be recovered from the hydrolysate by extraction with ether [23]. Alternately they can be supported on inert solid matrices like activated carbon [24], graphene and silica [25,26] making them easily separable from the hydrolyzate and can be reused.In addition to recovery from ether, HPAs can be reused by supporting it on catalyst supports or immobilizing it in membrane. Catalytic supports like activated carbon [24], silica gel [24,27–29], alumina [24,27,29], titania [24,29,30], magesia [27], aluminosilicate [27], mesoporous silica [31], activated clay [32], graphene nanoplatelets [33] are widely used. From solvents other than water and polar solvents, the HPAs can be readily recovered by filtration or centrifugation. Alternatively, HPAs can be encapsulated in the membrane matrices [34], encapsulated in the metal organic frameworks [35,36], supported onmagnetically recoverable catalysts [37] for heterogenous catalysis and easy recovery.

HPAs were employed as solid catalysts for the production of glucose from biomass, namely, miscanthus, sugarcane leaves, switchgrass, sunflower seeds and bamboo leaves.The biomass such as weeds like seaweed [38,39], water hyacinth [40], sugarcane leaves, bamboo leaves, cotton [41] and cow dung [42] can also be used. Practically, any material with cellulose can be used for ethanol production without food-fuel conflict. Use of corn for bioethanol production was successful in the USA [43]. But the use of food grains for fuel production created a situation known as fuel vs food conflict [44]. So, biomass with cellulose, collectively called as lignocellulosic biomass, is preferred.

Technology is advancing in areas like direct glucose fuel cells and bio-fuels like biodiesel and bioethanol. An attempt to develop alternative fuel from renewable biomass using heteropoly acid catalysts is made. The present work aims to use waste biomass as feedstock and maximise the glucose yield using acid catalysts. The objectives are to select biomass source which is a zero value waste, available in abundance, to select eco-friendly acid catalyst and to maximise the TRS production by choosing the best reaction parameters. In this work, five different biomass, namely, miscanthus [45], sugarcane [46], switchgrass [47], bamboo [48] and sunflower seeds, common plants found in major parts of India are selected to evaluate the feasibility for TRS production. The study involves the use of three different heteropoly acids; silicotungstic acid (HSiW), phosphotungstic acid (HPW) and phosphomolybdic acid (HPMo) for biomass hydrolysis to produce glucose. The article gives insight into the design of optimal glucose production process by the judicious selection of biomass and solid acid catalyst. The work also focuses on the optimization of process parameters such as reaction time, the catalyst to biomass ratio and the reaction temperature, for selecting the best reaction conditions.

2. Experimental

2.1. Materials and methods

2.1.1. Material

Locally grown switchgrass (SG), miscanthus (MC), bamboo leaves (BO), sugarcane leaves (SC), Bolivian sunflower seeds (SF) were selected. Silicotungstic acid ($H_4SiW_{12}O{\cdot}_{40}nH_2O$, HSiW, AR), phosphotungstic acid ($H_3PW_{12}O_{40}.nH_2O$, HPW, LR), phosphomolybdic acid ($H_3PMo_{12}O_{40}.24H_2O$, HPMo, AR) were purchased from Molychem, India. The chemicals were used without further purification. Hot air oven (Kemi), and UV–Vis spectrophotometer (Thermo scientific Genesys 10S UV–Vis spectrophotometer) and locally manufactured Teflon lined autoclaves (Shriram Enterprises Pvt. Ltd, Chennai) were used in the experiments and analysis. In addition, sulphuric acid (H_2SO_4, 98%), glacial acetic acid (CH_3COOH, 99.5%) and phenol (C_6H_5OH, 99.5%) were purchased from Loba Chemie India. Sodium hydroxide pellets (NaOH) from Spectrum chemicals, ethanol (C_2H_5OH, 99.9%) from Changshu Hongsheng Fine chemicals, China and benzene (C_6H_6, AR) from Merck were used. Sodium chlorite ($NaClO_2$, 80% puriss grade) was purchased from Sigma Aldrich and acetone ($(CH_3)_2CO$, LR) was purchased from Molychem India. All the chemicals were used without further purification.

2.2. Biomass content estimation

2.2.1. Compositional analysis of biomass

Biomass was ground to size range 20–80 mm. Then it was left for 8 h in the methanol, benzene mixture (1:1, v/v). The solid residue after decantation of the solvent was dried at room temperature and was used for the composition analysis.

2.2.1.1. Ash content. Ash content was estimated according to Tappi standard 211-om 85. A known amount of biomass was burnt in a pre-weighed porcelain crucible using muffle furnace. Initially, it was burnt for 30 min at 400 °C, then at 850 °C for 45 min. The change in weight was noted and the ash content was estimated.

2.2.1.2. Lignin content. A known amount of extracted biomass was mixed with 20 mL of 72% sulphuric acid in a beaker. The acid was added in a dropwise manner with continuous stirring of the resulting mixture using a glass rod. Once the fragmentation was complete, the reactant mixture was left in the beaker for overnight with a glass plate covering it. The beaker was maintained at room temperature during the period. The resulting mixture was then transferred to 1 L round bottom flask for further reactions. The mixture was then diluted to 3% acid and boiled for 4 h under reflux. The resulting solid was separated from the solution using ashless filter paper. Further, the solid was washed till neutrality using hot distilled water. The lignin was then weighed and ignited at 850 °C for 45 min. On subtraction of ash weight, ashless lignin content was determined.

2.2.1.3. Holocellulose content. The biomass was oven dried and ground in a laboratory mixer to pass a screen of mesh number 40 and then the extraction was carried out using alcohol benzene mixture of 1:1 proportion (v/v %) for 6 h. A known amount of the raw material was suspended in 150 mL water at 75 °C and the solution was stirred continuously for the set period. To the resulting mixture, 10 drops of glacial acetic acid and 1.5 g sodium chlorite were added with continuous stirring. The process was repeated three more times until the total reaction time was 4 h. The resulting mixture was cooled and then filtrate with distilled water until the filtrate was neutral, ensuring the filtride was free from residual chemicals. Later the mixture was treated with acetone solution and left to dry. The holocellulose was then estimated gravimetrically [49].

2.2.1.4. Alpha cellulose content. Alpha cellulose is the part of cellulose content which does not dissolve in 17.5% sodium hydroxide solution. Alpha cellulose content was determined according to Zellcheming Merkblatt IV/29. A known amount of the sample was placed in a 250 mL of porcelain beaker to which 25 mL of 17.5% NaOH was added dropwise and then the sample was kept for swelling for 4 min. The samples were pressed against the beaker with a glass rod for 3 min. Then 25 mL of NaOH was added and mixed until a homogeneous paste was obtained. The beaker containing the paste was kept at 20 °C for 35 min with a lid. 100 mL of distilled water was then added to the samples and were quickly filtered under suction using a sintered glass funnel. The filtrate was collected and then poured back on to the paste twice followed by washing with distilled water till neutrality. 100 mL of 10% (wt.% or vol%) acetic acid was added dropwise before adding distilled water. The entire experiment was performed at 20 °C. The amount of alpha cellulose was estimated gravimetrically after drying at 105–106 °C.

2.3. Pretreatment

2.3.1. Physical pretreatment

Physical pretreatment was carried out after cleaning the feedstock; namely, sunflower seeds, switchgrass, miscanthus, bamboo leaves and sugarcane leaves. The seeds and straw of the feedstock were used for the biomass conversion process. The plant matter of interest was chopped into pieces and dried in the hot air oven for three days at 80 °C. The oven dried straws were then ground to obtain course fragments. The fragments were then passed through mesh number 40 and the fragments that pass through the mesh were selected for further studies [50].

2.3.2. Hydrolysis

Acid hydrolysis of the biomass was performed with the selected feedstock. The hydrothermal reaction was performed in a stainless-steel reactor lined inside with Teflon. The optimization process involved variation of three reaction parameters, namely, the reaction time, temperature and acid catalyst concentration. The best catalyst was selected based on the TRS yield. The reaction was performed by maintaining constant temperature and time while the catalyst concentration was varied. Subsequently, effect of temperature was studied with varying temperature [4,51,52].

2.3.3. Phenol sulphuric acid method for the estimation of TRS content

TRS production from the biomass feedstock was quantitatively estimated using phenol-sulphuric acid method. In this method, 1 mL of 5% phenol and 5 mL of 96% sulphuric acid were added to 1 mL of the sample and incubated for 10 min at room temperature followed by 30 min of incubation in water bath. The resulting coloured solution was analyzed using UV–Visible spectrophotometry. Absorbance at 490 nm was a measure of the amount of TRS. The concentration of the carbohydrate in the analyte was deduced from the calibration plot derived using standard sugar samples [53–55].

3. Results and discussion

3.1. Biomass composition analysis

Table 1
Composition analysis of biomass.

Feedstock	Cellulose	Hemicellulose	Lignin	Ash
	~(Wt.%)	**~(Wt.%)**	**~(Wt.%)**	**~(Wt.%)**
Switchgrass	41.01	36.62	15.37	6.32
Miscanthus	50.15	35.06	10.45	3.27
bamboo leaves	51.32	31.10	8.34	8.4
sunflower seeds	22.10	68.50	4.36	4.31
sugarcane leaves	45.83	44.16	5.40	3.82

Composition analysis of the feedstock was performed on all the five feedstock, namely, sunflower seeds, switchgrass, miscanthus, bamboo leaves and sugarcane leaves. Relative amounts of various components in the biomass feedstock were shown in Table 1. Further selection of biomass for glucose production via acid hydrolysis was based on their chemical composition, namely, the holocellulose (carbohydrate) content. Holocellulose content was taken into account for TRS production but the lignin recovered could be used in vanillin production [56]. Composition analysis showed that sunflower seeds had the highest quantity of holocellulose. As a preliminary step for the selection of biomass, the hydrothermal process was carried out with sunflower seeds as feedstock because of the highest holocellulose content among the five selected feedstocks.

3.2. Biomass conversion using heteropoly acids

3.2.1. Selection of biomass based on TRS yield

The hydrolysis reactions were carried out for selecting the biomass feedstock and evaluating the best reaction parameters. The TRS production process at 120 °C from different biomass for different reaction time and the different catalysts of various concentrations is depicted in Fig. 1 (Figs. S1–S4). TRS yield was maximum for the reaction time of 3 h and temperature of 120 °C. Use of HPMo as catalyst with a catalyst to biomass ratio of 30:100 (wt./wt.%) yielded highest yield of TRS Fig. 1. For all the biomass namely, bamboo leaves, sugarcane leaves, sunflower seeds, miscanthus and switchgrass; the TRS yield was maximum at the above mentioned process conditions. A maximum TRS yield of 5.77 (wt./dry wt.%) was observed in switchgrass compared to other biomass at the same reaction parameters. Recently, Zhong et al. reported on the better performance of switch grass compared to mischanthus [57]. Glucose and xylose yields from switch grass are 32.37 and 16.28 g/L compared to 26.56 and 11.92 g/L respectively from mischanthus. Moreover, the crystallinity index of switchgrass (45%) is lower than that of mischanthus (51%). The potential of switchgrass (82 and 63%) is on a par with its other grass counterpart, namely, coastal Bermuda grass (87 and 59%) in terms of glucose and xylose yields [58]. Other characteristic features that motivated the authors to study switchgrass as resource for reducing sugar production include its abundance, low cost, rich holocellulose content, growth under various geographical and climatic conditions, resistance to drought and pests under degraded and contaminated soil conditions, ability to reduce soil erosion and to regenerate itself after it was cut for harvest, potential to fix CO_2 in the soil [58]. Owing to specific advantages like high productivity, low water and nutritional requirement, suitability in marginal land quality and positive environmental benefits, switch grass is classified as a model energy crop by the United States department of energy [59]. As a result, switch grass is chosen as the representative example of grasses in our study. However, the TRS yield at the catalyst concentration of 20:100 was found to be economical because of reduced amount of catalyst concentration for higher yield of TRS in comparison with 30:100.

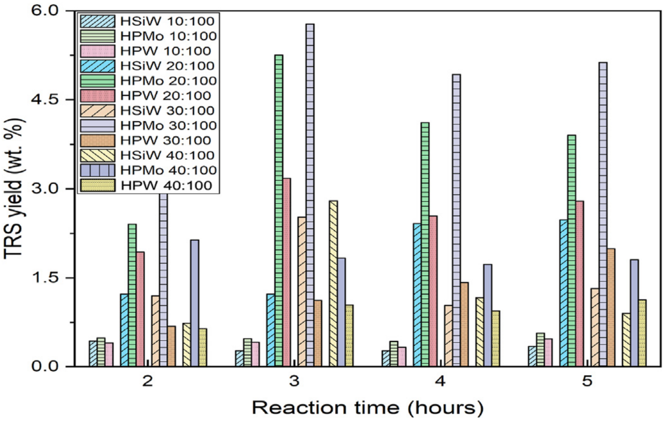

Fig. 1. Effect of acid type and acid concentration on the yield of TRS from switchgrass at 120 °C.

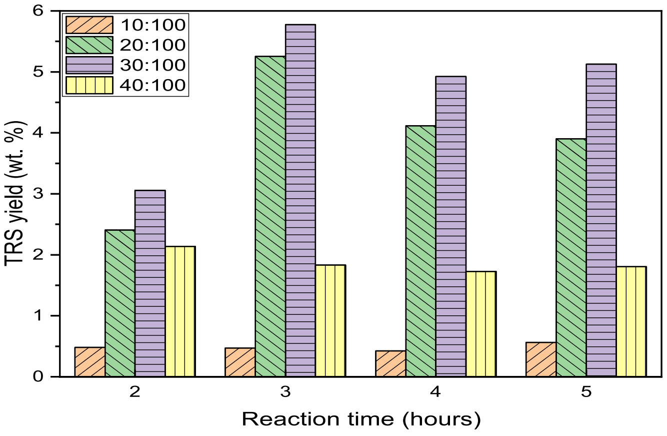

Fig. 2. Effect of catalyst concentration on TRS yield for HPMo at 120 °C.

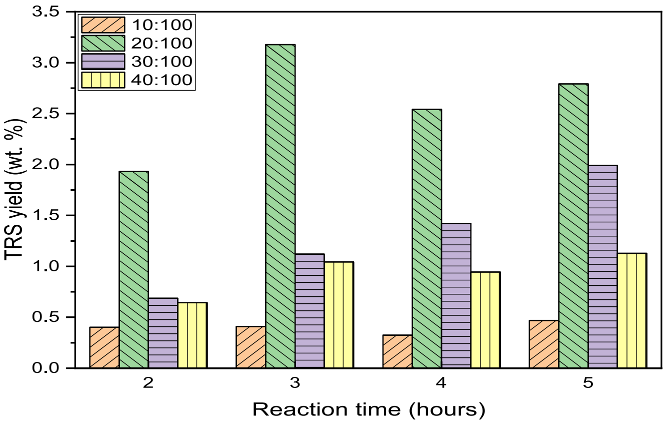

Fig. 3. Effect of catalyst concentration on TRS yield for HPW at 120 °C.

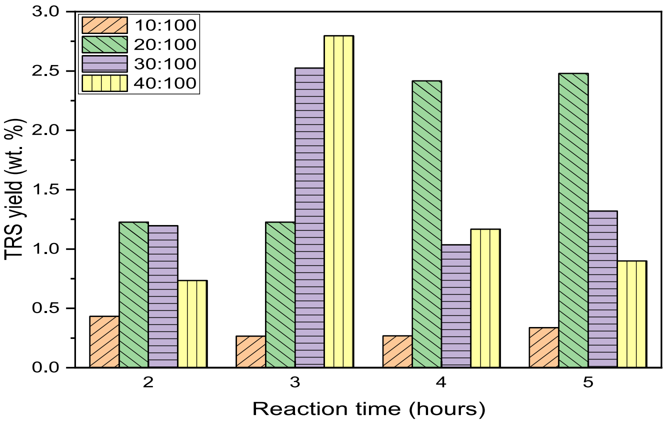

Fig. 4. Effect of catalyst concentration on TRS yield for HSiW at 120 °C.

3.2.2. Effect of nature and acid strength of catalyst on the yield of TRS

The hydrolysis reaction of biomass was carried out at 120 °C for 3 h by varying the catalyst type, namely, HPW, HSiW and HPMo with different biomass feedstock. The hydrolysates derived were tested for TRS using UV–Vis spectroscopy. The TRS produced was estimated by phenol-sulphuric colorimetric method. From Fig. 1 it can be reported that for hydrolysis conditions of 120 °C temperature for 3 h of reaction time, and the respective catalyst concentration of three different catalysts, the TRS yield was maximum for the switchgrass (Figs. S1–S4). Hence, switchgrass was considered for further studies. Moreover, among the three catalysts studied, HPMo was the best, yielding high TRS amounts irrespective of the biomass used. The Brønsted acidity of heteropoly acids is significantly higher than the conventional mineral acids. So they are termed as “super acids” [60]. Hammet and Deyrup defined acidity function (H_0) to measure the acid strength (in terms of basic indicators) of any solution whose acidity lies between that of dilute aqueous solution and that of 100% sulphuric acid. The H_0 value of pure sulphuric acid (100%) is −10.60. H_0 values of HPAs are usually lower than −12 [61]. The acid strength of heteropoly acids is stronger than the conventional mineral acids (HCl, HNO_3 and H_2SO_4) as revealed from the acid dissociation constants. Tungstun based HPAs are usually stronger than molybdenum based HPAs [62]. The dissociation constants of heteropoly acids at 25 °C are as follows: $H_3PW_{12}O_{40}$ (pK_1, 1.6; pK_2, 3.0; pK_3, 4.0); $H_4SiW_{12}O_{40}$ (pK_1, 2.0; pK_2, 3.6; pK_3, 5.3) and $H_3PMo_{12}O_{40}$ (pK_1, 2.0; pK_2, 3.6; pK_3, 5.3). For comparison the pK value of H_2SO_4 is 6.6. These values indicate that the acid strength of the tested catalysts varies in the following order: $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} \geq H_3PMo_{12}O_{40}$ [63]. Usually, owing to high acidity, HPW was expected to perform well and yield highest TRS. But the experiments showed that the TRS yield is not purely based on acid function but also on the redox function of the catalyst. HPMo possess both acidic and redox properties and so resulted in a high yield of TRS from diverse biomass feedstock [64].

3.2.2.1. Effect of time of reaction and catalyst concentration. The effect of reaction time and the concentration of the catalysts for the conversion of switchgrass to TRS was studied. For the catalyst HPMo, HPW and HSiW, the ratio of catalysts to biomass (wt./wt.%) −10:100, 20:100, 30:100 and 40:100 were varied. The yield of TRS as a result of variation of catalyst amount and reaction time for HPMo, HPW and HSiW are shown in Fig. 2, Fig. 3 and Fig. 4 respectively. With HSiW, the best reaction conditions were found to be a reaction time of 5 h with a catalyst to biomass ratio of 20:100 (wt/wt %). With HPW, the best reaction conditions were a reaction time of 3 h with a catalyst to biomass ratio of 20:100. The decrease in the reaction time with HPW catalyst relative to HSiW catalyst from 5 to 3 h was due to the increased acidity of the HPW catalyst compared to HSiW. With HPMo, the best reaction conditions were reaction time of 3 h and a catalyst to biomass ratio of 30–100. The increased amount of HPMo required for the highest yield of glucose was reasonable as HPMo was least acidic in the series of catalysts used. Even though, the ratio of HPMo to biomass of 30:100 for 3 h

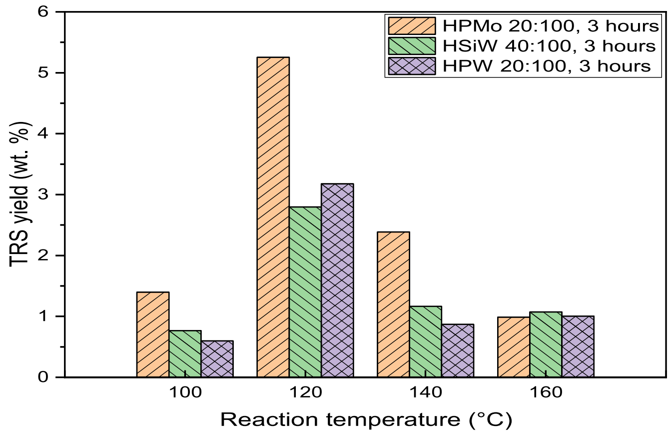

Fig. 5. Effect of temperature on TRS yield for catalyst concentration of HPMo (20:100), HPW (40:100) and HSiW (20:100).

yielded highest TRS yield, there was no much variation in the yield of TRS obtained when the catalyst to biomass ratio was 20:100. So a ratio of HPMo to biomass of 20:100 was chosen as the optimum value with a reaction time of 3 h for further experimentation. However, HPMo, outperformed HSiW and HPW, as the yield of TRS was nearly twice with HPMo compared to either HPW or HSiW with same ratio of catalyst to biomass (20:100) and a reaction time of 3 h. The observed high activity of HPMo for the hydrolysis of switchgrass to TRS was due to the synergistic activity of acid and redox function of HPMo catalyst [64]. The ratio of catalyst to biomass should be as low as possible while retaining the highest product yield under modest reaction conditions (temperature and pressure) in an ideal catalytic process with an energy return on energy invested (ERoEI) value greater than 1 [23].

3.2.2.2. *Effect of temperature.* The effect of temperature on the TRS production by switchgrass was studied by conducting the hydrolysis reaction at different temperatures of 100, 120, 140 and 160 °C with other parameters being constant. The results shown in Fig. 5 depicted that, as the reaction temperature was increased from 100 to 120 °C, the TRS production increased and then with a further rise in temperature, the yield decreased showing the least values of TRS yield for the temperature 160 °C. Irrespective of the nature of the catalyst, the optimum temperature of the hydrolysis of switchgrass was 120 °C. The observed enhancement in the yield of TRS (~ 3.5–7 fold, depending on the catalyst used) with an increase in reaction temperature from 100 to 120 °C is in accordance with the rate law that for every 10 °C raise in reaction temperature, the reaction rate is doubled. The acceleration of the reaction rate of the hydrolysis of holocellulose to monosaccharides (glucose and xylose) caused the observed enhancement in the yield of TRS (Fig. 5) when the reaction rate is increased from 100 to 120 °C. However, beyond the reaction temperature of 120 °C, the monosaccharides (glucose and xylose) are further converted to products like fructose, 5-hydroxy methyl furfural (5-HMF) and levulinic acid by the isomerization, dehydration and rehydration of glucose respectively and to furfural by the dehydration of xylose, resulting in the observed decrease in the yield of TRS [65].

4. Conclusion

Bioethanol has been widely accepted among scientists around the globe as an alternative to fossil fuels. When produced from a biomass, ethanol serves as a carbon neutral fuel which is the focus of current scenario at global level. From the present work, it can be reported that switchgrass yields highest amount of TRS when compared to other biomass that were selected for the study. Furthermore, switchgrass is available in abundance with an added advantage of minimal growth period and cellulose percentage. Heteroployacids are green acids whose acidity can be altered based on requirement. In this work, HPMo was found to be the most effective catalyst for the application (TRS production) with the yield of the wt.% yield of TRS from switchgrass. The study was also conducted for the selection of optimum process parameters. The optimal hydrolysis conditions were a reaction time of 3 h at 120 °C with a HPMo to switchgrass ratio of 20:100 (wt./wt. %). Thus, switchgrass and HPMo were recommended as preferred biomass and solid acid catalyst for the high yield production of TRS.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Abhishek Nayak: Investigation, Writing - original draft. **Indra Neel Pulidindi:** Supervision, Writing - review & editing. **Chinta Sankar Rao:** Supervision, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.renene.2020.05.129.

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