

Preparation of Activated Carbons from Rice Straw and Hydrogenolysis of Glycerol over Activated Carbon Supported Ru Bi-Functional Catalysts

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ABSTRACT: Activation of biochars obtained from rice straw by using $(\text{NH}_4)_2\text{HPO}_4$, KOH, HNO_3 , H_3PO_4 , KMnO_4 reagents by modifying surface properties is carried out. Activated carbon with highest surface area is used for preparation of Ruthenium bifunctional catalyst for hydrogenolysis of glycerol. Among all the catalysts studied, Ru/C-UR3-5 shows maximum activity. Influence of solid acid co-catalyst on activity of Ru/C catalysts by using various metal oxides like TiO_2 , Nb_2O_5 , ZrO_2 etc. were studied. Ru/C catalyst in presence of TiO_2 yields better conversion of glycerol. Effect of quantity of Ru/C and TiO_2 on conversion of glycerol was also studied. As the wt. of catalyst and co-catalyst increases the percentage of conversion of glycerol to 1,2 PDO also increased.

KEYWORDS: Biochar, Activated carbon, Hydrogenolysis, Solid acid, 1,2 propane diol (1,2 PDO)

1. INTRODUCTION

Biomass is a renewable energy resource and has a growing interest as a chemical feedstock source. Biochar is a new scientific term with various definitions in the literature. Biochar can be well-defined as “a carbon rich product when biomass such as wood, manure or leaves is heated in a closed container with little or unavailable air”. Agricultural wastes or residues are wide available low-cost raw material to produce biochar, as well as bio oil and gases. Rice straw is one of the main categories of agricultural by-products. Large quantities of straws accumulate due to agricultural practices in Asia. Although some residues are used as feed, fuel or straw returned to the fields, millions of tons of rice straws are burnt annually in Asia especially in southern region through wildfires, post-harvest burning of cultivation fields, and domestic uses for cooking and heating. This represents a main source of source of air pollution. Since past one decade, several researchers began to focus on developing biochar from straw. However, limited knowledge is available for the surface modification of biochar. The surface modifications result in variation of surface reactivity, physicochemical and structural properties. Surface modification of biochar using alkali or acid results in changing of surface areas plus functional groups characteristics on biochar. Further investigation on biochar modification is important owing to necessity to develop it for special applications. The objectives of this work is i) modification of biochar prepared from Rice straw by using various solvents/reagents ii) investigation of modification effects on the pore structure and surface properties of the products iii) determination of the optimum experimental conditions for the preparation of materials with desired surface properties and adsorption capacities iv) activation of biochar under different conditions to produce activated carbons v) application of these activated carbons as support materials for glycerol hydrogenolysis.

Researchers and industry have been looking for new technologies to convert glycerine into value-added chemicals to

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replace petrochemicals as a source of chemical raw materials. Of late, there have been an impressive series of achievements made in the value-addition of glycerol and it is now becoming established as a major platform for the production of chemicals and fuels [1]. Recently, a series of novel catalytic conversion processes that transform glycerol into useful chemicals have been reported in the literature [2,3]. New opportunities and challenges still exist for researchers and industry to improve both the catalytic materials and technologies needed for the efficient transformation of glycerol into valuable chemicals [3]. The mass production of biodiesel leaves about 50–88% pure glycerol [4]. The usage of low-grade quality of glycerol obtained from biodiesel production is a big challenge as this glycerol cannot be used for direct food and cosmetic uses [5]. The conventional application cannot cope up with the excess production of glycerol as costly purification steps are required to bring it to 98% purity. An effective usage or conversion of crude glycerol to specific products will cut down the biodiesel production costs [6].

With a focus on recent developments in the conversion of glycerol into value-added chemicals, new chemistry of glycerol will be developed which plays a crucial role in future bio-refineries, as its derivatives find uses in sectors as diverse as fuels, chemicals, automotive, pharmaceutical, detergent, and building industries. Value-addition of glycerol will increase profitability of biodiesel industry [7-15]. A variety of reactions are used to produce valuable chemicals from glycerol.

One of the important glycerol conversions is selective hydrogenolysis of glycerol. Hydrogenolysis is a catalytic chemical reaction that breaks a chemical bond in glycerol with the simultaneous addition of a hydrogen atom to the resulting propanediol. Since hydrogenolysis uses hydrogen as a reactant, the hydrogenolysis catalyst must have an ability to activate hydrogen molecules. Noble metals are well known to be able to activate hydrogen molecules and are widely used in hydrogenation catalysts. Activated carbon supported Rh, Ru, Pt and Pd were used for glycerol hydrogenolysis earlier [16]. Glycerol can be converted to 1,2-propanediol and 1,3-propanediol and ethylene glycol. These products are valuable starting compounds for the production of polymers. The second objective of present work is to develop catalytic methods for the production of above products selectively from glycerol. The activated carbons produced will be used as supports for metal precursors like Ruthenium to develop a suitable catalyst. As glycerol hydrogenolysis reaction follows two step mechanism, a co-catalyst is also required to improve conversion rates of glycerol. When Ru is supported on acid catalyst itself, then the hybrid catalyst avoids the requirement of a separate solid acid catalyst to reaction medium.

II. RELATED WORK

- i. Researchers and industry have been looking for new technologies to use glycerine into value-added chemicals to replace petrochemicals as a source of chemical raw materials. Of late, there have been an impressive series of achievements made in the value-addition of glycerol and it is now becoming established as a major platform for the production of chemicals and fuels.
- ii. The main objective of the work is to use low cost Bio-waste, especially agricultural by-products like Rice Straw for preparation of activated carbons.
- iii. The surface properties of carbons were modified by using $(\text{NH}_4)_2\text{HPO}_4$, KOH, KMnO_4 , HNO_3 , H_3PO_4 etc. as activating agents.
- iv. The prepared activated carbons are used as support materials for Ru metal catalysts.
- v. Activities of Ru/C catalysts can be enhanced by using solid acid catalysts like TiO_2 , Nb_2O_5 , ZrO_2 as co-catalysts.
- vi. Ru/C catalysts supported on activated carbon prepared from rice straw are implied to study the conversion of Glycerol into 1,2 PDO, 1,3 PDO, Ethylene glycol etc. through hydrogenolysis reactions.
- vii. The reaction conditions of glycerol hydrogenolysis are optimized by varying catalyst and co-catalyst wts.

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III. EXPERIMENTAL METHODS

3.1 Materials

Rice straw was collected from Krishna province, Andhra Pradesh, India and was trimmed in to small pieces. These pieces were soaked in 2 wt.% NaOH solution for 24 hr to remove ash and water soluble substances. The straw was then washed with distilled water until the pH is neutral and then dried at 110°C overnight.

3.2 Preparation of Activated Carbons

A tubular furnace for carbonization provided with temperature programmer was used to prepare activated carbons. 10 gr of dried rice straw was heated in the furnace under nitrogen atmosphere at 10°C/min. from room temperature to a 600°C and maintained for an hour. After carbonization, the furnace was cooled to room temperature under continuous flow of nitrogen to avoid post oxidation process. Thus produced solids were washed with hydrochloric acid (1M) followed by thorough washing with hot distilled water to remove chloride ions and other residues until the pH became neutral. The purified solids were dried at 110°C for 10 hr. This sample is designated as UR-0. Thus produced UR-0 biochar is activated by using several reagents to modify surface properties as follows.

i) Activation of by $(\text{NH}_4)_2\text{HPO}_4$: a) This sample was further activated by using diammonium hydrogen phosphate. 5 gr. of UR-0 was calcined at 250°C for 2hr for oxidation under air. Then the sample is impregnated with 30wt.% $(\text{NH}_4)_2\text{HPO}_4$ solution using an impregnation mass ratio of 1:5 (straw/ $(\text{NH}_4)_2\text{HPO}_4$). This sample is designated as UR-1.

b) 5 gr. of UR-0 is first impregnated with 30 wt.% $(\text{NH}_4)_2\text{HPO}_4$ and then heated at 600°C under nitrogen atmosphere. This sample is named as UR-2. c) 5 gr. of UR-0 is first impregnated with 30 wt.% $(\text{NH}_4)_2\text{HPO}_4$ and then heated at 250°C under air for 2 hr. Then the same sample is subjected to heating at 600°C under nitrogen atmosphere for activation. This sample is named as UR-3.

ii) Activation by KOH: UR-0 biochar was treated with 1M KOH by boiling for 2h. The oxidized biochars were washed and then dried overnight at 110°C. This sample is designated as UR0/KOH

iii) Activation by HNO_3 : UR0 biochar was treated with 40 ml of 70 % nitric acid at 60°C under continuous stirring for 2 h. and washed with distilled water till the pH is neutral. Then the sample is dried overnight at 110°C. This sample is designated as UR0/ HNO_3 .

iv) Activation by H_3PO_4 : UR-0 biochar was treated with 2% H_3PO_4 at 60°C for 24 h. then washed with deionized water until pH was stable. Afterwards, the material soaked in 1% sodium bicarbonate solution overnight to remove residual acid. This sample is designated as UR0/ H_3PO_4 .

v) Activation by KMnO_4 : UR-0 biochar was treated by 50ml 0.1 N KMnO_4 solution at 50°C for 24h and washed with distilled water until the pH is stable. This sample is designated as UR0/ KMnO_4 .

3.3 Preparation of supported ruthenium catalysts by impregnation

Activated carbons prepared from rice straw are used as support for Ru catalysts. The catalysts were prepared by conventional impregnation using aqueous solution of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$. In the conventional method, calculated amounts of aqueous metal precursor solution was added to activated carbons with highest surface area UR-3 and after allowing overnight adsorption the excess solution was first evaporated to near dryness on a water bath and then the partially dried material was further dried in air oven at 120 °C for 12 h. The catalysts were reduced in H_2 flow at 300 °C for 2 h before its use for glycerol hydrogenolysis.

3.4 Preparation of bifunctional Ruthenium catalysts

The activity of Ru/C catalyst alone is very less when compared to the activity in presence of solid acid co-catalysts. Several solid oxides like ZrO_2 , TiO_2 , Nb_2O_5 and zeolites can be used as co-catalysts. The selected co-catalysts were crushed in to small particle of < 100 mesh size and mixed with Ru/C catalysts during activity studies.

3.5 Activity measurements

Hydrogenolysis of glycerol was carried out in an autoclave. In this experiment, the required quantities of glycerol diluted with de-ionized water and catalyst were taken. Prior to the experiment, the catalysts were reduced at suitable temperature for 3 h with H_2 flow (30 ml/min). In a typical run, 50 g of the aqueous glycerol solution and required quantity of the catalyst were loaded into the reactor. The autoclave purged with H_2 flow to drive off the air present in

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Vol. 6, Issue 9, September 2017

autoclave. After the purge, the reaction temperature and hydrogen pressure raised to required temperature and pressure. During the reaction the decrease in hydrogen pressure and was made up to maintain the pressure constant. After the reaction, the autoclave was cooled, the gas products were collected in a Teflon bag, and the liquid products were separated from the catalyst by filtration.

3.6 Product analysis

After the reaction the system was allowed to cool down to room temperature and the gas products were collected in a gas bag and the liquid phase products were separated from the catalyst by filtration. These products were analyzed using a gas chromatograph equipped with a flame ionization detector (FID). The GC column used was aInno wax capillary column (30 m X0.32 mm X 0.5 mm).The Products were also identified by using GC–MS. The gas phase products were analyzed by a gas chromatograph equipped with Porapak Q column and thermal conductivity detector. The products identified during glycerol hydrogenolysis are 1,2- propanediol (1,2-PD), acetol, 1-propanol (1-PO), and 2-propanol (2-PO) as hydrogenolysis products and ethylene glycol (EG), ethanol, methanol, ethane and methane are as degradation products.

IV. RESULTS AND DISCUSSIONS

4.1 Surface area and Pore volume

The surface area of pure activated carbon prepared from rice straw UR-0 is $376 \text{ m}^2 \text{ g}^{-1}$. As the wt.% of Ru increases from 1 to 7, the surface area and pore volumes gradually decreased. The change in pore volume and average pore diameter is marginal. Based on the activity studies the highest activity is shown on Ru/C-UR0-5 catalyst which was reported in our earlier studies [17]. The surface area's of pure activated carbons UR-0, UR-1, UR-2 and UR-3 shown in Fig.1, are gradually increasing. It is interesting to see that when UR-0 is further activated by KOH, HNO_3 , H_3PO_4 and KMnO_4 , there is varied trend in surface properties shown in Fig.2. Although the N_2 adsorption isotherms are similar for all samples, the adsorption capacities are significantly different according to the strength of activating reagent. The sample treated with KOH and KMnO_4 shows higher surface area than UR-0. From this it is well recognized that during activation with KOH and KMnO_4 , pores are opening up due to oxidation of organic volatile matter. Decreasing in surface area of acid treated samples is due to presence oxygen functional groups located at the entrance of pores which hinder nitrogen molecules to go inside of the pores. Reduction of BET surface area in acid treated biochars may also be due to excess water released due to dehydration in pores. This leads to produce an over gasification of biochar by converting micropores in to macropores.

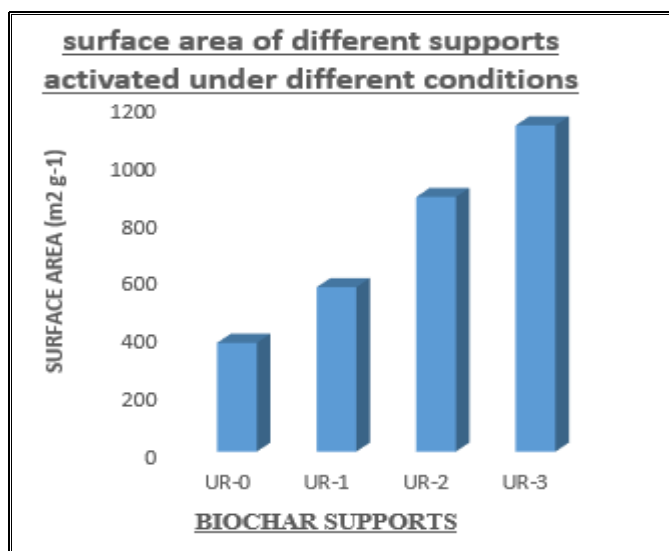


Fig.-1 Surface areas of different Biochar supports

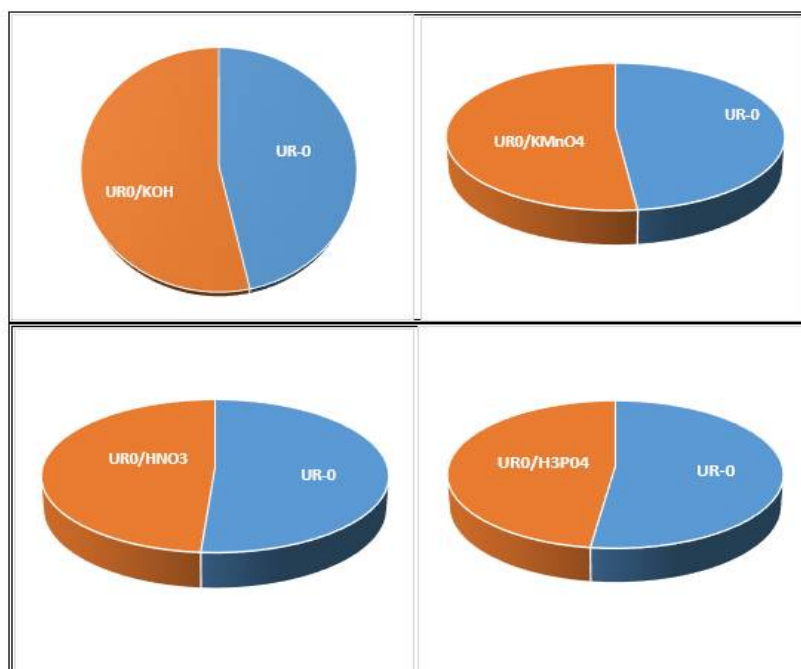


Fig.-2 Comparitive surface areas of pure UR-0 and activated surface

4.2 Evaluation of metal functionality of carbon supported Ru metal catalysts

The selectivity to 1,2-PDO, 1,3-PDO and EG were discussed in our previous paper [17]. The activity results of glycerol hydrogenolysis are listed in Table-3. Highest conversion of glycerol is observed for Ru/C-UR3-5 clearly presented in Table-1, however the conversion rates are less.

Table-1 Glycerol hydrogenolysis activity of Ru/C catalysts on different supports

Catalyst	Conv. %	Selectivity				
		1,2-PDO	EG	1,3-PDO	Acetol	Others
Ru/C-UR0-5	2.5	20.3	65.4	3.2	0.9	8.1
Ru/C-UR1-5	3.9	21.2	52.1	10.4	0.4	12.4
Ru/C-UR2-5	6.3	19.5	57.2	4.8	0.2	12.7
Ru/C-UR3-5	8.5	18.4	64.1	0.5	0.1	10.2

Reaction conditions: 20 wt % Glycerol aqueous solution: 50 ml; H₂ Pressure: 60 bar;

Reaction Time: 8 h; Catalyst Weight: 0.3 g (5%); Reaction Temperature: 120° C.

Glycerol hydrogenolysis activity of Ru/C catalysts were very poor. In order to achieve high glycerol conversions, solid acids were added to reaction medium along with noble catalysts [18]. Amberlyst was used as a solid acid additive in combination with carbon supported noble metal catalysts for glycerol hydrogenolysis. The combination of Ru/C with Amberlyst was found to be effective for glycerol hydrogenolysis under mild reaction conditions compared to Rh/C, Pt/C, and Pd/C catalysts [19]. To know the influence of acidity of solid acid catalyst on the reactivity of proven superior catalyst Ru/C-UR3-5 (end numerical indicates wt. % of Ru metal), various solid acids with varying acid strengths such as Nb₂O₅, TiO₂, ZrO₂, were selected for the hydrogenolysis reaction.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

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Vol. 6, Issue 9, September 2017

The results enhanced hydrogenolysis activity than supported metal catalysts when used alone. These acid co-catalysts enhanced conversion and selectivity. Highest conversion percentage is observed for Ru/C-UR3-5 in presence of TiO₂. The order of % conversions of glycerol is TiO₂> Nb₂O₅> ZrO₂> pure catalyst. The results indicated that glycerol hydrogenolysis is the result of two reaction stages, dehydration to acetol and hydrogenation to 1,2-PDO. It can be seen from Table-2, that when TiO₂ was used as solid acid the conversion of glycerol was more compared to the other acid catalysts. Moreover the selectivity towards 1,2-PDO and ethylene glycol was also high. Nb₂O₅ and ZrO₂ catalysts also showed almost similar conversion and selectivity.

Table-2 Glycerol hydrogenolysis activity of Ru/C-UR3-5 catalysts

Catalyst	Co-Catalyst	% conv.	Selectivity		
			1,2-PDO	EG	Others
Ru/C-UR3-5	--	8.5	18.4	64.1	17.8
Ru/C-UR3-5	Nb ₂ O ₅	39.7	51.6	30.4	18.6
Ru/C-UR3-5	ZrO ₂	27.6	58.9	33.4	7.9
Ru/C-UR3-5	TiO ₂	45.2	64.0	27.5	8.5

In order to optimize the yield and selectivity during glycerol hydrogenolysis, the reaction was studied by varying the reaction parameters using different catalysts of Ru/C with TiO₂ as co-catalyst. The results show that Ru/C-UR3-5 catalyst yields superior conversion of glycerol than others shown in Table-3.

Table-3 Glycerol hydrogenolysis activity of different Ru/C catalysts in presence of TiO₂ co-catalyst

Catalyst	Acid	% conv.	1,2-PDO	EG	Others
Ru/C-UR0-5	TiO ₂	15.4	44.8	36.8	20.4
Ru/C-UR1-5	TiO ₂	19.6	50.3	27.5	24.6
Ru/C-UR2-5	TiO ₂	34.1	58.2	31.4	10.9
Ru/C-UR3-5	TiO ₂	45.2	64.0	27.5	8.5

Reaction conditions: 20 % Glycerol aqueous solution: 50 ml, H₂ Pressure: 60 bar; Reaction Time: 8 h, Ru/C Wt. : 0.3 g (3 %), Solid acid wt: 0.6 g (6%), Reaction Temperature: 180° C.

4.3 Effect of catalyst weight on glycerol hydrogenolysis

To understand the synergetic effect of both the catalysts on the reaction, the hydrogenolysis was carried out by changing both the weights of the two catalysts and the results are shown in Table-4. The glycerol conversion remarkably increased by increasing the amounts of both the catalysts. The selectivity towards 1,2-PDO also increased in the present case. However, the selectivity to EG decreased with increase of the catalysts amount. These results support the formation of acetol and its subsequent hydrogenation to 1,2-PDO. The decrease in EG could be explained as due to higher hydrogenation activity on Ru/C. There were no excess Ru sites to cleave 1,2-PDO to EG. These results confirm the synergistic and bi-functional nature of glycerol hydrogenolysis.

Table-4 Effect of variable wts. of Ru/C and TiO₂ catalyst on hydrogenolysis of glycerol.

Wt. of catalysts (mg)		Conversion %	Selectivity (%)		
Ru/C	TiO ₂		1,2 PDO	EG	Others
150	300	25.0	60.4	32.1	7.9
300	600	45.2	64.0	27.5	8.5
450	900	56.1	66.3	23.7	10.6
600	1200	61.1	67.8	21.5	11.2

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(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 9, September 2017

V. CONCLUSIONS

- Surface properties of activated carbons prepared from rice straw can be modified by KOH, HNO₃, H₃PO₄ and KMnO₄ reagents.
- The best activated carbon prepared from rice straw is UR-3 and relatively best catalyst is Ru/C-UR3-5 for glycerol hydrogenolysis.
- Conversion of glycerol is clearly influenced by solid acids as co-catalyst over Ru/C-UR3-5 during hydrogenolysis
- The activity of glycerol hydrogenolysis depends up on the amount of the acidity of solid acids.
- Among different acid catalysts studied, TiO₂ is showing moderate acid sites and executed better activity.
- Increase of total weight of Ru/C and solid acid catalysts lead to substantial increase in both glycerol conversion and selectivity to propyleneglycol.
- A synergistic effect was observed between solid acid and Ru/C catalyst towards glycerol conversion and selectivity to 1,2-PDO.

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