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Enhancing the sugars production yield by supporting $H_3PW_{12}O_{40}$ heteropoly acid on activated carbon for use as catalyst in hydrolysis of cellulose

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ABSTRACT

In this work, two catalysts were produced to be used in hydrolysis of cellulose reactions to obtain glucose, a raw material used in the production of bioethanol. The heteropoly acid, $H_3PW_{12}O_{40}$ (HPW), reported as strong and thermally stable acid, was supported on activated carbon (AC) in a ratio varying from 1:1 to 2:1 to produce the catalysts AC-HPW (1:1) and AC-HPW (2:1). The catalysts were tested in cellulose hydrolysis evaluating some reaction variables and the results show the remarkable dependence of reaction temperature, amount and acidity of the catalyst. The results indicate the advantage of supporting HPW on carbonaceous material for using as catalyst in hydrolysis of cellulose, showing better conversion rate into sugars comparing with unsupported HPW.

Keywords: heteropoly acid; activated carbon support; hydrolysis of cellulose.

1. INTRODUCTION

The production of renewable fuels has grown significantly in recent decades, motivated by environmental, political and economic issues [1,2]. Second generation ethanol is a renewable source of fuel that is in full development [3].The raw material for production originates from biomass which, after undergoing treatment processes, fermentation and distillation, provides alcohol for fuel [4,5]. Therefore, technologies involved in the production processes must follow the variety of feedstock.

Biomass is essentially composed of cellulose, hemicellulose and lignin [6]. Cellulose, the most abundant polymer on earth, is composed of units of D-glucose linked by glycosidic bonds and functions as the support structure in plants [7]. When the glycosidic bonds are hydrolyzed, the monomers of glucose become available for enzymatic fermentation [8].

One of the biggest drawbacks encountered during the hydrolysis reaction is the high crystallinity associated with large amounts of intra and intermolecular hydrogen bonds present in cellulose. This feature makes cellulose insoluble in bases, acids and organic solvents, which results in difficulty of accessing the glycosidic bonds to be hydrolyzed [6]. The hydrolysis reaction may occur by several processes using bases, acids, oxidizing agents or by the action of microorganisms [9]. Acid hydrolysis using mineral acids offers good yields; however, acid effluents are generated, which cause equipment corrosion and is difficult to stop the reaction producing degradation compounds [10]. In addition, although hydrolysis with microorganisms is very selective, it is expensive and needs stable and well-controlled reaction conditions like pH, temperature, etc [11].

Recently, many studies show the hydrolysis of cellulose with solid acids. Solid acid catalysts have advantages comparing with liquid acid catalysts as easier product separation and reduce waste generation because of reuse [4,12-14]. Some studies have been used heteropoly acids as catalysts in the hydrolysis of cellulose, with promising results [15].

Heteropoly acids are ionic clusters with redox properties, thermally stable, very acid and soluble in water and organic solvents [16]. One of them is $H_3PW_{12}O_{40}$ (HPW) which has the high thermal stability and acidity. They can be used in homogeneous, heterogeneous and biphasic reactions [17]. In heterogeneous

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phase, different supports for heteropoly acids have been studied. Activated charcoal, a carbonaceous material with high surface area, has good interaction with heteropoly acids and is able to produce catalysts with high acidity [18].

Since the use of HPW for the hydrolysis of cellulose is well known in the literature [19-21] the purpose of this work was to produce and characterize heterogeneous catalysts of HPW supported on activated carbon (AC) in different ratios, to be used as catalysts in hydrolysis of cellulose and verify if it increases the conversion of cellulose in sugars.

2. MATERIALS AND METHODS

2.1 Synthesis of catalysts

To produce the catalyst AC-HPW (1:1), 3.0 g of AC (Fluka) were added to 30 mL of an aqueous solution containing 3.0 g of HPW (Sigma Aldrich). The mixture was stirred for 24 hours and dried at 105°C. The material was pyrolyzed in a nitrogen atmosphere (10 mL min^{-1}) at 400°C for 3 hours. The same procedure was used for the catalyst AC-HPW (2:1); however, the ratio of 3.5 g of AC to 1.75 g of HPW was employed instead.

2.2 Characterization of catalysts

Fourier transform infrared spectroscopy (FTIR) was performed on an IR Affinity using KBr pellets. Thermogravimetric analysis (TGA) was performed using a Shimadzu DTG-60AH TGA. Samples (approximately 10 mg) were heated under synthetic air atmosphere in the range of 40 to 900℃ with a heating rate of 10℃ min^{-1} and a gas flow rate of 30 mL min^{-1}. Differential scanning calorimetry (DSC) was performed on a Shimadzu DSC-60A, in the range of 40 to 600°C. Scanning electron microscopy (SEM) was acquired with a LEO EVO 40XVP device, using a voltage of 25 kV. Energy dispersive X-ray spectroscopy (EDS) was performed in a device SEM coupled with EDS/INCA 350. The surface area analysis based on the BET method, was performed with an AUTOSORB-1, Quantachrome. To analyze the functional groups, a potentiometric titration was completed using an equipment Metrohm model Titrando 888 based on Boehm method [22].

2.3 Hydrolysis of cellulose

The cellulose hydrolysis reactions were performed in a closed system, with stirring for 2 hours, and varying the amount of catalyst and temperature. The catalysts employed were commercial HPW without further modification (homogeneous), AC-HPW (1:1) and AC-HPW (2:1) (both heterogeneous). The amount of substrate used was 0.1 g of microcrystalline cellulose (Synth), with different amounts of catalyst and water up to 10 mL total volume. Reaction conditions are shown in Table 1. The catalyst on reaction 19, named AC-HPW (1:1) reused, was the same catalyst of reaction 8 that was recovered by filtration and washed until pH 7.

The products of the reactions were analyzed in a Shimadzu UV-1800 UV/Vis spectrophotometer and the total reducing sugar content (%TRS) was quantified by the dinitrosalicylic acid (DNS) method [23] at a wavelength of 540 nm.

Table 1: Reaction conditions for the hydrolysis of cellulose.

REACTION	CATALYST	TEMPERATURE (°C)
1	-	120
2	-	150
3	0.30 AC	120
4	0.15 HPW	120
5	0.30 HPW	120
6	0.30 HPW	150
7	0.30 AC-HPW(1:1)	100
8	0.30 AC-HPW(1:1)	120
9	0.30 AC-HPW(1:1)	150
10	0.15 AC-HPW(1:1)	120
11	0.15 AC-HPW(1:1)	150

12	0.45 AC-HPW(1:1)	120
13	0.45 AC-HPW(1:1)	150
14	0.30 AC-HPW(2:1)	100
15	0.30 AC-HPW(2:1)	120
16	0.30 AC-HPW(2:1)	150
17	0.15 AC-HPW(2:1)	120
18	0.45 AC-HPW(2:1)	120
19	0.30 AC-HPW (1:1) reused	120

3. RESULTS AND DISCUSSION

3.1 Materials characterization

Materials supported on activated carbon present different acid sites on the surface as carboxylic acids, phenolic groups and lactones, and the contribution of each of these groups provides the total acidity of the catalysts. The catalysts showed higher acidity compared to the support (AC) and HPW (Table 2). This result should be related to the total contribution of acid sites in AC and HPW. The AC-HPW (1:1) showed higher acidity than AC-HPW (2:1) because the proportion of HPW was larger. The acidity of the materials directly reflects the energy required to remove a proton from a Brønsted acid. Thus, the higher Brønsted acidity of the catalyst, the lower the energy required for the reaction [24].

The surface area using the BET method was studied to determine the influence of the amount of HPW impregnated on the surface of the material. The AC demonstrates a larger surface area when compared to the catalysts (Table 2). The surface area decreases when larger is the amount of HPW showing the impregnation of the support by the HPW. Among the as-prepared catalysts, the AC-HPW (1:1) showed the lower surface area due to the larger amount of HPW.

Table 2: Total acidity and BET area of materials.

MATERIALS	**ACIDITY (mmol H^+ g^{-1})**	**S_{BET} (m^2 g^{-1})**
HPW	1.00	10 [25]
AC	0.89	1126
AC-HPW 1:1	1.64	272
AC-HPW 2:1	1.24	444

The presence of HPW impregnated on the surface of the AC-HPW catalysts is confirmed in the FTIR spectra of AC, HPW, AC-HPW (1:1) and AC-HPW (2:1) (Figure 1). Bands attributed to the Keggin anion were observed in the catalysts produced (between 700 and 1200 cm^{-1}) and as the HPW content increased, the intensity of the bands also increased. In addition, characteristic bands related to four different types of oxygen atoms in HPW structure were observed at 797 cm^{-1}, referring to stretching of W–O–W on the edges, at 890 cm^{-1}, referring to W–O–W stretching at the vertices, at 972 cm^{-1}, the asymmetric W–O stretching with terminal oxygen atoms and at 1079 cm^{-1} referring to asymmetrical P–O stretching [26].

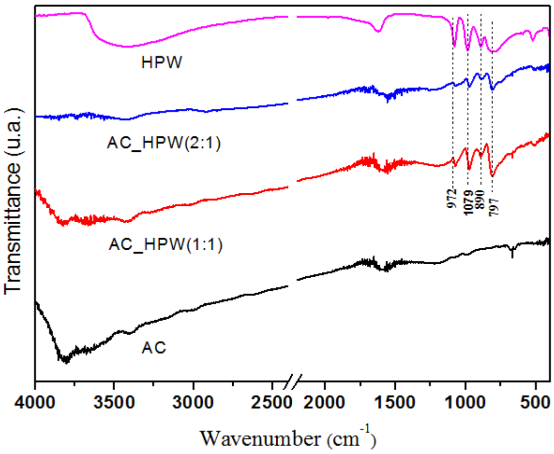

Figure 1: Fourier transform infrared spectroscopy (FTIR) spectra of HPW, AC-HPW (2:1), AC-HPW (1:1) and AC.

The SEM micrographs provide information about the morphology of the catalysts and EDS spectra quantify the elements present, as shown in Figure 2 for (a) HPW, (b) AC, (c) AC-HPW (1:1) and (d) AC-HPW (2:1) materials. The SEM micrographs of the catalysts (2c and 2d) highlight the presence of the HPW impregnated on the surface of AC support. The EDS spectrum of HPW identifies the peaks of the constituent elements, such as phosphorus, tungsten and oxygen. In the spectra of the catalysts, there are peaks relative to both the AC support (carbon and oxygen) as well as HPW.

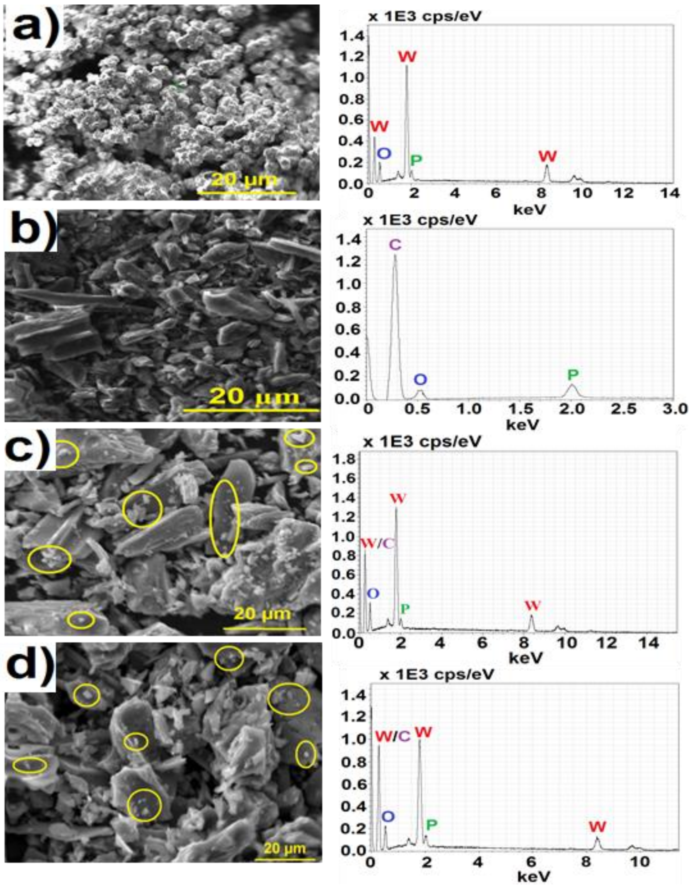

Figure 2: SEM images and EDS spectra of a) HPW, b) AC, c) AC-HPW (1:1), and d) AC-HPW (2:1). The circles on figures 2c and 2d highlight the HPW on CA.

The amount (%) of each element identified by EDS for the samples are shown in Table 3. The AC-HPW (1:1) catalyst showed a lower amount of carbon compared to AC-HPW (2:1) due to a lower proportion of AC in the catalyst. The tungsten content in AC-HPW (1:1) was higher than in AC-HPW (2:1), confirming a larger amount of HPW on the support. In both catalysts, the tungsten content was close to the calculated value (%W*) indicating its efficient impregnation over the support and no significant loss during the process.

Table 3: EDS quantification of elements present in the catalysts.

MATERIALS	%C	%O	%P	%W	%W* (calculated)	TOTAL
HPW	0	9.1	6.9	84.0	76.6	100
AC-HPW (1:1)	56.9	3.0	2.3	37.8	38.3	100
AC-HPW (2:1)	72.0	3.0	0.4	24.6	26.0	100

Thermogravimetric analysis showed that cellulose thermally decomposes in two stages; at low temperatures (<300°C), degradation occurs gradually with low mass loss, which relates to dehydration of cellulose. At high temperatures (>300°C), cellulose loses mass rapidly and effective degradation occurs (the rate of degradation stabilizes after 530°C) with 98% mass lost. AC showed small weight loss (ca. 100°C) due to water release and good thermal stability up to 400°C. After this temperature, there is high mass loss (90%) and the rate of degradation stabilizes at 650°C. HPW (Figure 3a) shows total mass loss of 5%, which occur via two-step process related to removal of different types of water at the initial temperatures and remaining stable to higher temperatures [27]. The loss of water can be confirmed by DSC analysis (Figure 3b) occurring an energy variation (endothermic process) at 100°C related to loss of crystallization water and a second variation (endothermic process) at 250°C related to constitutional water of material. At 300°C, an exothermic process occurs due to Keggin anion decomposition [28], without appreciable weight loss, since this was not observed in TGA analysis.

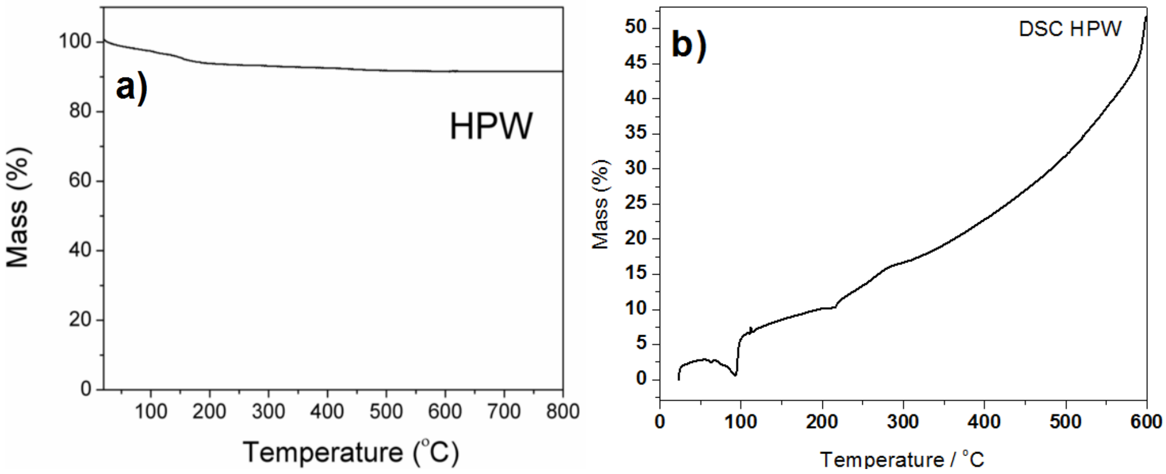

Figure 3: a) TGA and b) DSC graphics of the HPW heteropoly acid.

Both catalysts (Figure 4) are thermally stable up to 420°C, when the catalysts mass starts to decrease. After this, AC-HPW (1:1) shows a mass loss of 50% and AC-HPW (2:1) of 85% indicating that a higher mass loss occurs when the AC content is higher. The rate of degradation stabilizes at 520°C for each catalyst. These important results show that the catalysts can be used at temperatures lower than 420°C, and they would be stable in hydrolysis reactions at 100, 120 and 150°C.

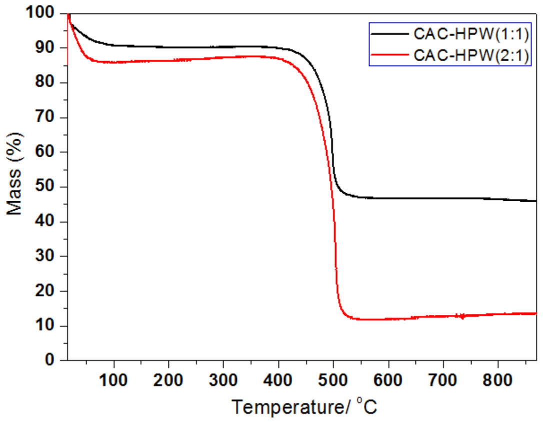

Figure 4: TGA graphics of AC-HPW (1:1) and AC-HPW (2:1).

3.2 Hydrolysis of cellulose

The results from the hydrolysis of cellulose, in %TRS (Figure 5), were calculated using the standard curve of glucose. The experiments were performed focusing on studying the influence of the variables: type and amount of catalyst, temperature of the reaction and catalyst reuse. All these variables affect the results in %TRS. The importance of the catalyst in hydrolysis of cellulose can be confirmed in Figure 5; reactions with no catalyst (1 and 2) and using only the AC support (3), results in low conversions of %TRS comparing with homogeneous reactions using as catalysts commercial HPW without further modification (4 to 6) and heterogeneous reactions using as catalysts AC-HPW (1:1) and AC-HPW (2:1) (7 to 19). The catalyst is necessary to access the crystalline sites of cellulose and break the glycosidic bonds to produce sugar.

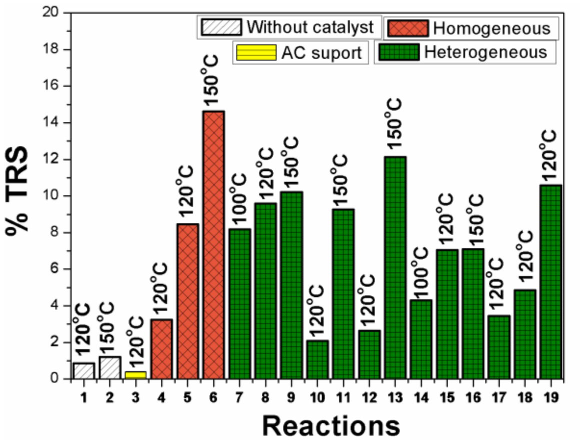

Figure 5: Results in %TRS from the hydrolysis of cellulose using the catalysts produced.

3.3 Effect of temperature

The influence of temperature can be observed comparing the reactions with the same amount of catalyst at different temperatures (5 and 6 for HPW; 7, 8 and 9 for AC-HPW (1:1); 14, 15 and 16 for AC-HPW (2:1)); higher temperature results in higher %TRS in homogeneous and heterogeneous phase. Even when no catalyst is used the influence of temperature can be observed although the conversion in %TRS are lower.

When reactions at the intermediate temperature (120°C) were compared (5, 8 and 15), it was observed that although the amount of HPW used in reaction 5 is higher than that used in reactions 8 and 15 (0.30 g, 0.15 g and 0.10 g, respectively), a better conversion was obtained in reaction 8, showing the advantage of supporting the catalyst. This trend can be attributed to an increase in the acidity of the catalyst supported, as shown in Table 2, which a higher amount of H^+ is available to react. At high temperatures (150°C), with the same amount of catalyst (6, 9 and 16), higher conversions are obtained for HPW in homogeneous phase (6) (Figure 6). It can be explained by the high solubility of HPW in water, which can dissociate protons, increasing the amount of H^+, freely available to interact with the oxygen atom in the ether linkage of cellulose [14].

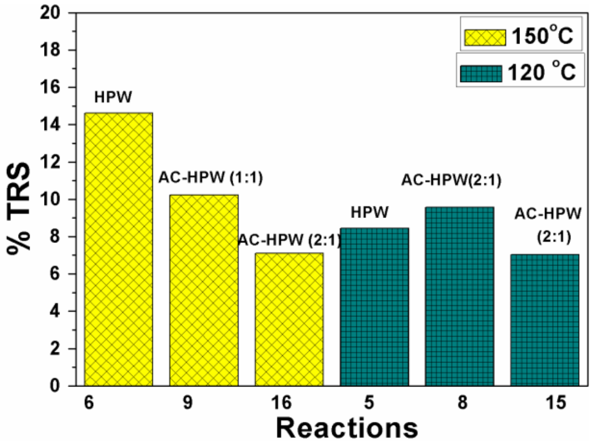

Figure 6: Relationship between temperature and the catalyst phase using 0.30g of each catalyst.

The results show the advantage of supporting the catalyst since the support increases the surface area, providing more catalytic sites for reaction. Although reaction 6 showed the highest conversion in %TRS, the amount of HPW in the middle needs to be observed; comparing reaction 4 with 8, in which the amount of HPW (0.15g) and temperature (120°C) are the same, when the HPW is supported the efficiency is higher than that in the homogeneous reaction. This result can be explained by the higher acidity of the catalyst supported on AC compared with pure HPW. Moreover, we could not expect different results if HPW reused is used, since the amount of soluble HPW would be the same in both reactions.

3.4 Effect of amount of catalyst

The amount of catalyst is another important variable in the hydrolysis reactions. Comparing reactions using AC-HPW (1:1) at the same temperature (8, 10), it was observed that an increase in amount of catalyst results in an increase in %TRS. However, an excessive increase (reaction 12) did not result high sugar production yield (Figure 7). This trend also occurs for reactions using the AC-HPW (2:1) catalysts (15, 17 and 18). These results suggest the existence of an optimum amount of catalyst for the reaction instead of a direct relationship where more catalyst produces a higher conversion. A large amount of catalyst may difficult the mobility of reagents in the medium reaction resulting in a lower conversion in %TRS.

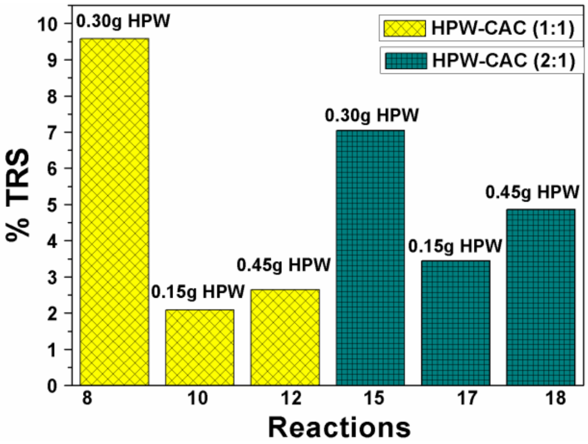

Figure 7: Relationship between the variation in the amount of catalyst and the %TRS in reactions performed at 120°C.

Furthermore, at higher temperatures (150°C) using the AC-HPW (1:1) catalyst (9, 11, 13), larger amounts of catalyst resulted in higher conversions, independent of the quantities used (Figure 8). Additionally, the %TRS are relatively equal, indicating that, at higher temperatures, the mobility of the reactants is higher, so changes in catalyst amounts do not produce substantial differences in yield of conversion to sugars.

Studies show the high solubility of HPW in water suggesting that the reaction is homogeneous even using the heterogeneous catalyst. In order to verify if the HPW is leached in water during the hydrolysis another reaction was performed (19) using the AC-HPW (1:1) reused from reaction 8 as catalyst. Comparing reactions 9 with 19 (Table 1) with the same conditions but different temperatures, the results show similar %TRS, even at lower temperature (reaction 19) indicating that HPW was not leached during hydrolysis reaction and it could be reused to convert more cellulose into TRS (Figure 8).

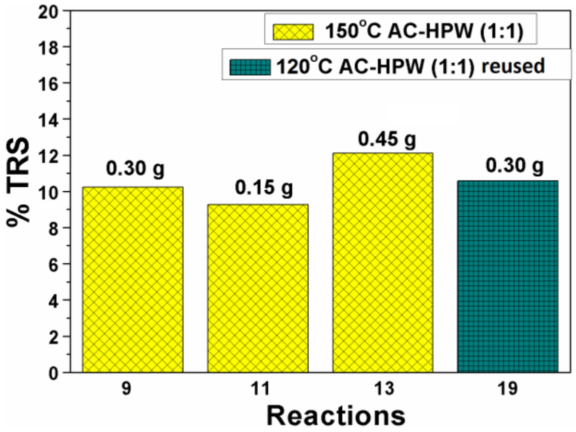

Figure 8: Conversion of cellulose at elevated temperatures with AC-HPW (1:1) catalyst.

4. CONCLUSION

The catalysts with different ratios of AC and HPW were synthesized and the results of characterization, BET, FTIR, MEV-EDS and TGA, confirm the impregnation of HPW in AC. The catalysts present higher acidity comparing with unsupported HPW, increasing the yield of conversion in sugar production. The hydrolysis reactions show better results in %TRS at high temperature, optimum amount of catalyst and heterogeneous phase. The HPW supported on activated carbon is more effective in terms of conversion to total reducing sugar (%TRS) comparing with unsupported HPW. The leaching test showed a good stability of HPW and the catalyst can be reused. The aim of the catalysts prepared in this work was to offer alternatives to the different reactions used for producing fuels by renewable sources.

5. ACKNOWLEDGMENTS

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