

Study on the Reuse of the Catalyst $\text{NbOPO}_4 \cdot n\text{H}_2\text{O}$ in the Conversion of Sugarcane Biomass into Furfural

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The reuse study of niobium phosphate catalyst ($\text{NbOPO}_4 \cdot n\text{H}_2\text{O}$, abbreviated as NbP) in furfural production from sugarcane bagasse (SCB) in an aqueous medium is the aim of this project. The heterogeneous NbP catalyst was exploited to hydrolyze the SCB biopolymers and dehydrate the major released carbohydrate, i.e., xylose, into furfural. The compounds were separated and quantified by high-performance liquid chromatography (HPLC). At the end of each reaction, the catalyst was separated from the SBA by sieving and pre-treated with water (A), 5 ml of acetone (B), 10 ml of acetone (C) or calcined at 550 °C (D). After pretreatment, the catalyst was reused for another cycle. An analysis of variance was performed to compare the difference in productivity between cycles statistically. The catalyst was analyzed for its morphology by SEM images and XEDS. For the release of xylose, at a significance level of 0.01, the pretreatments A, B, and D in the reactions at 150 °C were efficient to reactivate the catalyst's active sites. Cycles 1 and 2 produced about 15 g kg⁻¹ xylose at 110 °C and 80 g kg⁻¹ furfural at 150 °C. The results with pretreatment A at 150 °C are promising from an economic and environmental point of view since the other pretreatments either use a toxic, more costly solvent or consume electricity.

1. Introduction

The increase in the price of crude oil has resulted in an interest in searching and developing alternative sources of fuel and chemicals (Mamman et al., 2008). Towards sustainable growth, the global trend aims to develop different technologies and processes based on renewable sources to produce fuel, energy, and chemicals as an alternative to the oil-based economy. Brazil has a vast arable area and favourable climates that highlight significant advantages for developing various crops in different regions. As a result of the country's agricultural diversity, ethanol and biodiesel production as alternatives to fossil fuels is facilitated. In addition, the excess lignocellulosic residue from such processes is used to produce-generation bioenergy and high value-added chemical inputs with a wide range of applications (Aranda et al., 2009). In this scenario, lignocellulosic biomass is the most promising and abundant renewable source to achieve these goals (Catrinck et al., 2020).

Furfural is industrially produced from lignocellulosic materials such as corn cobs and sugarcane bagasse (SCB). It is currently the only furan compound obtained directly from lignocellulosic biomass on an industrial scale (Mika et al., 2018). In addition to its use as a secondary fuel precursor, the main uses for furfural include the extractive distillation of hydrocarbons, as a solvent for refinery oil, in the manufacture of plastics, and pesticide and germicide formulations. Therefore, a strategy to increase yields and reduce energy costs in furfural production and from the hydrolysis of lignocellulosic biomass is very important to the fuel and fine chemical industries. Hydrolysis is aided by a catalytic process that converts the carbohydrates present in the biomass (cellulose and hemicellulose fraction) into fermentable sugars. These sugars, mainly glucose, xylose, and arabinose, can be later converted, for example, via fermentation and/or dehydration, to products with high added value. Therefore, the availability of these carbohydrates in the reaction medium is essential for higher yields of the products of interest. Several methods presented in the literature propose using xylose as a model substrate to improve or

develop new strategies to increase furfural yield. These methods alter the catalyst and solvent to make the process more efficient and environmentally sustainable (Catrinck et al., 2020). Niobium-based catalysts are recognized as water-tolerant solid acid catalysts. Applications have been found in several catalytic processes that require strong acidic properties, even in aqueous media. As they have Lewis (LAS) and Brønsted (BAS) acid sites, these catalysts accelerate the isomerization and conversion of pentose in reactions involving lignocellulosic materials. Niobium phosphate, for example, has LAS and BAS with the advantage that these properties are preserved in an aqueous medium and at high temperatures (Carniti et al., 2006; Catrinck et al., 2020). Considering the advantages of heterogeneous catalysis, the replacement of water-soluble acids by solid acids is highly desirable in the chemical industry. Solid acids are ecologically sound concerning corrosiveness and safety, and their separation and recovery are facilitated. However, when using water-insoluble substrates, such as SCB, two aspects must be considered: catalyst separation and reuse. To our knowledge, no study in the literature has used, separated, and reused the niobium phosphate catalyst to produce furfural directly from the SCB. Catrinck et al. (2020) show that niobium phosphate is an excellent catalyst to produce furfural from SCB; however, the authors did not report separation and reuse results for this catalyst. Thus, the specific objectives of this work are: i) to produce furfural from SCB using niobium phosphate; iii) to separate the catalyst from the biomass, and iv) to investigate its reuse.

2. Materials and Methods

2.1. Materials

NbOPO₄.nH₂O (NbP) was supplied by Companhia Brasileira de Metalurgia e Mineração (CBMM, Brazil) and washed to remove excess phosphoric acid from the surface. Acetone (Fmaia 99.5 %) will be used as supplied. The sugarcane bagasse (SCB) used as substrate was supplied by the Sugarcane Genetic Improvement Program (PMGCA) of the Department of Plant Science at the Federal University of Viçosa, UFV. The SCB was ground, sieved, and removed its extractives before the experiments. The bagasse supplied was characterized with the following composition: 27.7 % cellulose; 25.26 % hemicellulose; 18.34 % lignin. Of the amount of hemicellulose, 19.56 % is made up of xylose and 5.69 % of arabinose (Barbosa, 2018).

2.2. Methods

2.2.1. Catalytic reactions

The catalytic reactions were developed in glass tubes with a conical bottom coupled with a temperature control heating plate and a magnetic stirring system. Initially, 0.3 g of SCB, 0.3 g of catalyst, and 5 ml of deionized water were added to the tubes of the first cycle, and a blank was also made, i.e., without addition of catalyst. The interaction between the mixture components was increased by vigorously shaking the tubes before the reaction using a tube shaker (CORNING – LSE). The reactions were studied at two temperatures, 110 and 150 °C. The tubes were placed in a glycerine bath, whose temperature was controlled to ensure the accuracy of each temperature. The reaction time was five hours. After completion of the reaction, the samples were cooled to room temperature, transferred to Falcon tubes, and taken to a centrifuge (Quimis) for five minutes.

2.2.2. Liquor analysis

After completion of centrifugation, an aliquot of the supernatant was filtered using a 0.45 µm Nylon syringe filter into a 1.5 mL vial and taken for analysis on the HPLC in a Shimadzu Prominence chromatograph. Two detectors were used: the evaporative light scattering detector (ELSD) for carbohydrate detection and the photodiode array (PDA) for the furan analysis, i.e., HMF and Furfural. A volume of 20 µl was injected. Compounds were separated at a flow rate of 0.8 mlmin⁻¹ on a Bio-rad Aminex HPX-87H column (300 mm × 7.8 mm, 9 µm particle size) maintained at a temperature of 60 °C. A pre-column of the same material was used. The mobile phase used in isocratic mode (85:15, v/v) was an aqueous solution with 0.08 % acetic acid and 15 % acetonitrile. The temperature of the ELSD detector was 50 °C at a carrier gas pressure of 350 kPa. The total running time was 19 min. Shimadzu's Labsolution Software was used for method setup, injection, analysis, construction of the calibration models and predictions. The answer used to verify carbohydrate release and conversion to furfural is given by Eq(1).

$$Productivity = \frac{Mass\ p}{Mass\ SCB} \quad (1)$$

where Mass p is the predicted mass of the compound (carbohydrate or furan) in the reactor and Mass SCB is the mass of sugarcane bagasse weighed.

2.2.3. Solid-phase treatment

The catalyst/biomass mixture remaining in the tube was washed with 8 ml of water, and new centrifugation was carried out for two minutes. After washing with water, a study of different pretreatments was conducted to verify the most suitable for removing impurities from the catalyst. The following pretreatments were studied: A - additional washing with 8 ml of water followed by centrifugation for 2 min; B - washing with 5 ml of acetone followed by centrifugation; C - two washes with 5 ml of acetone; each followed by centrifugation for 2 min; D - calcination at 550 °C in a muffle (SP LABOR – SP 1200) for 5 h using porcelain crucibles. These pretreatments were chosen based on previous works found in the literature, which studied the removal of humins deposited on the active sites of solid acid catalysts (Bernal et al., 2014). The supernatant from each wash was discarded. Pretreatments A, B, and C were performed twice. After pretreatments A, B, and C, the solids were oven-dried at 80 °C for 12 h. Subsequently, the catalyst was separated from the biomass using an 80-mesh sieve. The fraction that passed through the sieve was identified as the recovered catalyst and found a percentage of 80 % recovery, on average. The solids removed from the muffle were the recovered catalyst for pretreatment D. The second cycle was carried out from the recovered catalyst mass. The added bagasse mass was calculated proportionally to the recovered catalyst mass, considering the same reaction conditions of the first cycle. An analysis of variance (ANOVA) was performed, considering the cycles as a variable for all pretreatments and both temperatures. Four repetitions of the productivity values were used for each cycle.

2.2.4. Scanning electron microscopy analysis

The solids separated in pretreatments A, B and C, in addition to the catalyst recovered in pretreatment D, were placed on a double carbon adhesive tape glued to metallic stubs. The stubs were taken for metallization of the samples with gold in a metallizer (Quorum Q150R S). After metallization, the samples were analysed in a scanning electron microscope (JEOL - JSM-6010LA). During electron microscopy, elemental analysis of the catalysts was performed using energy-dispersive X-ray spectroscopy (XEDS).

3. Results and Discussion

After liquor analysis, it was noted that there was low or no release of glucose, arabinose and low or no production of HMF. Thus, this work will be limited only to the results obtained for xylose and furfural.

3.1. Liquor analysis

The productivity values obtained for xylose and furfural in the two cycles and the different pretreatments are shown in Table 1. For the pretreatments highlighted with an asterisk (*), significantly different values are observed between cycles 1 and 2 to one 0.01 significance level. Conversely, for non-highlighted pretreatments, values between cycles 1 and 2 are statistically equal to a significance level of 0.01.

The values in parentheses are the coefficients of variation, which indicate the precision in the replicates. Overall, the accuracy was relatively good, as the studied system is complex.

Table 1: Average yields and respective coefficients of variation for xylose and furfural in cycles 1 and 2 in different catalyst pretreatments

Treatments	Xylose (g kg ⁻¹)		Treatments	Furfural (g kg ⁻¹)	
	C1	C2		C1	C2
A110*	25.81 (18 %)	7.47 (09 %)	A110	1.87 (22 %)	1.22 (07 %)
A150	16.66 (05 %)	14.45 (08 %)	A150	75.54 (02 %)	76.47 (05 %)
B110	16.81 (25 %)	11.97 (14 %)	B110	1.46 (23 %)	1.78 (17 %)
B150	18.18 (15 %)	13.33 (17 %)	B150	80.62 (10 %)	63.01 (14 %)
C110*	11.97 (14 %)	4.46 (05 %)	C110	1.87 (22 %)	0.98 (27 %)
C150*	13.33 (17 %)	30.23 (15 %)	C150	63.01 (14 %)	60.39 (15 %)
D110*	17.19 (12 %)	4.50 (05 %)	D110*	1.34 (05 %)	0.75 (09%)
D150	17.17 (17 %)	18.07 (16 %)	D150	78.91 (18 %)	82.68 (17 %)

*Different at the 0.01 significance level. Values in parentheses are coefficients of variation calculated from four replicates. C1 and C2 are cycles 1 and 2, respectively.

The results presented in Figure 3 show the variation in xylose and furfural productivity in cycles 1 and 2 and at the two temperatures studied. The ANOVA results for xylose are shown in Table 2.

It can be observed for xylose that for catalysis at a temperature of 110 °C, from the first to the second cycle, there was a deactivation of the catalyst's active sites for pretreatments A, C, and D. This result is confirmed by ANOVA since the variation between the groups was significant at a level of significance 0.01. It is possible to observe that, for pretreatment B at 110 °C and a significance level of 0.01, the productivity of cycle 1 is

statistically equal to that of cycle 2. This result shows that pretreatment B can be efficient for catalyst regeneration at this temperature.

In contrast, for catalysis at a temperature of 150 °C, the ANOVA results at a significance level of 0.01 show that there is no statistical difference between cycles 1 and 2 for pretreatments A, B and D. Therefore, these results prove that the pretreatments used were efficient to reactivate the catalyst's active sites. The temperatures of 150 °C and these pretreatments are promising since they indicate a possibility of catalyst recovery in direct catalysis with raw SCB. From an economic and environmental point of view, pretreatment A is the most viable since B uses a more costly and toxic solvent and D uses calcination, which consumes electricity.

In Figure 3C, it is observed that the xylose productivity increased in the second cycle, an unexpected behaviour for the temperature of 150 °C. These results were obtained from replicates; there is probably an anomalous behaviour for releasing xylose when the catalyst is recovered using pretreatment C.

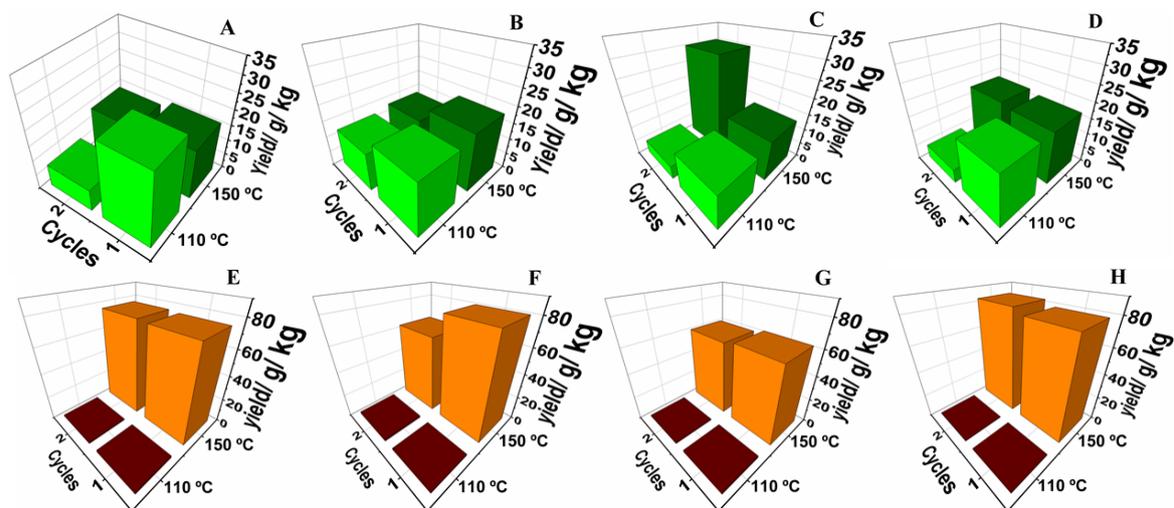


Figure 3: Xylose (A-D) and Furfural (E-H) productivity at two temperatures (110 and 150 °C) in cycles 1 and 2 and different catalyst treatments. A/E: washing with water, B/F: washing with acetone, C/G: washing with excess acetone, D/H: calcining in the muffle.

Table 2: Analysis of variance of cycles for xylose release in the different pretreatments

Xylose – A110						Xylose – A150					
Source of Variation	QS	GL	MQ	F	Value-P	Source of Variation	QS	GL	MQ	F	Value-P
Between groups	673.2	1	673.2	62.6	0.00022	Between groups	9.74	1	9.74	9.58	0.021
In groups (error)	64.5	6	10.7			In groups (error)	6.10	6	1.02		
Xylose – B110						Xylose – B150					
Source of Variation	QS	GL	MQ	F	Value-P	Source of Variation	QS	GL	MQ	F	Value-P
Between groups	46.8	1	46.8	4.47	0.08	Between groups	46.83	1	46.83	4.47	0.079
In groups (error)	62.9	6	10.5			In groups (error)	62.88	6	10.48		
Xylose – C110						Xylose – C150					
Source of Variation	QS	GL	MQ	F	Value-P	Source of Variation	QS	GL	MQ	F	Value-P
Between groups	148.6	1	148.6	38.4	0.00082	Between groups	174.8	1	174.8	1.41	0.279
In groups (error)	23.2	6	3.9			In groups (error)	742.0	6	123.7		
Xylose – D110						Xylose – D150					
Source of Variation	QS	GL	MQ	F	Value-P	Source of Variation	QS	GL	MQ	F	Value-P
Between groups	381.6	1	381.6	79.2	0.00011	Between groups	26.17	1	26.17	0.55	0.488
In groups (error)	28.9	6	4.8			In groups (error)	287.4	6	47.90		

The results presented in Figure 3 (E-H) show the variation in furfural productivity in cycles 1 and 2 and at the two temperatures studied. The ANOVA results for furfural are shown in Table 3.

It can be observed that for catalysis at a temperature of 110 °C, from the first to the second cycle, there was a low furfural production for all pretreatments, as observed in Figure 3 (E-H). This result was expected because, at this temperature, the reaction of dehydration from xylose to furfural is not thermodynamically favorable. When checking the ANOVA, it is observed that there was significant variation between cycles for pretreatment D.

Despite this significant variation, it is noted that the values are low; therefore, this ANOVA result should be disregarded.

In contrast, for catalysis at a temperature of 150 °C, ANOVA noted no significant difference between cycles at a significance level of 0.01 for all pretreatments. Therefore, the active catalyst sites were not significantly affected by these pretreatments. The results for a temperature of 150 °C for all pretreatments are promising and indicate a possibility of catalyst recovery in direct catalysis with raw SCB.

From an economic and environmental point of view, pretreatment E is the most viable since F and G use a more costly and toxic solvent, and H uses calcination, which consumes electricity.

Table 3: Analysis of variance of cycles for furfural release in the different pretreatments

Furfural – A110						Furfural – A150					
Source of Variation	QS	GL	MQ	F	Value-P	Source of Variation	QS	GL	MQ	F	Value-P
Between groups	0.853	1	0.853	9.35	0.022	Between groups	1.74	1	1.74	0.19	0.681
In groups (error)	0.547	6	0.091			In groups (error)	56.25	6	9.37		

Furfural – B110						Furfural – B150					
Source of Variation	QS	GL	MQ	F	Value-P	Source of Variation	QS	GL	MQ	F	Value-P
Between groups	0.21	1	0.21	2.11	0.197	Between groups	620.0	1	620.0	8.92	0.024
In groups (error)	0.59	6	0.10			In groups (error)	416.8	6	69.5		

Furfural – C110						Furfural – C150					
Source of Variation	QS	GL	MQ	F	Value-P	Source of Variation	QS	GL	MQ	F	Value-P
Between groups	2.57	1	2.57	11.06	0.016	Between groups	627.8	1	627.79	1.20	0.314
In groups (error)	1.40	6	0.23			In groups (error)	3126.9	6	521.15		

Furfural – D110						Furfural – D150					
Source of Variation	QS	GL	MQ	F	Value-P	Source of Variation	QS	GL	MQ	F	Value-P
Between groups	1.22	1	1.22	16.31	0.0068	Between groups	571	1	571.2	0.56	0.482
In groups (error)	0.45	6	0.075			In groups (error)	6102	6	1016.9		

3.3. Scanning electron microscopy analysis and Energy Dispersive X-Ray Spectroscopy

A morphology with a larger particle size and disaggregated particles was observed for pure NbP. After catalysis, there was a significant change in morphology for NbP after pretreatment with water at 150 °C, acetone and calcination in a muffle at both temperatures. After pretreatment with water at 110 °C the catalyst structure did not change significantly from the pure.

In general, for pretreatment with water at 150 °C, and acetone and calcination in a muffle at both temperatures, the particle size has decreased, the particles appeared to be more aggregated, and, therefore, there is a larger contact surface. The appearance of residual organic particulates (humins or lignocellulosic material) is not observed in the Figure 4, which shows that the pretreatments effectively cleaned the surface.

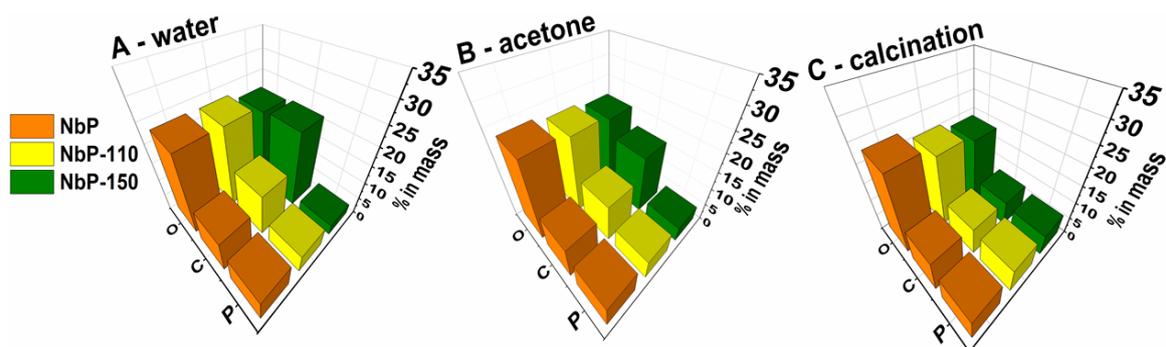


Figure 4: Elemental analysis of oxygen (O), carbon (C), and phosphorus (P) in the catalyst in different pretreatments using XEDS. Pretreatments: A) with water; B) with 10 ml of acetone; C) calcination.

The relative quantification of the elements oxygen, carbon, and phosphorus in percentage by mass in the NbP catalyst was accessed for the different pretreatments (i.e., with water, acetone and after calcination) by XEDS (Figure 4). It was noted for all pretreatments, proportionally, the amounts of oxygen and phosphorus decreased

and that of carbon increased, which the carbon strip can explain used to perform the procedure. This shows the formation of humins on the catalyst, which justifies the increase in carbon.

The results for calcination pretreatment (Figure 4-C) indicate that it promotes burning of humins, loss of water, and volatilization of phosphorus compounds.

By performing the two temperatures comparison, it can be observed that, for all pretreatments, there was a more significant increase in carbon at the temperature of 150 °C. This result suggests greater catalyst activity with xylose dehydration to furfural and, thus, greater humin production.

There is probably a loss of sites from the catalyst to the solution during the catalytic reaction for calcination pretreatment. This loss was more significant at 150 °C since the mass percentage was lower at this temperature after calcination.

4. Conclusions

The study of the reuse of the heterogeneous catalyst $\text{NbOPO}_4 \cdot n\text{H}_2\text{O}$ in converting SCB into furfural was successfully carried out. The results showed that it is possible to produce furfural and reuse the catalyst even using raw SCB. Furthermore, the work showed that it is possible to separate the catalyst from the biomass by simple sieving. Regarding reuse, the study pointed out that at 150 °C, there is a more outstanding production of furfural and that the pretreatment carried out using only water is enough to regenerate the catalyst in at least one cycle.

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