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Effect of KOH Pretreatment on Lignocellulosic Waste for the Reduction of Nitrobenzene to Aniline without Metal

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Abstract: A green reduction of nitrobenzene to aniline was carried out using lignocellulosic biomass as a hydrogen source in a subcritical polar protic solvent, such as water and alcohol. The method is simple to implement, inexpensive, and easily applicable on a larger scale. The present method does not demand elaborated experimental conditions nor any metal catalyst. Optimal conditions provided aniline with a 90% yield by reduction of nitrobenzene in the presence of sawdust impregnated by KOH in subcritical methanol at 240 °C for 6 h.

1. Introduction

Aromatic amines are important intermediates which are employed in the chemical industry as dyes and agricultural and pharmaceutical chemicals [1]. Among the amino derivatives having aromatic core, aniline is a platform molecule used for the industrial production of rigid polyurethane (PU) foams [2]. Aniline is also an intermediate employed for the synthesis of a number of molecules of interest present in different areas, such as rubber products, agriculture, consumer goods, transportation, textile, packaging, adhesives/sealants, manufacturing, coatings, electronics, photography, pulp and care, and pharmaceutics [3,4]. Most of these aromatic amines are prepared through the reduction of the corresponding nitroaromatic compounds using a metallohydride reagent or by catalytic hydrogenation [5]. Many reductive agents have been recommended [6–9] for this transformation and the most classic and practical reductants are zinc, tin, or iron [10,11]. These processes mainly utilize potentially explosive H_2 [12,13] or reducing agents such as hydrazine hydrate [14–22], silane [23–25], sodium hydrosulphite [12,13], formate [26], decarborane [27–30], and glucose [31,32]. In the context of sustainable development, lignocellulosic biomass was treated by a hydrothermal liquefaction process to successively furnish macromolecules and smaller chemicals [33]. It is noteworthy that H_2 can also be produced from the decomposition of lignocellulosic biomass [34] in critical water. Using the hexose D-glucose as a hydrogen donor and as a moiety of cellulose, the inexpensive and easy scale-up production of amines having an aromatic core from nitroarene under catalyst-free conditions in water was reported [33]. In order to provide a more sustainable synthesis of aniline derivatives and as a continuity of our previous work [35], herein we disclose a novel reduction of nitrobenzene into the corresponding aromatic amine without added metal and without added dihydrogen in the presence of bio waste under different polar protic solvents in critical conditions.

2. Experimental Section

2.1. Material and Methods

Substrates were purchased from Acros (Aniline 99%, Nitrobenzene $\geq$ 99%, *p*-Xylene $\geq$ 90%, acetone, butan-1-ol, ethanol, methanol, propan-1-ol and propan-2-ol, phosphoric acid), and potassium hydroxide for use as a reference was purchased from Fisher Scientific. All materials were used without further purification. For all experiments, the water used was of Millipore Milli-Q grade.

2.2. Catalyst Preparation

Firstly, sawdust was chemically activated by both acid and basic routes. The latter was carried out using potassium hydroxide (sawdust-KOH) (1:2, wt/wt). The sawdust (20 g) was first immersed in aqueous KOH (300 mL) with stirring at room temperature for 12 h. The liquid was then separated by filtration and the sawdust, activated by the base, was dried at 110 °C for 12 h.

The acid activation was carried out using phosphoric acid (H_3PO_4). The sawdust was impregnated with a solution of 85% H_3PO_4 with a mass ratio of 1:2 and stirring at room temperature for 12 h. The liquid was then separated by filtration and the sawdust, activated by the acid, was dried at 110 °C for 12 h.

2.3. Catalyst Characterization

The characterization of sawdust is based on a few basic physicochemical indices—Ash content (Cd %) (ASTM International, 2006).

Scanning Electron Microscopy–Energy Dispersive X-ray Diffraction (SEM–EDX) analysis of the sawdust was executed on a Quanta FEG 250 (FEI) equipped with a microanalysis detector for EDX (Brucker). SEM micrographs were acquired in secondary electron mode at low vacuum, 15 kV accelerating voltage, and a 10 mm working distance. EDX spectra were obtained at a 30° angle, 15 kV accelerating voltage, and a 10 mm working distance.

XPS measurements were performed in an ultrahigh vacuum (UHV) multipurpose surface analysis system (SpecsTM model, Germany), operating at pressures of <10−10 mbar using a conventional X-ray source (XR-50, Specs, Mg K, 1253.6 eV) in a "stop-and-go" mode. The study and detailed Fe and Cu high-resolution spectra (pass energy 25 and 10 eV, step size 1 and 0.1 eV, respectively) were recorded at room temperature with a Phoibos 150-MCD energy analyzer. Powdered samples were placed on a sample holder using double-sided adhesive tape and were subsequently evacuated under vacuum (<10−6 Torr) for 12 h. Finally, the sample holder containing the degassed sample was placed in the analysis chamber for XPS studies. After recording the spectra, the detailed element XPS (typically C, O, and S) were recorded and the data were processed with the program, Casa XPS.

2.4. General Procedure for the Reduction of Nitrobenzene in Subcritical Methanol

In a typical experiment, a 100 mL a batch reactor (autoclave), charged with methanol (55 mL) and nitrobenzene (3.70 g, 30 mmol), pretreated basic biomaterial (sawdust 2 g and KOH 4 g). The autoclave was successively sealed, placed in the heating collar, and heated to the selected temperature for the selected time. The temperature of the reaction mixture inside the autoclave was measured by the temperature probe. The autoclave was cooled down to 40 °C at the end of the reaction and the aqueous phase was diluted in 100 mL of ethyl acetate under magnetic stirring (500 rpm). After separation, the organic phase was filtered through a syringe filter (PTFE, 0.45 μm, VWR) and then analyzed. All experiments were repeated three times, and the deviation was lower than 5%.

2.5. Product Analysis

Each sample of the reaction mixture was analyzed separately by means of a GC with a mobile phase, N_2 and a column oven, 40 °C. The products were detected with a FID detector. Nitrobenzene conversion (*X*) and Aniline yield (*Yi*) were calculated by the following Equations (1) and (2):

$$X = \frac{(Initial\ nitrobenzene\ amount\ (mol) - Final\ aniline\ amount\ (mol))}{Initial\ nitrobenzene\ amount\ (mol)} \times 100 \qquad (1)$$

$$Yi = \frac{Final\ aniline\ amount\ (mol)}{Initial\ nitrobenzene\ amount\ (mol)} \times 100 \qquad (2)$$

3. Results and Discussion

Preliminary studies were realized for nitrobenzene conversion (10 mmol) using a pretreated basic biomaterial (sawdust (1 g) and KOH (2 g)) in water (55 mL) at 310 °C under generated pressure for 6 h as a model reaction, as shown in Figure 1. The characterization of the sawdust was described using conventional SEM, EDX and XPS analyses as shown in Figures S1–S5 and Tables S1 and S2 in the Supporting Information. With our preliminary experimental conditions, aniline was obtained in 60% yield with a quantitative conversion of nitrobenzene. A similar reduction of nitrobenzene using pretreated lignocellulosic waste with H_3PO_4 furnished the aniline in poor yield (5%) with a quantitative conversion of the starting material. In our hands, the effect of acidic treatment with H_3PO_4 on lignocellulosic waste did not have an impact on the formation of the target aromatic amine. The temperature and pressure are important parameters in this metal-free developed process. When the temperature is between 100 °C and 374 °C and the pressure between 0.1 and 22.1 MPa, the reduction of the nitroarene takes place in subcritical water conditions. In these conditions, water has particular physicochemical properties in terms of density equivalent to that of the liquid, viscosity approaching that of the gas, a diffusion coefficient at least ten times higher as compared to the liquid, and a transfer coefficient and dielectric constant which is close to that of organic solvents. The alteration of the physical properties of subcritical water leads to the different behaviors of solvents [36,37]. In this work, the effects of substrate, sawdust/KOH and KOH loadings, temperature, time, and solvent were studied.
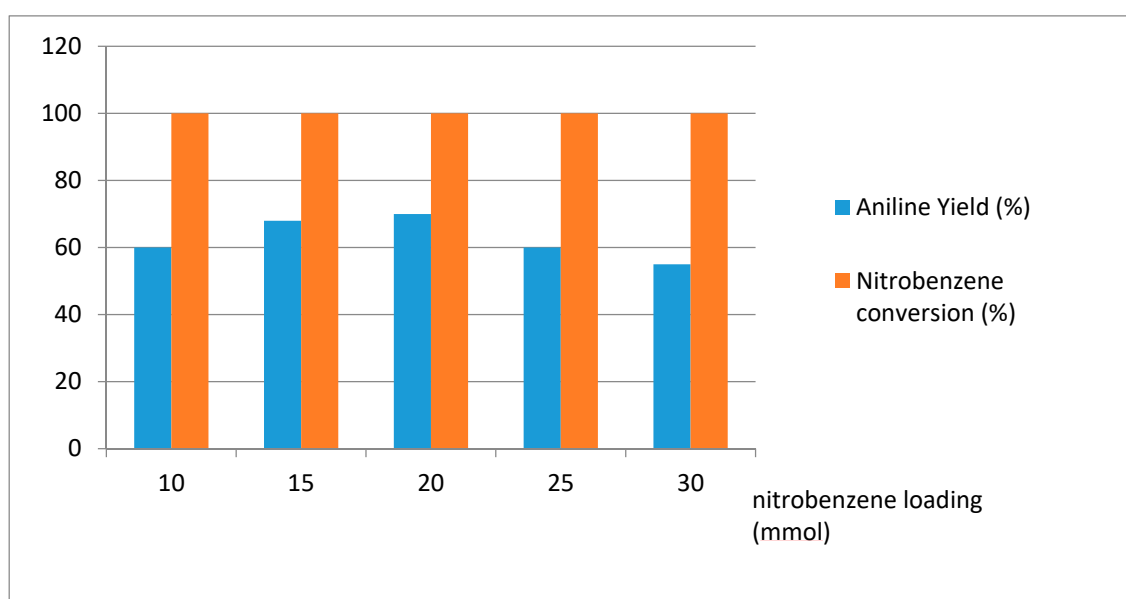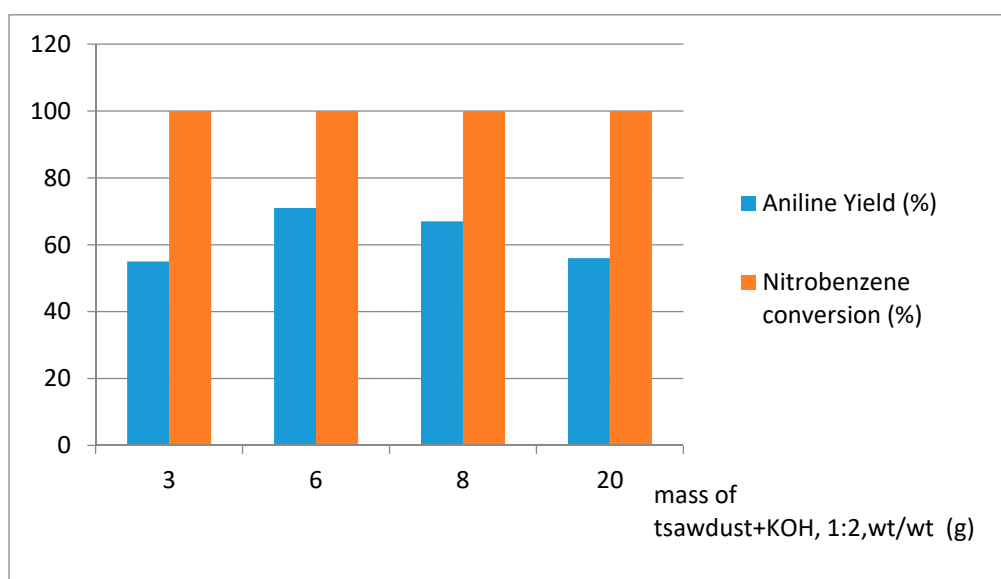

Figure 1. Effect of nitrobenzene concentration on reduction of nitrobenzene to aniline. Reaction conditions: Nitrobenzene (10–30 mmol), sawdust + KOH (3 g, 1:2, wt/wt), water (55 mL), 310 °C, 90–130 bar, 6 h.

3.1. Effect of Substrate Loading

Variation in the nitrobenzene loadings (10 to 30 mmol) in the presence of pretreated bio-based waste (sawdust 1 g + KOH 2 g) was then studied to find if the concentration of nitrobenzene can have a major role on aniline yields, as shown in Figure 1. With the increase in nitrobenzene loading from 10 mmol to 20 mmol, aniline yield was higher (60% vs. 70%) with complete conversion. Even if the yield obtained, starting from concentrated nitrobenzene (30 mmol), was lower (55% vs. 70%), the higher concentration was conserved for the next step due to a better productivity.

3.2. Effect of Sawdust + KOH Loading

The effects of the pretreated bio-based waste (sawdust + KOH (1:2, wt/wt)) were studied to optimize the reduction of aqueous nitrobenzene (0.54 M) at 310 °C for 6 h. Sawdust + KOH loading was tested with 3 g to 20 g and its effect on aniline yield and nitrobenzene conversion was studied, as shown in Figure 2. With the increase in powder loading from 3 g to 6 g, the aniline yield increased by ~15%, and the highest yield achieved was 71% with the complete conversion of nitrobenzene with 6 g pretreated bio-based waste (sawdust 2 g + KOH 4 g). Nevertheless, it was observed that aniline yield and the conversion of nitrobenzene decreased when more basic sawdust powder was used (20 g, 1:2, wt/wt). Our results show that the yield of aniline depends on the amount of KOH in the reaction medium since, when the pH increases, the yield also increases up to an optimum (4 g, KOH) under the conditions described previously. The pH values of the mixture after 1 min and 6 h of reaction were 10 and 7, respectively, meaning that the KOH amount was consumed during the reduction of the nitrobenzene probably due to its interaction with the biopolymer of sawdust.
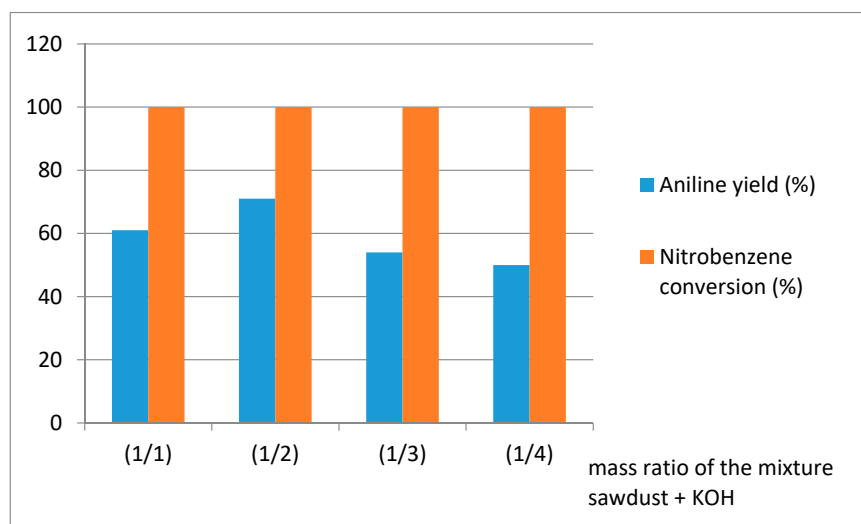

Figure 2. Effect of sawdust + KOH concentration on the reduction of nitrobenzene to aniline. Reaction conditions: Nitrobenzene (30 mmol), sawdust + KOH (3–20 g, 1:2, wt/wt), water (55 mL), 310 °C, 100–130 bar, 6 h.

3.3. Effect of KOH Loading

Due to the decrease in pH during the reduction (from 10 to 7), the effect of the ratio between sawdust and KOH was studied to optimize the reduction of nitrobenzene (0.54 M) at 310 °C for 6 h. Sawdust + KOH loading was tested from 1:1, wt/wt to 1:4, wt/wt and its effect on aniline yield and nitrobenzene conversion was studied, indicated in Figure 3. As shown, with the increase in the base loading from 1:1, wt/wt to 1:2, wt/wt, the aniline yield increased by ~10%, and the highest yield achieved 71% with the complete conversion of nitrobenzene. It should be noted that the aniline yield

and conversion of nitrobenzene decreased when the ratio of sawdust + KOH was 1:4, wt/wt. It can therefore be deduced that the mass ratio of sawdust + KOH (1:2, wt/wt) is the ideal ratio for the KOH to react with all of the biopolymers that constitute biomass.

Figure 3. Effect of KOH concentration on reduction of nitrobenzene to aniline. Reaction conditions: Nitrobenzene (30 mmol), sawdust + KOH (6 g, 1:1 to 1:4, wt/wt), water (55 mL), 310 °C, 100–130 bar, 6 h.
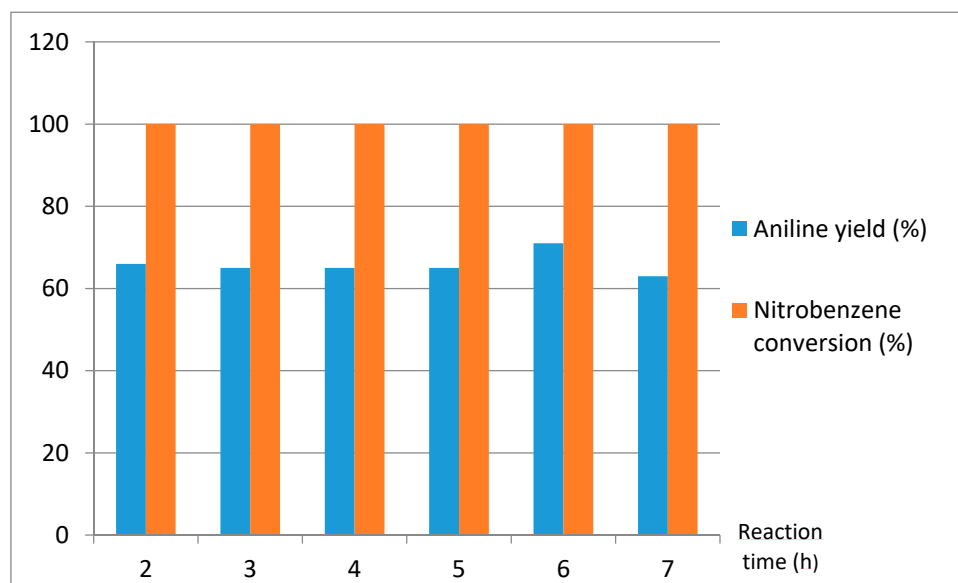
3.4. Effect of Reaction Temperature

Reaction temperature is a key factor for the reduction of nitrobenzene, especially to the status of subcritical water. In order to determine the most favorable reaction temperature, the variability of temperature from 270 °C to 310 °C was investigated in a batch process through conventional heating and generated pressure (90–130 b) using the previous optimized conditions (nitrobenzene (30 mmol), sawdust + KOH (6 g, 1:2, wt/wt), water (55 mL), 270–310 °C, 130 bar, 6 h), as shown in Figure 4. A temperature of 270 °C was insufficient for the conversion of nitrobenzene to aniline in 6 h. An increase in the reaction temperature to 310 °C benefitted aniline production (71% yield and quantitative conversion). However, aniline yield severely decreased to 63% when the reaction temperature increased to 320 °C, and this may be due to the degradation of organic compounds.
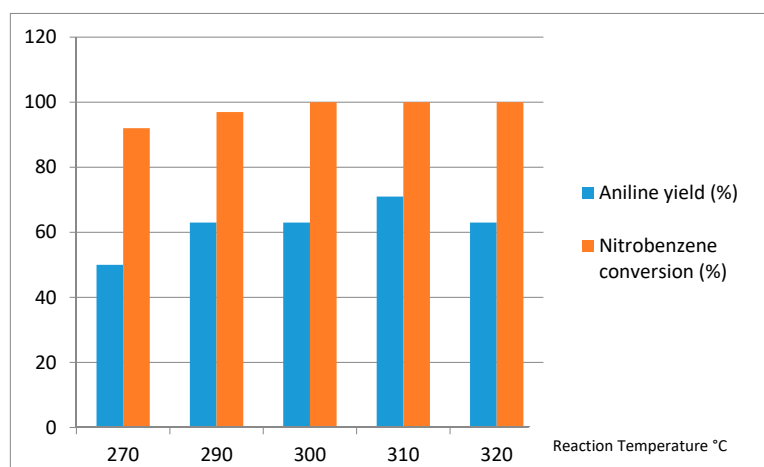
Figure 4. Effect of temperature on reduction of nitrobenzene to aniline. Reaction conditions: Nitrobenzene (30 mmol), sawdust + KOH (6 g, 1:2, wt/wt), water (55 mL), 270–320 °C, 90–130 bar, 6 h.

3.5. Effect of Reaction Time

The kinetic study of the reaction aimed to optimize the reaction time for the reduction of nitrobenzene. The experiments were carried out for various reaction times ranging from 2 h to 7 h at 310 °C and 130 b, as shown in Figure 5. At 310 °C, the results show that the yield of aniline increased with reaction time, with a peak value of 71% for 6 h and 100% nitrobenzene conversion. At shorter times, the reaction did not have time to finish, and at times greater than 6 h (longer heating) there is a risk of the decomposition of the organic matter. In any case, possible degradation products and recombination have not been studied.
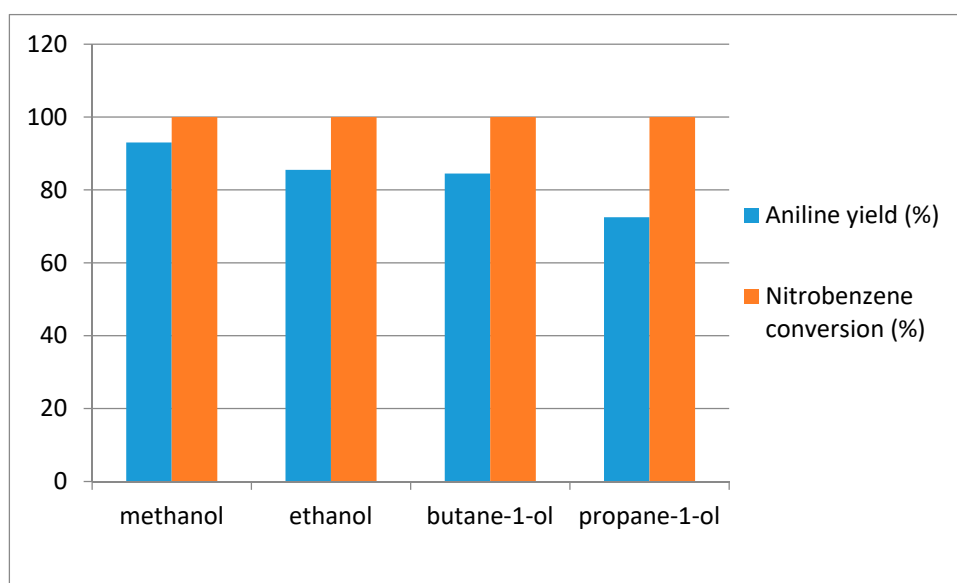

Figure 5. Effect of reaction time on reduction of nitrobenzene to aniline. Reaction conditions: Nitrobenzene (30 mmol), sawdust + KOH (6 g, 1:2, wt/wt), water (55 mL), 310 °C, 130 bar, 2–7 h.

3.6. Effect of the Nature of the Solvent

Other polar protic solvents (methanol, ethanol, propan-1-ol, and butan-1-ol) have been tested as green solvents for the reduction of nitrobenzene to aniline in sub-critical conditions, shown in Figure 6 and Table 1. Compared with water, all of the tested alcohols were permitted to reach aniline in better yield (>72%). The best was obtained when methanol was used (93% yield and 100% conversion). This may be due to the ability of organic solvents to extract the biopolymers of sawdust. Indeed, we can cite, for example, the organosolv pretreatment process, which uses an organic solvent or mixture of organic solvents to extract biopolymers at critical temperatures depending on the type of biomass [38,39].

Using our optimized reaction conditions (nitrobenzene (30 mmol), sawdust + KOH (6 g, 1:2, wt/wt), solvent (55 mL), 240 °C, 40–80 bar, 6 h), different nitroaromatic derivatives, having different steric and electronic demands, were evaluated. For all of the reductions, the conversions are quantitative (>99%). Unfortunately, only traces of pure aniline could be observed, whatever the position (ortho, meta, and para) and the ring substituents (F, I, Cl, COOH, NHCOCH$_3$, CHO, COO CH$_3$). Efficient degradation (mineralization) occurred and no other product was detected. To date, the reported successful process is exclusive for nitrobenzene.

Figure 6. Effect of solvent on reduction of nitrobenzene to aniline. Reaction conditions: Nitrobenzene (30 mmol), sawdust + KOH (6 g, 1:2, wt/wt), solvent (55 mL), 240 °C, 40–80 bar, 6 h.

Table 1. Critical temperature and critical pressure of the tested alcohols.

	Critical Temperature (°C)	Critical Pressure (bar)
methanol (CH_4O)	239	80
ethanol (C_2H_6O)	240	61
propan-1-ol (C_3H_8O)	263.6	51
butan-1-ol ($C_4H_{10}O$)	289.8	44

3.7. Plausible Mechanism Pathway for the Generation of H_2

In light of the literature [40], a plausible reaction mechanism for the reduction of nitrobenzene to aniline in the presence of lignocellulosic biomass can be proposed. In critical fluid, biomass is transformed to hexose and pentose, which produce dihydrogen and carbon monoxide after ten and eight steps, respectively. In the case of glucose, decarbonylation afforded the corresponding pentitol, and then dehydrogenation produced the corresponding pentose. These sequential reactions continued until the formation of dihydrogen and carbon dioxide in the last step. In the presence of critical water, water gas shift reaction produced an additional dihydrogen for each carbon monoxide, as shown in Scheme 1.
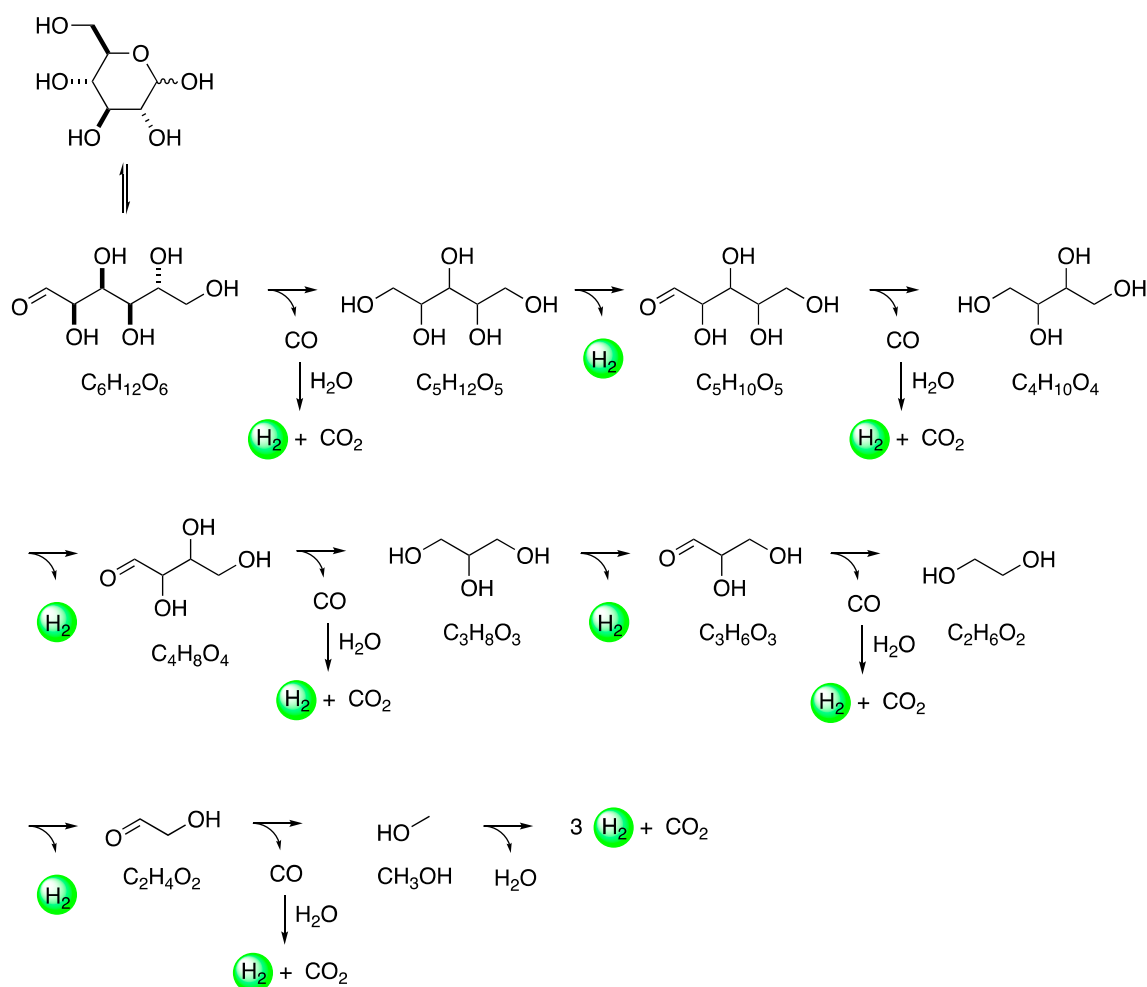
Scheme 1. Plausible mechanism reaction for hydrogen production from glucose and the corresponding pentose via aqueous phase reforming reactions.

4. Conclusions

An efficient selective protocol has been optimized for the production of aniline, starting from nitrobenzene under subcritical conditions using polar protic solvents, such as water and methanol. The proposed methodology features an efficient and practical method, employing lignocellulosic biomass impregnated by KOH as the hydrogen source without the added transition metal. A high yield condition allowed us to obtain the target aniline with quantitative yields using methanol as a solvent for the reaction. The scope of the ecological reduction of nitrobenzene will be translated into different nitroarene derivatives in continuous flow.

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