International Scientific Journal
Journal of Environmental Science
http://environment.scientific-journal.com/

Conversion of waste agricultural biomass into furfural and HMF using $AlCl_3$ catalyst

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***Abstract*—Different lignocellulosic biomasses (hazelnut shells, poppy stalks and sunflower stalks) were directly converted to fine chemicals in the presence of 0.02 M $AlCl_3$ catalyst at 180 ^{0}C for 2 hours in one-step synthesis. Maximum conversion of poppy stalks into HMF and furfural was achieved as 2.21% 10.75%, respectively. HMF productivity was followed by hazelnut shells (%) and sunflower stalks, furfural productivity was followed by sunflower stalks and hazelnut shells. Levulinic and formic acid were also produced. Among the different biomasses maximum levulinic acid (3.37%) and formic acid (1.01%) was converted from hazelnut shells.**

Keywords—Biomass, furfural, HMF, cataytlic conversion

I. INTRODUCTION

Lignocellulosic biomass is renewable feedstock for sustainable production of chemicals and fuels. It is also the most abundant resource with its great potential of production and net zero carbon emission (1). Biomass may serve as a promising raw material for production of fuels and chemicals. Lignocellulosic materials (such as agricultural residues) were converted to several products used in energy, food, feed, chemical, and fuel industries (2).

C5 and C6 sugars were produced by depolymerization of polysaccharides with the presence of an acid catalyst. These sugars were further hydrogenated to polyols on metal catalysts. Functional metal catalysts, on the other hand, are capable of combining this two-stage process into a single-pot conversion (3).

Catalytic conversion of cellulosic biomass into various platform molecules, especially furan-based chemicals, is one of the important pathways. Furfural and 5-Hydroxymethylfurfural (HMF), are considered to be a very promising platform chemicals. Both furfural and HMF can be synthesized from sugar derivatives using a wide range catalysis including metal catalysts [4]. However, their direct conversion from raw biomass using green catalysis remains challenging because of the low yield of products. Aluminum chloride ($AlCl_3$), which is soluble in many organic solvents and is cheap, is the most commonly used Lewis acid. Due to its ability to strong compound Lewis base products it should be used in reagent quantities [4]. The aim of this study is to investigate the catalytic performance of $AlCl_3$ for the conversion of different lignocellulosic biomasses into fine chemicals including furfural, hydroxy methyl furfural (HMF), formic acid and levulinic acid.

II. MATERIAL AND METHODS

A. Material

Hazelnut shells, sunflower stalks, poppy stalks used in this study were purchased from Trabzon, Trakya region of Turkey and Afyon Alkaloids Factory in Turkey, respectively. The materials were dried to a final 9% moisture content. Then they were grounded by grinder and screened with a sieve shaker to obtain particle sizes between 0.224-0.850 mm. commercial cellulose was purchased from Sigma-Aldrich. The Aminex HPX 87H column for the HPLC analysis was purchased from Bio-Rad Laboratories (California, USA). All chemicals used were standard analytical grade. The standard reagents of xylose, glucose, furfural, HMF, formic acid, and levulinik acid were purchased from Sigma-Aldrich.

B. Catalytic Conversion of Commercial Cellulose and Biomass

Catalytic conversions were performed in a high temperature-high pressure stainless steel reactor (PARR,USA) with 0.02M $AlCl_3$ at 180°C and for 120 min. The solution was kept liquid under N_2 atmosphere. At the end of the treatment, the slurry was collected and filtered using filter paper to separate the solid and liquid fractions for further analysis. Compositions of liquid products were analyzed by high-performance liquid chromatography (HPLC).

C. Analytical Methods

The chemical composition of raw and pretreated hazelnut shells were determined according to NREL methods (5). 0.3 g solid was hydrolyzed by 3 ml of 72% (w/w) H_2SO_4 at 30^{o}C for 60 minutes, then, the reaction mixture was diluted to 4% (w/w) and autoclaved at 121^{o}C for 60 minutes. Lignin was determined by solid residue, cellulose and hemicellulose amounts were determined from the filtrate by using High Performance Liquid Chromatography (Agilent 1100). The HPLC system was mainly equipped with a Bio-Rad Aminex HPX-87H column (300 mm × 7.8 mm), and a refractive index detector. The analytical column was operated at 60°C. The mobile phase contained 0.2 μm filtered, 0.005 M H_2SO_4 solution with a flow rate of 0.6 ml/min (6). Glucose, HMF, levulinic and formic acid conversions were calculated based on the initial cellulose content of raw biomass; xylose and furfural were calculated based on the initial hemicellulose content of raw biomass. Solid conversion was also calculated on the remained solid residue after the reaction.

III. Results and Discussion

The compositions of the three biomasses were analyzed and the cellulose, xylan and lignin contents of these lignocellulosic biomasses are shown in Table 1. Sunflower stalks are cellulose- and xylan- rich biomasses, while the major component of the hazelnut shells is lignin.

TABLE I. LIGNOCELLULOSIC COMPOSITION OF DIFFERENT BIOMASSES

Table Head	*Cellulose (%)*	*Xylan (%)*	*Lignin (%)*
Poppy stalks	24.36	7.41	19.79
Sunflower stalks	32.44	13.63	15.57
Hazelnut shells	16.67	9.78	51.25

We studied effect of $AlCl_3$ catalyst on the conversion of three different biomasses and commercial cellulose. Solid conversions were ranged between 43.78-71.61% as shown in figure 1. Maximum solid conversion was obtained for cellulose (71.61%). It was followed by sunflower stalks (59.03%), poppy stalks (53.11%) and hazelnut shells (43.78%).

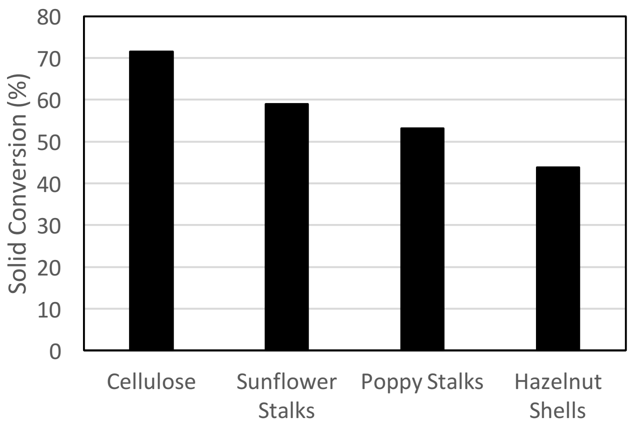

Fig. 1. Solid conversion of different biomasses and cellulose with $AlCl_3$ catalyst

During the catalytic conversion of the biomasses glucose and xylose, which are main intermediates for furfural and HMF production, were liberated. The production of these sugars from different biomasses is illustrated in Figure 2 and 3. Maximum glucose in the reaction medium was obtained during the conversion of hazelnut shells, while the least amount was observed for cellulose, indicating that cellulosic glucose was further converted to fine chemicals.

Since cellulose does not contain any xylose units, xylose production was only observed for the biomasses. After the catalytic conversion, the maximum amount of xylose (8.34%) left in the reaction medium was seen in the poppy stalks mixture. This indicates that, having the least xylan content (Table 1), poppy stalks' xylan was hydrolyzed but xyloses were not efficiently converted.

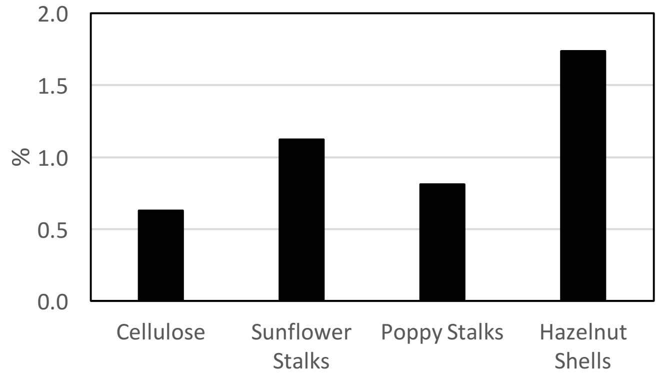

Fig. 2. Glucose production from different biomasses with $AlCl_3$ catalyst.

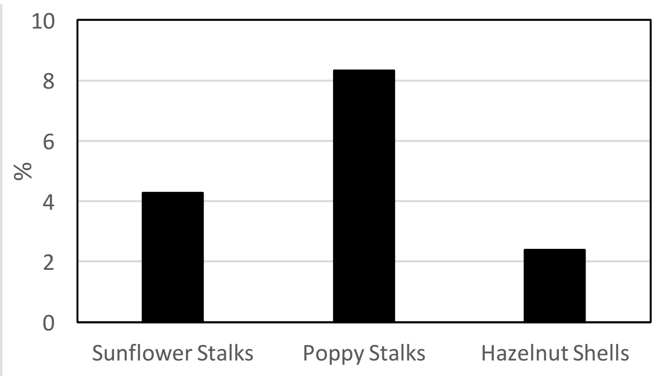

Fig. 3. Xylose production from different biomasses with $AlCl_3$ catalyst.

HMF was produced from glucose and according to figure 4 maximum HMF conversion was obtained from poppy stalks (2.21%). The remaining glucose after the catalytic conversion was minimum for poppy stalks (Figure 2), this means that glucose to HMF conversion rate is better than other biomasses and glucose was effectively converted to HMF. This was followed by hazelnut shells and sunflower stalks. The direct conversion of commercial cellulose to HMF was only 0.44%, this may be due to conversion of HMF to levulinic and formic acid (figure 6).

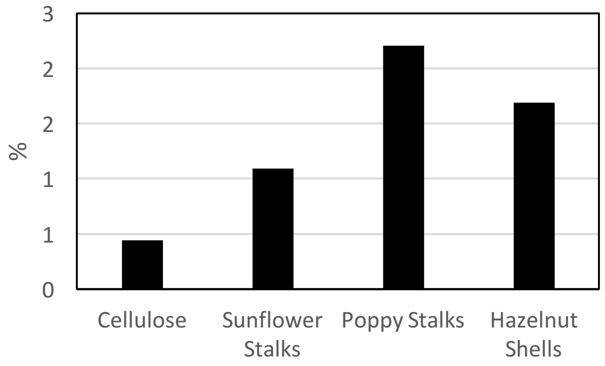

Fig. 4. HMF production from different biomasses with $AlCl_3$ catalyst

Figure 5 shows that furfural production have same trend with xylose production. While 10.75% furfural was produced from poppy stalks, 5.01% conversion was achieved with sunflower stalks. The least furfural production of 4.71% was observed for hazelnut shells.

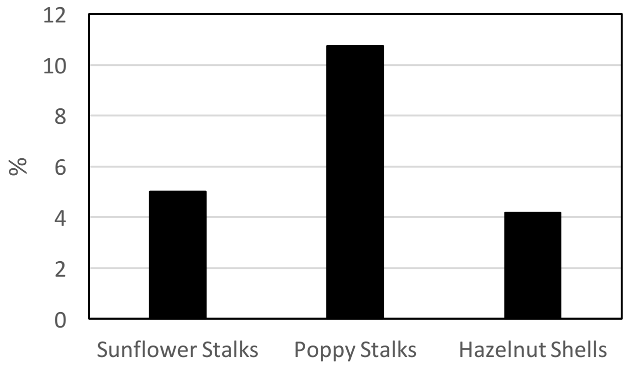

Fig. 5. Furfural production from different biomasses with $AlCl_3$ catalyst

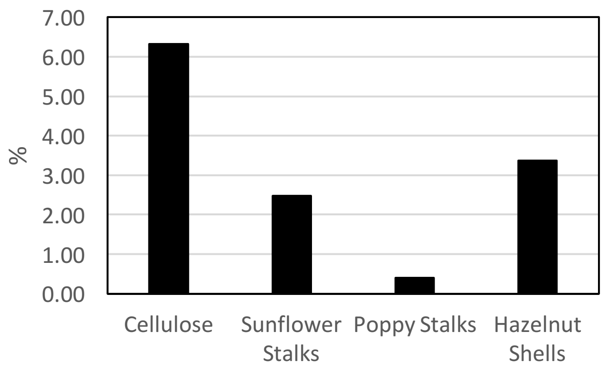

Fig. 6. Levulinic acid production from different biomasses with $AlCl_3$ catalyst

Maximum levulinic acid (6.32%) conversion was obtained from the direct conversion of commercial cellulose (Figure 6). Comparetively significant amounts of levulinic acid were produced from Hazelnut shells (3.37%) and sunflower stalks (2.47%), while , leuvenic acid from poppy stalks was in trace amount (0.4%).

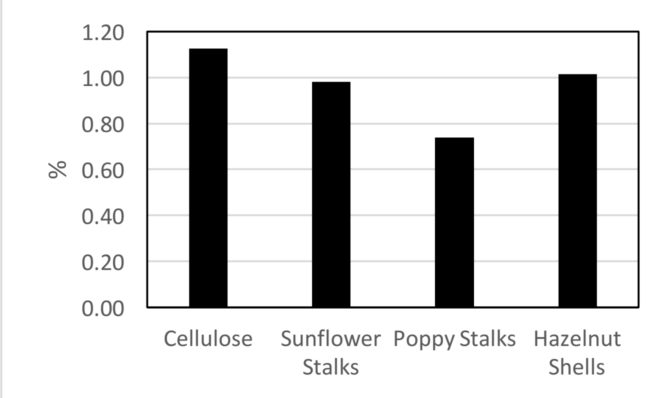

Fig. 7. Formic acid production from different biomasses with $AlCl_3$ catalyst

During the $AlCl_3$ mediated conversion of biomass, production of formic acid was also observed. Cellulose resulting in maximum 1.13% formic acid formation was followed by hazelnut shells (1.01%), sunflower stalks (0.98%) and poppy stalks (0.74%) (Figure 7.).

As a conclusion, all of the biomasses were efficiently converted to fine chemicals in the presence of AlCl3 catalyst. The highest HMF (2.21%) was obtained from poppy stalks, followed by hazelnut shells (1.69%) and sunflower stalks (1.09%). Similar trend was also observed for furfural yield, being10.75%, 5.01%, and 4.17% for poppy stalks, sunflower stalks and hazelnut shells, respectively. The study demonstrates the potential for production of fine chemicals from lignocellulosic waste materials. It also exhibits the promising role of $AlCl_3$ as an effective catalyst for single-step conversion of biomass.

ACKNOWLEDGMENT

This study was supported by Anadolu University Scientific Research Projects Commission under the grant no: 1505F198

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