Characterization of Chemicals by Cellulose Degradation in Near Critical Water

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This study aims the characterization of the intermediates produced in the near critical water extraction of cellulose. The experiments are conducted using a batch type reactor at 225°C, 300°C and 375°C. The effect of the catalysts such as K_2CO_3 and ZSM-5 on the results is also investigated at 375°C. The key chemicals detected in the aqueous phase such as furfurals, phenols, acids and aldehydes are characterized by various analytical techniques. An explanation of possible formation and degradation pathways of the intermediates is given.

INTRODUCTION

Global warming is mainly sourced by the use of fossil fuels. Furthermore, the stocks of fossil resources start to run out [1]. As a result of this, the number of the Investigations on the renewable energy resources is increased and biomass resources will become more important as alternative to fossil resources. Biomass is the renewable energy resource and carbon dioxide is fixed by photosynthesis through regeneration. In addition, valuable chemicals may be able to replace from biomass resources [2]. Cellulose is a model biomass and it is a component of at least a third of advanced plants. Therefore, cellulose is the most abundant naturally occurring reproducible organic compound. In recent years, research regarding the conversion of cellulose and cellulosic biomass to valuable chemical using water at hydrothermal and supercritical conditions has been reported [3,4,5]. Cellulose is the main unit of biomass like materials. In order to give a realistic response to formation and degradation

pathways of the intermediates, the researchers should be focused on identification of these compounds which are the key compounds for biomass conversion.
In this study decomposition of cellulose in near and sub-critical water (225 ºC, 300ºC, 375ºC) is studied. Effect of the experimental conditions such as temperature and catalysts addition (HZSM-5, K_2CO_3) on the results is investigated. Products such as fructose, furfurals, phenols, acids and aldehydes are identified and possible reaction pathways for their formation and degradation are given.

MATERIALS AND METHODS

In the experiments, micro-crystalline Cellulose (ACROS) is used as the starting material. Catalysts used in the experiments are K_2CO_3 (MERCK) and H-ZSM5 (ACROS ORGANICS). The experiments are conducted in an autoclave (1 L of capacity) with a magnetic stirrer equipped by an electrically heated furnace. 8 g of Cellulose and 400 ml of water are charged in the autoclave. 2 MPa of nitrogen is used to purge the residual air. After 1 h of reaction time, the autoclave is cooled down to the room temperature and the autoclave is opened. In the vessel, solid particles and aqueous phase are found and the particles are separated by filtration from the aqueous phase. The amounts of different phenols are determined calorimetrically by a UV-VIS spectrometer (Cadas 200 photometer, Dr. Lange Company). The amounts of organic acids and furfurals are measured by an ion chromatograph equipped with and high-performance liquid chromatograph pump, an Aminex TMHPX-87 H column by Biorad for organic acids, a RP-18 column by Merck for furfurals, and a L-4250 UV-Vis detector by Merck.

RESULTS

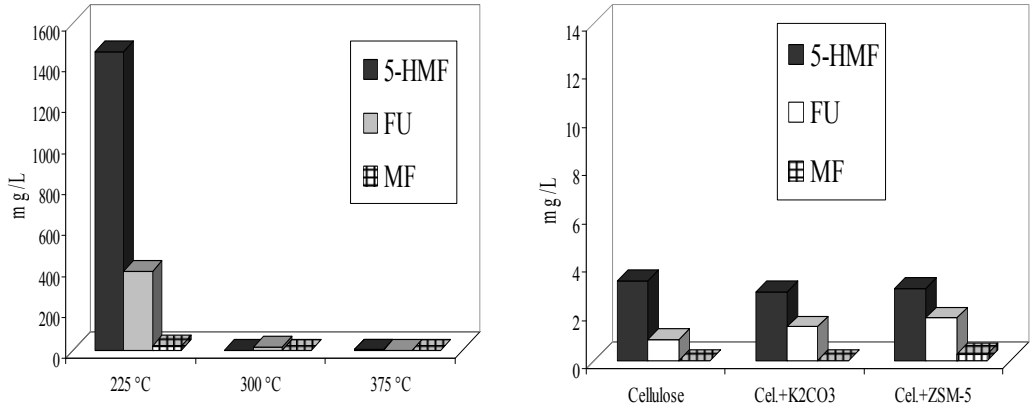

Figure 1. Content of Furfurals (5-HMF: hyroxymethyl furfural, FU: furfural, MF: methyl furfural) of aqueous phase (a) temperature effect, (b) catalyst effect at 375ºC

Furfurals are one of the important intermediates. According to Figure 1, an increase in temperature leads to a decrease in amount of furfurals as a result of conversion of furfurals to other intermediates such as acids and aldehydes. Furfurals especially 5-HMF are formed with ionic reaction at near critical temperature. 5-HMF is degraded to furfural and phenol derivatives. No clear effect of catalysts on the amount of furfurals is observed during the catalytic run conducted at 375^0C.

Phenols are degradation products of furfurals and they are very stable [6]. Phenol content of aqueous phase increased with increasing temperature as can be seen in Figure 2. This is consistent with Figure 1, which shows the decreased amount of furfurals with temperature. Degradation of Phenols and phenol derivatives is accelerated by Catalysts as a result of hydrogenation.

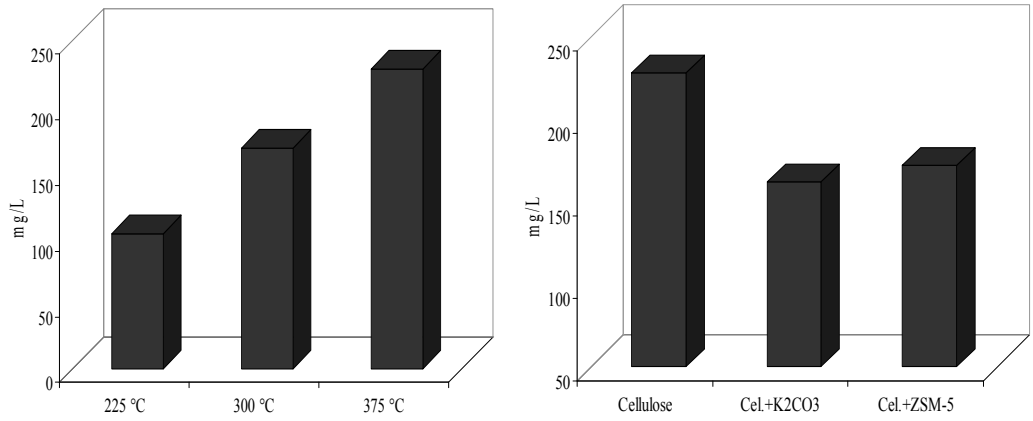

Figure 2. Total phenol contents of the aqueous phase at the end of the hydrothermal conversion of cellulose (a) temperature effect, (b) catalyst effect at 375ºC

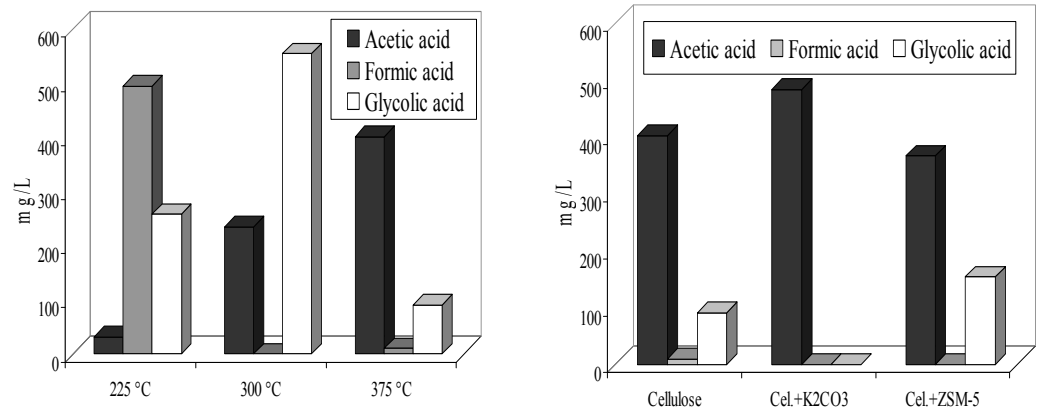

Figure 3. Acid content of aqueous phase at the end of the hydrothermal conversion of cellulose (a) temperature effect, (b) catalyst effect at 375 ºC

An increase in temperature leads to an increase in acetic acid amount. The huge amount of acetic acid is obtained at highest experimental temperature of 375 ºC. The reason of this variation is possibly stable structure of acetic acid [7]. The maximum amount of Glycolic acid is found at 300 ºC. Further temperature increase leads to a significant decrease in Glycolic acid amount. Glycolic acid is mainly decomposed to phenols and gases at this temperature. A significant degradation of formic acid to gases is remarkable by temperature.
Acetic acid amount is increased while no formic and glycolic acid are found in the presence of K_2CO_3. In presence of K_2CO_3 glycolic acid is not seen but glycolic acid amount is increased in the presence of ZSM-5. No Formic acid is found in the presence of catalysts. This is evident that degradation of formic acid to gases is accelerated by catalysts.

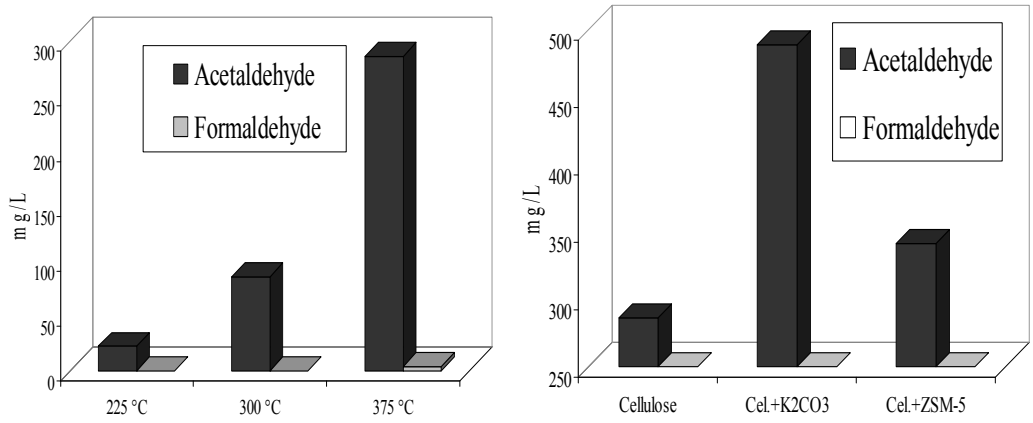

Figure 4. Aldehyde concentration of the aqueous phase at the end of the hydrothermal conversion of cellulose (a) temperature effect, (b) catalyst effect at 375ºC
Acetaldehyde has stable structure [8] and is found in a huge amount in the aqueous phase at 375ºC. Unstable formaldehyde converted to gases and no formaldehyde is found in both cases. In the presence of K_2CO_3 acetic acid is not depredated and its amount is very high.

In the presence of the K_2CO_3 which is a basic catalyst, acetaldehyde amounts are higher than that obtained by ZSM-5. The formation route of acetaldehyde is mainly via glyceraldeyde decomposition and ZSM-5 is more effective than K_2CO_3 in conversion of acetaldehyde to gases.

CONCLUSION

Near critical temperature promoted the conversion of cellulose into its derivatives as acids, aldehydes, furfurals. The catalysts play an important role for degradation or formation of intermediates. Based on these results, it is suggested that the near and sub-critical water application could become a useful method to transform cellulose to the valuable chemicals effectively.

ACKNOWLEDGEMENT

The Authors thank TUBITAK (The Scientific and Technological Research Council of Turkey) for providing financial support for this Work through the Project “106M412”. Our special thanks are to Dr. Andrea Kruse, S. Habicht, Mr. Habicht and A. Böhm (Forsungszentrum Karlsruhe – ITC - CPV) for the analysis.

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