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The Critical Role of Phenolics on Gasification of Biomass Hydrolysate

Bahar Meryemoglu[1*], Burcak Kaya Ozsel[2], Berna Nis[2]

[1] Cukurova University Central Research Laboratory Adana, Turkey.
[2] Department of Chemistry, Faculty of Engineering and Natural Sciences, Bursa Technical University, 16310 Bursa, Turkey.
Correspondence;
Bahar Meryemoglu
E-mail adress:
meryemoglubahar@gmail.com
ORCID No:
0000-0002-4785-5917

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Abstract

The study was designed to solubilize sorghum by water extraction and investigate the effect of phenolics depending on the time in sorghum hydrolysate for hydrogen gas production by aqueous-phase reforming. The Folin-Ciocalteau method was used to determine the total water soluble phenolics of the sorghum hydrolysate. There were no significant changes in the total amount of phenolic compounds during the first weeks. It was observed that the total amount of water soluble phenolic compounds of sorghum hydrolysates showed changes monthly (300-400 ppm). The gas volume produced reached up to 40-50 mL was obtained when the hydrolysates were gasified. APR of biomass hydrolysates in the presence of a reforming catalyst (Pt 5% on activated carbon) produced various amount of gas mixture which consisted of H_2, CH_4 and CO_2 gases. The results showed that the descrease in total water soluble phenolics of sorghum hydrolysate had no significant effect on gasification, depending on the time.

Keywords: *Phenolics, sorghum, gasification, biomass*

1. INTRODUCTION

Recently, interest in new and renewable energy sources has been continuously increasing. Biomass energy has an important place among these sources. At the same time, various energy conversion technologies are being applied and tested to produce energy from biomass. Catalytic hydrothermal gasification in the supercritical water is a very effective method based on the gasification of any aqueous organic mixtures at temperature and pressure conditions above the critical point of water (T = 374 ° C, P = 221 bar). In these conditions, organics, which has nonpolar properties, are miscible completely with water, and a single phase is observed. In addition, the hydrogen bondings between water molecules dissociate due to the high kinetic energy, and dielectric constant of water in supercritical conditions comes close to those of nonpolar organic solvents. The reactions can be carried out easily without mass transfer limitations. The molecules have high kinetic energy due to medium of supercritical water, and they come into collusion effectively because of density of the medium. Thus, it was obtained treatment efficiency up to 100 % in very short residence times by catalytic hydrothermal gasification in supercritical conditions of water. In a study, the treatment and gasification of olive mill wastewater was investigated using a Pt/Al_2O_3 catalyst in a packet bad reactor at supercritical water conditions. The treatment and elimination of the olive mill wastewater is accepted as an important environmental problem which has to be solved in mediterian countries. High amount of organic contaminant in the olive mill wastewater are considered as a biomass source, and while its gasification is carried out in supercritical water, its treatment is provided at the same time. As a result of this work, gases such as hydrogen, methane, ethane, propane, propylene which can be used as energy, were obtained. With developed process, either organic content has been removed from wastewater and obtained energy from a real biomass. In accordance with this purpose, the experiments were carried out at a constant pressure of 250 bar, different five reaction temperatures (400, 450, 500, 550 and 600°C) and different five reaction times (10, 15, 20, 25 and 30 s). Effects of experimental conditions on gas composition; gas flow rate, total energy amount and total organic carbon (TOC) exchange were investigated. Afterwards, experiments were made at 100, 150, 200, 250 bar pressure in order to examine effective of system pressure. The effects of reactant concentration on the same parameters were investigated at 2000, 4000, 8000, 10000 mg/L concentrations. Furthermore, using obtained experimental data, a kinetic model of catalytic decomposition reaction was developed (Kutluay, 2012).

Huelsman et al. (2014) investigated the gasification of phenol in the supercritical water at different temperatures, water and substrate concentrations and reaction times. Both gas and liquid analysis were made by determining the product composition. Gas phase consists of H_2, CO, CH_4, and CO_2, while in the liquid phase polycyclic aromatic hydrocarbons were generally observed. At high temperatures the gas content was enriched with H_2 and CH_4, as well as an increase in char formation (Huelsman et al, 2014).

In another study, the gasification of aqueous mixtures of glucose and phenol as the lignocellulosic material model compound was investigated under the supercritical water condition. Experiments were carried out at various concentrations at 400 ° C under 25.0 MPa pressure at different reaction times. The results showed that the phenol compound had a limiting effect on gasification. It was observed that phenol is not inert in the condition but reacts with other products formed in the liquid phase to form tar / solid (Castello et al. 2014).

Cellulose and lignin are model compounds of biomass. Cellulose and lignin mixtures were gasified in the presence / absence of K_2CO_3 catalyst under super-subcritical conditions in the range of 300-600 ° C and 90-410 bar. Gas and liquid analyzes were performed and the highest hydrogen and methane yields were obtained in the presence of K_2CO_3 catalyst at 600 ° C (Madenoglu et al., 2016).

Biomass derived model compounds have been used in gasification methods in the studies so far. However, methods that exhibit high activity in the conversion of water-soluble oxygenated model compounds such as sugars, sugar alcohols and glycerol unfortunately do not yield the same yield when applied to complex biomass hydrolysates containing various carbohydrate and lignin soluble products (Meryemoglu et al., 2010; Irmak and Ozturk, 2010). In order to better understand the chemistry of the gasification process using lignocellulosic hydrolysates, the water soluble phenolics of the hydrolysates were determined and followed. The effect of the change in phenolic concentrations due to waiting in hydrolysates was investigated.

2. MATERIALS AND METHODS

2.1. Materials

In this study, sorghum (Green Go) that supplied from May Seed, sown in April 2010 and harvested in October 2010, was used.

2.2. Methods

2.2.1. Sorghum Hydrolysis

In this method, 10 g of lignocellulosic material was hydrolyzed in 350 ml of water under reflux for 2 hours. The obtained hydrolysate was filtered and used for gasification reactions.

2.2.2. The Gasification of Sorghum Hydrolysates

The 50 mL hydrolysate was placed in 100 mL volume Parr 4590 model micro bench reactor. The reactor was purged with argon to minimize air in the rector. Gasification experiments carried out for 2 hours at 250°C with stirring at 1000 rpm in presence of catalyst. The gasification was started with the reactor reaching the desired temperature (250 °C). After the gasification was completed, the reactor was immersed in water and cooled rapidly to room temperature and it was assumed that the reaction was completed by immersion of the reactor in water. The gases were analyzed by Varian gas chromatography with two TCD detectors. Argon (Ar) and Helium (He) gases were used as carrier gases. In gasification experiments, 0.1 g of 5% Pt / Activated carbon was used as catalyst.

2.2.3. The Analysis of Sorghum Hydrolysates

Total phenolic compounds were determined by Folin-Ciocalteau method (Caboni et al., 1997). The total amount of phenolic compound was given as equivalent to the gallic acid standard. The 0.5 mL sample was mixed with 1 ml of a 10-fold diluted Folin-Ciocalteau reagent and vortexed by adding 2.0 mL of saturated Na_2CO_3 solution. The mixture was allowed to stand at room temperature for 30 minutes and then the absorbance value was measured on a spectrophotometer at a wavelength of 765 nm to determine the total amount of phenolic compound. GC-MSMS and LC-QTOFMS analyzes were performed in order to examine and identify the product composition formed to determine the content of hydrolysates.

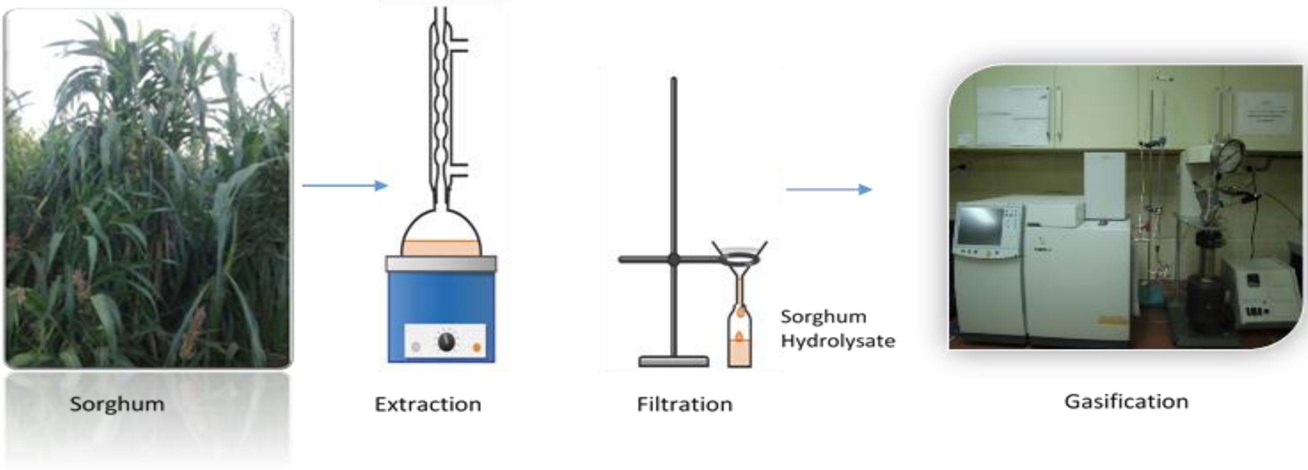

Figure 1. Schematic diagram of preparation samples

3. RESULTS AND DISCUSSION

3.1. Hydrolysis of Sorghum

Hydrolysis were performed under reflux for 2 hours. The hydrolysates were filtered for determining the total amount of phenolic compound. After filtration, the solid remained after hydrolysis was dried in the oven to determine the percentage of hydrolysis. Sorghum hydrolysis yield was 28.61 ± 0.25 %. The gas chromatography-mass spectroscopy (GC-MS) and high performance liquid chromatography (HPLC) uses for screening phenolic compound content of plants. GC-MS is a method that used to determine volatile phenolic compounds of leaves and flowers. For example when phenyl propenes can be separated using 20% Reoplex 400-Gas Chromium a Q column, Resorcinol-based cannabinoids seperated with 3% OV-17 Gas Chromium. Q (100-120 mesh) column (Harborne et al., 1982). They are usually converted to trimethylsilyl ethers as they increase the volatility of phenolic compounds (Greenway et al., 1988). In this study, the organic phase obtained by extraction of sorghum hydrolysate with diethyl ether was analyzed with GC-MS using HP-5MS column.

The GC-MS analysis of the sorghum hydrolysate showed that phenol, 2,2'-methylene bis [6- (1,1-dimethylethyl) -4-methyl- (antioxidant 2246) was the most common (Fig 2). This compound can generally prevent the aging and physical properties of natural rubber, synthetic rubber and synthetic resin from oxygen, hot, ultraviolet rays, metal compounds, and coloration of the resin. There was no other phenolic compound identified by GC-MS analysis.

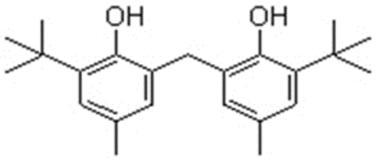

Fig 2. Antioxidant 2246

No pre-purification was performed for sorghum phenolic compounds in the analysis. As a result of LC-QTOFMS analysis of sorghum hydrolysate, no phenolic compounds were identified in the library screening. Furthermore, the chromatograms obtained from liquid chromatography before and after gasification of sorghum hydrolysates were found to be similar.

3.2. Determination of Total Water Soluble Phenolics in Sorghum Hydrolysates

In our study, total water soluble phenolics of sorghum hydrolysates were determined and followed. Firstly, total water soluble phenolics of the hydrolysates were examined and the samples gasified weekly. The change in the amounts of total water soluble phenolics were given in Table 1.

Table 1. Total water soluble phenolics of sorghum hydrolysate

Sorgum Hydrolysate	Total water soluble phenolics (ppm)
First day	400.00±0.56
1. week	395.00±0.36
2.week	375.02±0.32
3.week	320.45±1.23
4.week	334.00±0.45

As seen in Table 1, the total water soluble phenolics of sorghum hydrolysates did not show much change in the first weeks but depending on the time at the end of the 4th week (1 month) a decrease was observed. When this situation was examined in terms of the color of the solutions, the hyrolysate starting color was dark brown, gradually turned into yellow. A large group of flavonoids is also responsible for the color of foods. The fact that the color changes from dark to light can be an indication that the content of phenolic substances is reduced. Proantocyanidins from flavonoids are colorless if the chain length is short. As the chain length increases, they gain color changing from yellow to brown.

No significant changes were observed in the total water soluble phenolic compounds of sorghum hydrolysates obtained in the first weeks. For this reason, the amount of total water soluble phenolic of sorghum hydrolysates were examined monthly (Table 2). As a result of monthly measurements, it was observed that amount of total water slouble phenolics decreased gradually. The results showed that total water soluble phenolic compound amounts changed monthly. Sorghum hydrolysates showed higher values (334.00ppm) at the first months. The lowest amount of total water soluble phenolics were also obtained after 6 months (30.52ppm).

Table 2. Monthly total water soluble phenolic of sorghum hydrolysate

Sorgum Hydrolysate	Total water soluble phenolics (ppm)
1 month	334.00±0.45
2 month	275.36±1.65
3 month	230.40±2.10
4 month	211.00±1.0
5 month	35.81±2.30
6 month	30.52±4.20

3.3. The Gasification of Sorghum Hydrolysates

In the study, 50.0 mL sorghum hydrolysate was gasified at a constant temperature of 250 ° C in the presence of 5% Pt /Activated carbon catalyst for 60 min. The gasification results were given in Table 3. The gas volume produced 50. 0 mL at the first day. The hydrogen yield of this gas was 53.5%. No significant changes were observed on gas volume and composition as a result of gasification of sorghum hydrolysates performed monthly. The highest gas volume was obtained by using sorghum hydrolysate with high total water soluble phenolic on the first day.

The total water soluble phenolics of sorghum hydrolysates were also investigated after gasification. As a result of monthly gasification experiments, it was observed that the amount of total water soluble phenolics in sorghum hydrolysates decreased compared to the initial.

In the literature, biomass and phenol were gasified under supercritical condition. The gas mixture of these experiment consisted of H_2, CO, CH_4, CO_2. They also observed the formation of polyaromatic hydrocarbons in the liquid phase. It was found that the gas phase enriched with hydrogen methane and char formation were increased at the high temperatures (Chad et al., 2014). Similar results were obtained as a result of gasification of sorghum hydrolysates in this study (Table 3). Sorghum hydrolysate contains a complex structure; aliphatic compounds (oils and waxes) terpenes (sterol and resin) and terpenoids, fatty acids, tannin, quinine, aldehyde, alcohol, coloring pigments, steroids and phenolic compounds, cellulose, hemicellulose. According to the results, it can be said that the least contribution to gasification in this complex structure is phenolic compounds.

4. CONCLUSIONS

The effect of the change in the concentration of phenolics on the gasification was investigated depending on the time in sorghum hydrolysate obtained by water extraction. Total water soluble phenolics were determined by a spectroscopic method. According to results, total water soluble phenolic compounds decreased in the time period. When these hydrolysate solutions were gasified monthly, no significant changes were observed in the gas composition. It was concluded that the decrease in total water soluble phenolic compounds of sorghum hydrolysate had no effect on gasification. In further studies when more information about the phenolic compound content of a plant is desired extraction with various solvent systems and paper chromatography can be performed.

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Table 3. The monthly gas composition of sorghum hydrolysate

Time	**Gas volume (mL)**	**Gas composition (%)**			
		H_2	CO_2	CO	CH_4
First day	50.0±0.5	53.5±0.2	39.6±0.6	5.4±0.3	1.5±0.2
1 month	47.0±1.0	40.5±1.1	53.3±2.3	5.8±0.4	0.4±0.3
2 month	46.0±0.5	39.5±0.2	54.2±1.3	5.5±0.1	0.8±0.2
3 month	44.0±1.0	38.5±0.5	54.3±1.3	7.0±0.3	0.2±0.1
4 month	40.0±0.5	36.1±0.3	56.1±1.3	7.2±0.2	0.6±0.1
5 month	40.0±0.5	38.6±0.2	54.8±1.2	6.4±0.4	0.2±0.1
6 month	43.0±0.5	39.8±0.3	55.7±1.3	4.0±0.3	0.5±0.1

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