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GASIFICATION OF OLIVE MILL WASTEWATER WITH WATER PLASMA

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Abstract: Olive mill waste water(OMW) is formed as a result of olive oil production. Due to the abundance of organic matter, suspended solids, oil and grease and existence of phenolic compounds, it is a significantly dangerous type of wastewater. Since the pollution rate in OMW is high, its disposal and energy recovery from organic compounds within should be enabled. In this study, OMW is used as a raw matter and gasified with water plasma. Obtainable ideal gas composition is theoretically examined and results acquired from experimental studies are compared. The aim of this study is to identify the uncalculated effect of plasma by comparing the experimental studies with theoretical calculations. In theoretical studies, during gasification process, four basic reactions were used, compound equivalence has been established and gasification process has been simulated using MATLAB program with conversion balance. Ideal syngas composition was established at temperatures between 850 – 1000 K working within 0,05-0,7 S (water vapor/dry fuel) ratios. Experimental studies with low mass flow range olive mill wastewater feed were performed and in order to examine gas composition, gas chromatography analysis was executed. Results are proven to be consistent and when compared to the conventional gasification methods same ratio of syngas compounds have been achieved by plasma gasification at much lower temperatures. Since there is no literature on the gasification of OMW with plasma technology, this article carries a quintessential role in the study of waste recycling technology for energy recovery.

Keywords: Plasma gasification; syngas, olive mill wastewater.

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INTRODUCTION

Industrial wastewaters that emerged after the world's industrial development have become one of today's most important environmental problems as they contain components with high-polluting properties. As a result of olive oil production obtained industrial wastewater known as the Olive Mill Wastewater (OMW) contains organic matter, suspended solids, oil, and grease. Therefore, the treatment and disposal of olive mill wastewater is very important (1). The quantity and characteristics of OMW vary depending on olive species, climate, harvest time, and degree of maturity (2). 1 m^3 olive mill wastewater is equivalent to approximately 200 m^3 domestic wastewater (1).

Due to the high content of organic matter in the OMW, oxygen in water dissolves very quickly. Thus, aquatic macro- and micro-organisms are unable to survive. As the light permeability of water due to the color of the wastewater, it restricts the ability of photosynthesis of aquatic plants. The most significant damage to the atmosphere is a peculiar smell of OMW. Fermented OMW can evaporate from little ponds, plants, and soil to the atmosphere causing odor emissions. (3).

In order to reduce or eliminate the pollutant effect of OMW, many laboratory and industrial scale studies are being carried out and different treatment technologies are being developed both in Turkey and all over the world.

In literature, some examples of OMW treatment, disposal, or reduction of its harmful nature are listed below:

- Distillation (4),
- Adsorption (5,6),
- Electrolysis (7,8),
- Evaporation (9),
- Chemical Treatment (10,4,11),
- Aerobic Biological Treatment (12,4,13),
- Anaerobic Biological Treatment (14-18),
- Advanced Treatment Processes (19-23),

OMW, which is seen as a waste because of its properties, is actually an important energy source because of organic compound content and in addition to disposal, it will contribute to the national economy with efficient, valuable products through its evaluation. Studies on energy recovery are restricted due to moisture content in the raw material. For the studies on energy production from OMW liquor, gasification process was performed by Kipçak *et al*. in supercritical water conditions (24).

GASIFICATION TECHNOLOGY AND PLASMA GASIFICATION

Generally speaking, gasification is a technology that allows production of energy from solid or liquid fuels or of various chemicals. With conventional gasification processes, the raw material is treated with steam and a certain amount of oxidizer at a high temperature and pressure. Under these conditions, at a certain temperature value, volatile content of the raw material disappears and the remainder of the carbon reacts to form carbon monoxide, carbon dioxide, and hydrogen.

In this study, the energy required for the realization of the exothermic gasification reaction met with plasma technology. Plasma technology involves the formation of an electrical arc passing an electrical current through the gas. Since plasma gasification technology provides gasification with high purity and partial oxidation, it is usually known as "pure gasification" (25-27). Some of the advantages offered by the technology of plasma gasification technology are listed below:

-Clean and efficient synthesis gas with a high calorific value is obtained and it can be adjusted by controlling the content of the synthesis.

-Plasma, which has high energy density, is sufficient to provide energy for gasification in a short time and the reaction rate is increased because of its charged species. With the increase reaction rate, it reaches steady state conditions prematurely. It makes it possible to have a quick starting and stopping times.

-Can be used to dispose a wide range of waste types consisting of solid, liquid, and gas (28-33).

The high moisture content of Olive Mill Waste Water prevents the use of traditional methods for waste treatment technology aimed at energy recovery. However, for plasma technology the moisture content of the raw material is not important and as a result of plasma thermo-chemical process by ionizing raw material at a high temperature plasma gas is obtained.

MATERIALS AND METHODS

Apparatus

A 1.5 kW DC arc plasmatron was used during the experiments (patent no: 2012/03912). In order to provide efficient heat transmission, the feed head was specifically designed from copper material. 0.5 mm diameter holes located in the feed head has led to longer interaction between OMW and plasma flame. In the experimental studies, lab-scale stainless steel fixed bed reactor, where the gasification reaction is carried out, was used. Plasma thermo-chemical reactions take place in the reactor and plasma gas rich in hydrogen and free radicals was formed as a result. Moisture within a plasma gas was removed and cooled by passing through a gas cooler. In the next phase, plasma gas was transferred to the gas chromatograph for component analysis.

EXPERIMENTAL PROCEDURE

MATLAB Simulation Studies

Gasification simulation analyses were performed by using MATLAB. Newton-Raphson numerical method, which is known as non-linear equation solving techniques, was used to obtain the simulation results. Newton-Raphson method used to obtain the given node balance for each load is given in Figure 1.

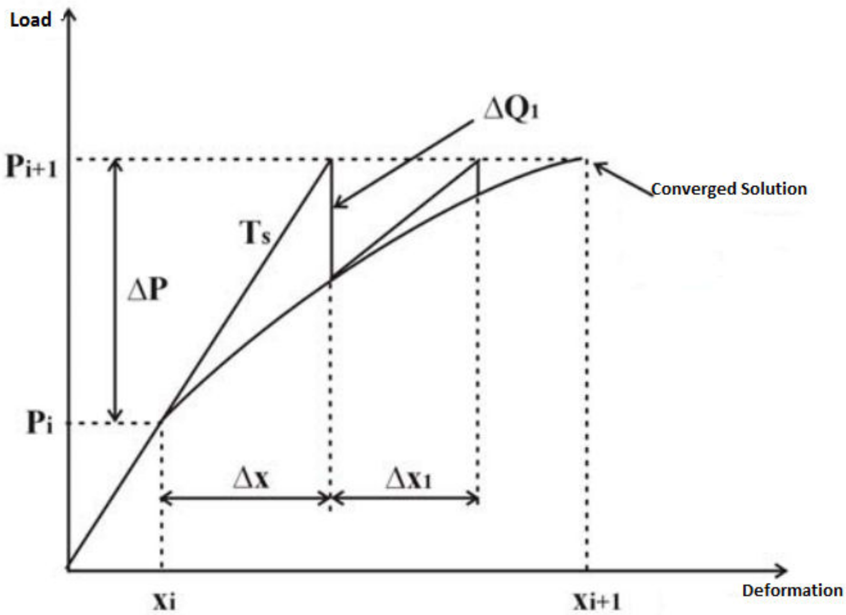

Figure 1. Calculation steps for non-linear analysis (34)

Simulation parameters were determined as change between 850-1000 K for temperature and mass parameters (S= kg steam/ kg dry fuel) ratio in the range of 0.05 to 0.7. It examined the effect of the parameters on the plasma gas composition. Elemental analysis values of the fuel used in the study is given in Table 1.

During simulation studies, while identifying the synthesis gas composition, kinetic data related to the 'Water Gas Reaction', 'Boudouard Reaction', 'Water Gas Shift Reaction' and 'Methanation

Reaction' and mass balance for H_2, N_2, CO, CO_2, CH_4, H_2O compositions were simultaneously solved in MATLAB program.

Table 1. Elemental analysis values of the fuel used (%) (35).

	DRY BASED
C, %	42.85
H, %	5.88
O, %	21.15
N, %	2.08
S, %	-
Ash, %	28.04
Moisture, %	80.0

$$C + H_2O \leftrightarrows CO + H_2 \quad \text{(Eq. 1)}$$

$$C + CO_2 \leftrightarrows 2CO \quad \text{(Eq. 2)}$$

$$CO + H_2O \leftrightarrows H_2 + CO_2 \quad \text{(Eq. 3)}$$

$$C + 2H_2 \leftrightarrows CH_4 \quad \text{(Eq. 4)}$$

Experimental Studies

In experimental studies, waste treatment technology for energy recovery was used to gasify OMW with plasma method. The aim of this study is to compare experimental with theoretical studies.

In the experimental study, plasma gasification of OMW, low mass OMW flow was performed with specially designed feed head with 0.5 mm diameter holes and it interacted with the plasma flame closest to the plasmatron area.

Water was used as a plasma agent and S ratio (steam / dry fuel) was fixed at 0,2. During the experiments, average temperature was 850-1000 K and studied under atmospheric pressure. In order to study the gas composition of formed plasma gas, it was cooled and analyzed by the gas chromatography analyzer. OMW plasma gasification test system is given in Figure 2.

Figure 2. Plasma gasification test system.

RESULTS AND DISCUSSION

MATLAB Simulation Study Findings

Investigation of Water Vapor and Temperature Effects

The effect of temperature and water vapor are investigated under constant atmospheric pressure. Examples of component concentrations at different temperatures with a value of S = 0.2 at atmospheric pressure are shown on Figure 3. With the increase in temperature, H_2-CO rate is increased and CH_4-CO_2 rate is decreased.

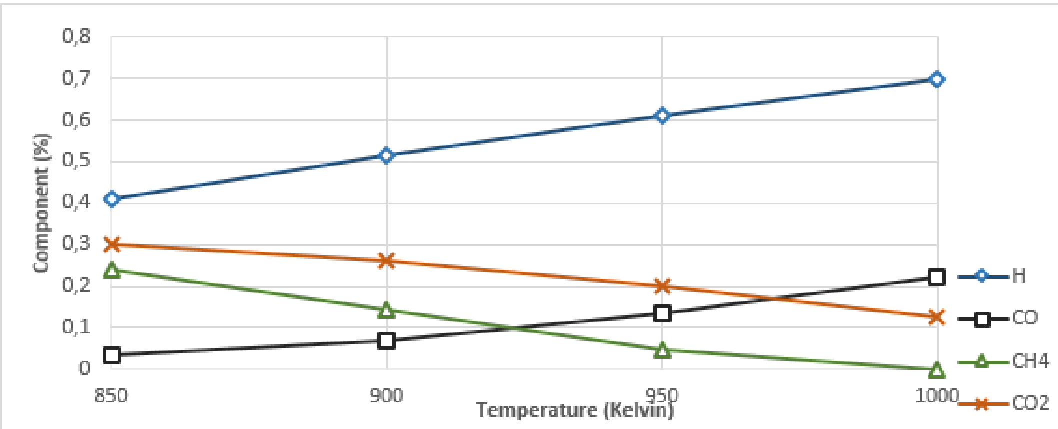

Figure 3. Temperature for S=0.2 % component replacement (P=1 atm).

Findings of Experimental Studies

Experimental studies were performed at atmospheric pressure and at constant steam/dry fuel at a 0.2 ratio. Due to the difficulties in temperature control of plasma, the average temperature values of the reactor were measured. The average temperature within the reactor is between 850-1000 K.

When considering the results obtained from experimental studies, probable fatty acids found in OMW suffered a thermochemical decomposition and carbon compounds turned into a hydrogen-rich gas plasma. The results are shown in Table 2 (1000 K).

The comparison of theoretical and experimental studies is shown in Table 3. The results of theoretical and experimental studies were obtained within the ratios of 1000 K and S value of 0,2.

In the theoretical studies while temperature was constant, with the increase of steam ratio, H_2/CO ratio has also been observed to increase. Increase of the temperature had similar effects on H_2 and CO. However, CH_4 and CO_2 concentration decreased.

The results from the comparison of theoretical and experimental studies are seen to be compatible. Other gases, apart from nitrogen, given in the results of the experimental study ethylene, propane, *etc*. are gases with combustion value and when comparing the calorific value, studies done with plasma technology are seen to be more efficient.

Theoretical and experimental studies have been carried out with this study and the possibility of energy recovery from Olive Mill Wastewater with high moisture content has been observed.
Given the limited work done and available in this subject (24) this study has proven to be innovative and important.

Table 2. Experiment Results (1000 K),

	Experiment 1	Experiment 2	Experiment 3	Experiment 4	Experiment 5	Mean Value	StDev
Compound	(%v/v)	(%v/v)	(%v/v)	(%v/v)	(%v/v)	(%v/v)	
H_2	63.97	64.45	64.53	66.18	64.98	64.82	0.75
CO_2	7.81	13.1	10.56	10.03	6.82	9.66	2.20
CH_4	0.29	0.14	0.42	0.32	0.58	0.35	0.15
CO	1.34	1.86	1.57	1.49	2.18	1.68	0.29
Other	26.59	20.45	22.92	21.98	25.44	23.48	2.25

Table 3. Comparison of experimental and theoretical studies,

	Experimental Studies (1000 K)	Theoretical Studies (1000 K)
Compound	(%v/v)	(%v/v)
H_2	64.82	65.09
CO_2	9.66	12.75
CH_4	0.35	0.01
CO	1.68	22.4

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Türkçe Öz ve Anahtar Kelimeler

GASIFICATION OF OLIVE MILL WASTEWATER WITH WATER PLASMA

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Öz: Zeytinyağı üretimi sonrasında zeytin karasuyu açığa çıkmaktadır. Zeytin karasuyu; organik madde, askıda katı madde, yağ ve gres içeriği oldukça yüksek olan ve fenolik bileşikler sebebiyle çevre için önemli derecede tehlike oluşturan bir atık su çeşididir. İçerisinde bulunan yüksek kirlilik oranı ile hem bertarafı gerekmekte hemde içerisindeki organik bileşikler (yağ asitleri vs.), zeytin karasuyundan enerji elde edilebilmesine imkan tanımaktadır. Bu çalışmada, hammadde olarak zeytin karasuyu kullanılarak su plazması ile gazlaştırma yapılmıştır. Elde edilebilecek ideal plazma gazı kompozisyonu teorik olarak incelenmiş ve deneysel çalışmalar yapılarak elde edilen sonuçlar karşılaştırılmıştır. Bu çalışmadaki amaç, teorik ile deneysel çalışmaların karşılaştırılarak plazmanın tanımlanmayan etkisinin belirlenebilmesidir. Teorik çalışmalarda gazlaştırma sırasında oluşan dört temel gazlaştırma reaksiyonlarından yararlanılmış, bileşen denkliği kurulmuş ve denge dönüşümleri ile MATLAB programı kullanılarak gazlaştırma prosesi simüle edilmiştir. 850-1000 K arasında farklı sıcaklıklarda, 0,05-0,7 S (su buharı/kuru yakıt) oranlarında çalışılarak ulaşılabilecek ideal sentez gazı kompozisyonu belirlenmiştir. Deneysel çalışmalarda düşük kütlesel debi aralığına sahip karasu beslenmesi ile plazma gazlaştırma deneyleri yapılmış ve gaz bileşiminin incelenmesi amacıyla gaz kromatografisinde analizi yaptırılmıştır. Deneysel sonuçlar ile teorik hesaplamalar karşılaştırıldığında sonuçların uyumlu olduğu, gazlaştırma sonucu aynı bileşen oranlarına plazma gazlaştırma ile daha düşük sıcaklıklarda ulaşıldığı görülmüştür. Zeytin karasuyunun plazma teknolojisi ile gazlaştırılması hakkında bir literatür bulunmadığından bu makale enerji geri kazanımı için atık geri dönüşüm teknolojisinin incelenmesinde son derece önemli bir rol oynamaktadır.

Anahtar kelimeler: Plazma gazlaştırma; sentez gazı, zeytin karasu

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