

Catalytic Gasification of Olive Mill Wastewater as a Biomass Source under Supercritical Conditions

Ekin Kıpçak, Mesut Akgün

Abstract—Recently, a growing interest has emerged on the development of new and efficient energy sources, due to the inevitable extinction of the nonrenewable energy reserves. One of these alternative sources which have a great potential and sustainability to meet up the energy demand is biomass energy. This significant energy source can be utilized with various energy conversion technologies, one of which is biomass gasification in supercritical water.

Water, being the most important solvent in nature, has very important characteristics as a reaction solvent under supercritical circumstances. At temperatures above its critical point (374.8°C and 22.1MPa), water becomes more acidic and its diffusivity increases. Working with water at high temperatures increases the thermal reaction rate, which in consequence leads to a better dissolving of the organic matters and a fast reaction with oxygen. Hence, supercritical water offers a control mechanism depending on solubility, excellent transport properties based on its high diffusion ability and new reaction possibilities for hydrolysis or oxidation.

In this study the gasification of a real biomass, namely olive mill wastewater (OMW), in supercritical water conditions is investigated with the use of Ru/Al₂O₃ catalyst. OMW is a by-product obtained during olive oil production, which has a complex nature characterized by a high content of organic compounds and polyphenols. These properties impose OMW a significant pollution potential, but at the same time, the high content of organics makes OMW a desirable biomass candidate for energy production.

The catalytic gasification experiments were made with five different reaction temperatures (400, 450, 500, 550 and 600°C) and five reaction times (30, 60, 90, 120 and 150s), under a constant pressure of 25MPa. Through these experiments, the effects of reaction temperature and time on the gasification yield, gaseous product composition and OMW treatment efficiency were investigated.

Keywords—Catalyst, Gasification, Olive mill wastewater, Ru/Al₂O₃, Supercritical water.

I. INTRODUCTION

SUPERCritical water gasification (SCWG) has recently received much attention as a potential alternative to energy conversion methods applied to aqueous/non-aqueous biomass sources [1]-[3] or fossil fuels such as coal [4], [5], due to the unique physical properties of water above its critical conditions (374.8°C and 22.1MPa). At supercritical conditions, water behaves both as an acidic and alkaline

precursor for acidic or basic reactions on account of the higher concentrations of H₃O⁺ and OH⁻ ions. This is due to the fact that the ionic product of subcritical and supercritical water at high pressures is some orders of magnitude greater than that of ambient water [6]-[8]. Therefore, supercritical water is considered both as a solvent for organic materials and as a reactant at processes such as the oxidative treatment of wastewaters, the gasification of aqueous organic solutions and production of fine metal oxide particles. Since organic compounds have complete miscibility and a high solubility in supercritical water due to its much lowered dielectric constant, chemical reactions with high efficiencies and without interfacial transport limitations can be obtained in the case of water-organic mixtures. Therefore, supercritical water offers a control mechanism depending on solubility, excellent transport properties based on its high diffusion ability, a low viscosity and new reaction alternatives for hydrolysis or oxidation [1], [9].

Energy production based on fossil fuels causes high import expenditures, environmental problems and a major consumption of the world's nonrenewable energy reserves. Hence, a growing interest has emerged on the development of new and efficient energy sources. Biomass energy is among these sources, which can be utilized with various energy conversion technologies. One of these technologies is biomass gasification in supercritical water that has many advantages, such as high gasification efficiency and considerable amounts of flammable component production in the gaseous effluent during the process. Extensive investigations have been conducted in the recent years on this topic, which included model compounds such as glucose, cellulose, lignin and some real biomass compounds [1], [3], [10], [11].

In this study, the catalytic gasification of a real biomass, olive mill wastewater, was investigated. OMW is a by-product obtained during olive oil production, which is a fundamental economic activity for countries along the Mediterranean coast. OMW is generally composed of the water content of the olive fruit, water used to wash and process the olives, soft tissues from the olive pulp and a very stable oil emulsion [12]. The annual OMW production in the Mediterranean countries is estimated to range from 10 to 30 million m³. This quantitative diversity results from different factors such as the oil extraction method, cultivation soil, the use of pesticides and fertilizers, olive harvesting time, degree of ripening, duration of aging, olive variety and climatic conditions [13]. The typical OMW composition by weight is 83-96% water, 3.5-15 % organic compounds and 0.5-2% mineral salts. The organic

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fraction includes sugars, tannins, pectins, lipids, organic acids, nitrogen compounds, polyalcohols and polyphenols. The complex composition stated above makes OMW a significant pollution potential. Its polyphenol content is responsible for several biological effects, as phenolic compounds of low molecular weight show toxicity on seed germination, aquatic organisms and bacteria. But at the same time, the high content of organics makes OMW a desirable biomass candidate for energy production.

The gasification experiments in supercritical water were conducted with the use of Ru/Al₂O₃ catalyst, at five reaction temperatures (400, 450, 500, 550 and 600°C), with five reaction times (30, 60, 90, 120 and 150s) under a constant pressure of 25MPa. With these experiments, it was aimed to find the effects of reaction temperature and reaction time on the gasification yield, biofuel composition and wastewater treatment efficiency. The results demonstrate that catalytic gasification of OMW under supercritical conditions can be employed both as a treatment process and as a way of energy recovery, in very short time intervals.

II. MATERIALS AND METHODS

A. Materials

The olive mill wastewater used in the experiments was supplied from an olive oil producing plant in Turkey, which was roughly filtered and diluted with distilled water in order to obtain the desired Total Organic Carbon (TOC) amounts. The characteristics of the OMW used in this work are presented in Table I.

B. Catalyst

The Ru/Al₂O₃ catalyst was commercially obtained (Alfa-Aesar), which contained 3.795% (wt.) ruthenium, 70.794% (wt.) aluminum, 7.905% (wt.) oxygen and 17.596% (wt.) chlorine. The catalyst tablets were in cylindrical shape, with a diameter and length of both 3.2mm. The density of the Ru/Al₂O₃ catalyst was measured as 1.82g/cm³. The SEM image of the catalyst, which was obtained from scanning electron microscope (JEOL-5410LV) using Bath Scatter Electron Detector and Secondary Electron Detector, is shown in Fig. 1. On the other hand, its XRF spectrum, which was obtained by using Energy Dispersive Spectroscopy (EDS), is presented in Fig. 2.

C. Experimental Setup

The catalytic gasification experiments were performed in the reactor system with a volume of 8.305mL, which was placed into a PID controlled split furnace (Protherm, model SPT 11/70/750). From the feed pump to the gas-liquid separator, all of the wetted parts of the system, such as tubing, fittings, etc., were made of 316 SS. OMW was pumped into the furnace by using a high pressure pump (Autoclave Engineers, Series III pump). After exiting the furnace, the effluent was cooled rapidly by passing through a heat exchanger, and the reaction immediately stopped.

TABLE I
THE CHARACTERISTICS OF THE OMW

| Parameters | Value |
|-----------------------------|-------|
| pH | 4.36 |
| Total Organic Carbon (mg/L) | 6138 |
| Inorganic Carbon (mg/L) | 30.1 |
| Total Nitrogen (mg/L) | 99.0 |
| Total Solid Matter (g/L) | 10.4 |
| Ash (g/L) | 2.9 |
| Phenols (g/L) | 3.7 |
| Ca (g/L) | 86.8 |
| Na (g/L) | 0.8 |
| K (g/L) | 452.2 |
| Mg (g/L) | 14.2 |
| Na (g/L) | 22.3 |

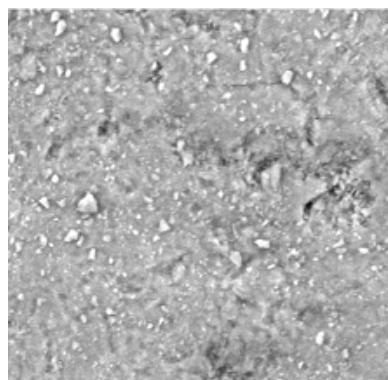


Fig. 1 SEM image of the Ru/Al₂O₃ catalyst (10 nm)

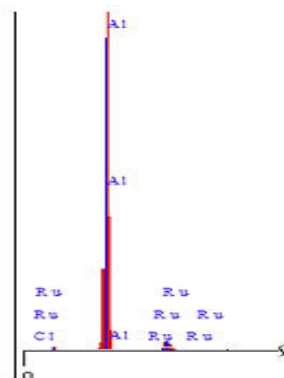


Fig. 2 XRF spectrum of the Ru/Al₂O₃ catalyst

The possible solid particles in the effluent, which would be formed presumably, were removed with a 0.5µm inline filter before the stream was depressurized by a back-pressure regulator (BPR) (GO Regulator Inc.). The system pressure was kept at a constant value (25±0.1MPa) by the BPR set at the exit of the reactor and monitored through a digital pressure indicator. The system temperature was also kept stable (±1°C) through the PID-controlled split furnace. The products leaving the BPR were separated by a gas-liquid separator. The gaseous effluent taken from the top portion of the separator was transported for quantitative analysis by a gas chromatograph

capable of online sampling. On the other hand, the samples taken from the liquid effluent leaving the system were sent for TOC analysis. The experimental setup is schematically demonstrated in Fig. 3.

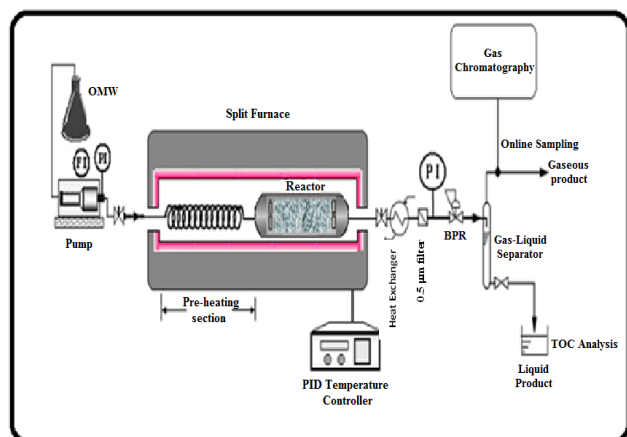


Fig. 3 Schematic demonstration of the experimental setup

D. Liquid Product Analysis

The liquid samples taken from the bottom of the gas-liquid separator were characterized for determining their treatment efficiencies by their TOC concentrations. TOC analyses were performed by a total organic carbon-total nitrogen analyzer (Hach-Lange IL550 TOC-TN), which is based on the combustion catalytic oxidation method, using a highly sensitive multi-channel, non-dispersive infrared detector (NDIR).

E. Gaseous Product Analysis

The gaseous product obtained from the top portion of the gas-liquid separator was taken to a gas chromatograph for quantitative analysis. The instrument used for this aim was a Perkin Elmer Arnel brand, Clarus 500 model gas chromatography device, coupled with one FID and two TCD detectors.

F. Other Analyses

The total phenolic content of the OMW was determined using the Folin–Ciocalteu method. Physicochemical properties of the wastewater such as total solids and ash in Table I was determined according to the Standard Methods.

III. RESULTS AND DISCUSSION

The experiments with $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst were made under a constant pressure of 25MPa, and it was aimed to investigate the effect of five different temperatures (400, 450, 500, 550 and 600°C) and five different reaction times (30, 60, 90, 120 and 150s) on the gasification yield, flammable component content and treatment efficiency of the wastewater.

As a result of the experiments, it was seen that gaseous effluent flow rates up to 16.7mL/min could be obtained by the catalytic gasification of OMW. However, the sole

interpretation of this can be quite misleading, as the OMW flow rates fed to the reactor were calculated considering the water density at supercritical conditions, in order to keep the reaction times constant. In other words, the OMW feed flow rates were greater at lower temperatures. Hence, it is more convenient to evaluate the gaseous effluent amount with respect to the unit amount of OMW fed to the system; i.e. the gas product yield (Fig. 4). As it can be seen from the figure, the gas product yield increased considerably with temperature, and began to decrease after 550°C. At 550°C and 30 s, a maximum gas product yield of 9.3 L/kg OMW was obtained.

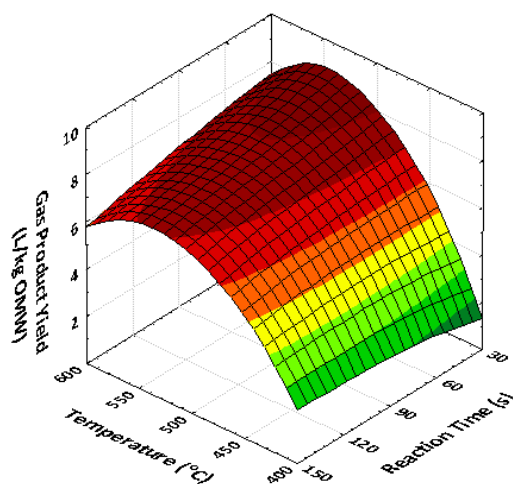


Fig. 4 The change of gas product yield with temperature and reaction time

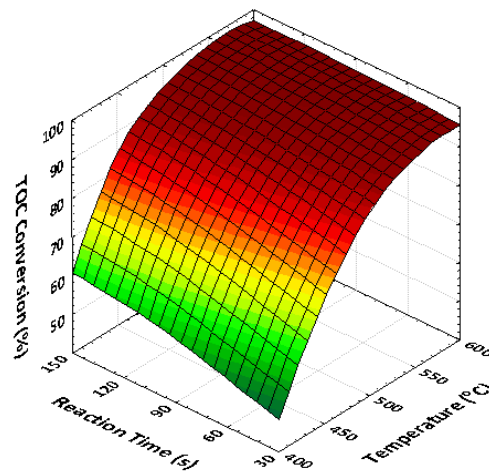


Fig. 5 The change of TOC conversion with temperature and reaction time

Fig. 5 shows the change of TOC conversion of the liquid effluent with temperature and time. Accordingly, it can be seen that TOC conversion increased with temperature and reaction time. This is an expected occasion, as the organic content of OMW reacted more and got through the gaseous phase, as the reaction temperature and duration increased. At elevated

temperatures and reaction times, about 98 % of the organic carbon present in OMW was transferred into the gaseous phase, enabling the treatment of the wastewater.

The gaseous effluents were mainly composed of methane, hydrogen, carbon dioxide and C₂-C₃ hydrocarbons (ethane, propane and propylene). Besides these products, scarce amounts of carbon monoxide, oxygen, nitrogen, n-butane, i-butane, 1-butene, iso-butene, T-2-butene, C-2-butene, 1,3-butadiene, n-pentane and iso-pentane were also obtained. Figs. 6 and 7 show the changes of the two main flammable gaseous products, methane and hydrogen, at different reaction conditions, respectively.

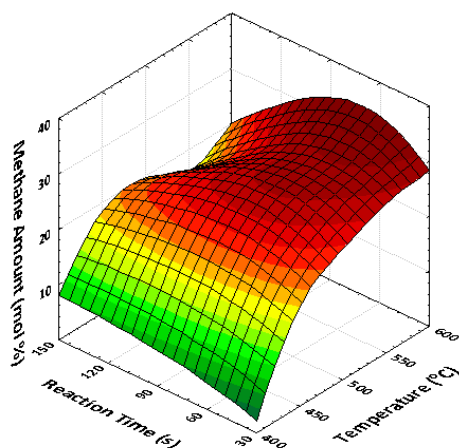


Fig. 6 The change of methane amount with temperature and reaction time

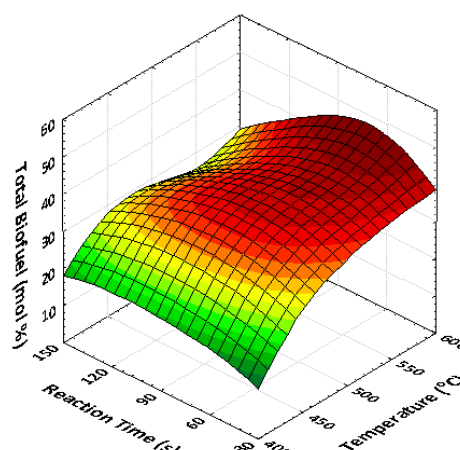


Fig. 8 The change of total biofuel amount with temperature and reaction time

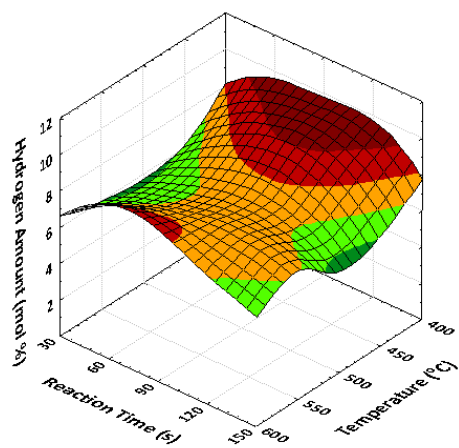


Fig. 7 The change of hydrogen amount with temperature and reaction time

Accordingly, the methane amount increased considerably with temperature, and it was seen that temperature had a much more prominent effect on methane production than reaction time. Methane showed an increasing tendency up to 60s, and then began to decrease. This shows the degradation of the formed methane to the final reaction products (carbon dioxide

and water) at elevated reaction times. The maximum amount of methane (38.0%) was obtained in the experiment performed at 600°C and 60s. Hydrogen showed a similar trend to methane, regarding reaction time, increasing up to 60-90 s and then decreasing. Considering temperature, it was seen that the amount of hydrogen in the gaseous effluent decreased at elevated temperatures. This situation shows the degradation of the formed hydrogen to the final reaction products at long reaction times and high temperatures. The maximum amount of hydrogen, 12.0%, was obtained at 400°C and 120s. But unlike methane, hydrogen did not show major deviations neither with temperature, nor with reaction time.

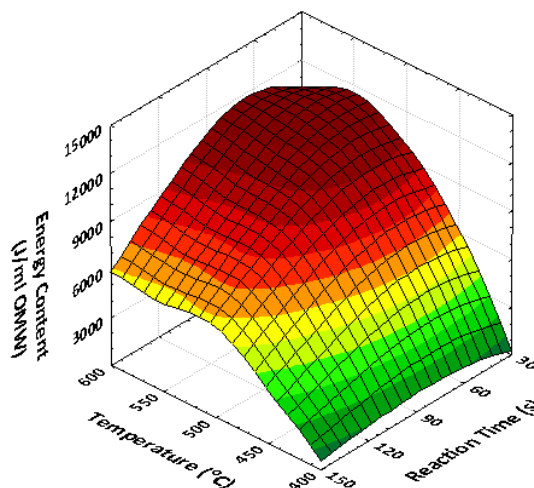


Fig. 9 The change in the energy content of the gaseous effluent with temperature and reaction time

The change in the total biofuel content of the gaseous effluent with respect to reaction temperature and time is given in Fig. 8. As it can be seen from the figure, 54.2% of the produced gas was composed of flammable components, which was obtained at 600°C for a reaction time of 60s. At these

conditions, a gas product yield of 7.1 L/kg OMW fed to the reactor was observed, which involved 38% methane, 11.0% hydrogen, 4.4% ethane, 0.3% propane, 0.2% propylene and 39.2% carbon dioxide.

Fig. 9 shows the energy content of the produced gaseous effluent at different reaction conditions. Accordingly, it can be seen that the reaction temperature was much more effective in increasing the calorific value of the gaseous product, rather than reaction time. The energy content showed an increasing tendency up to 60s, which shows the degradation of the flammable components to the final reaction products at higher reaction times. At 600°C and for a reaction time of 60s, the maximum calorific value of the gaseous product was obtained, which was 13284 J/ml OMW.

Fig. 10 presents the change of carbon dioxide content of the gaseous effluent with respect to temperature and time. Accordingly, it showed an increasing trend with decreasing temperatures and long reaction times. The maximum amount of carbon dioxide, which was 78.6%, was obtained at 400°C and for a reaction time of 30s. On the other hand, the minimum amount of carbon dioxide was obtained at the experiment carried out at 600°C and 60s; the conditions at which the maximum amount of flammable components was produced (39.2%).

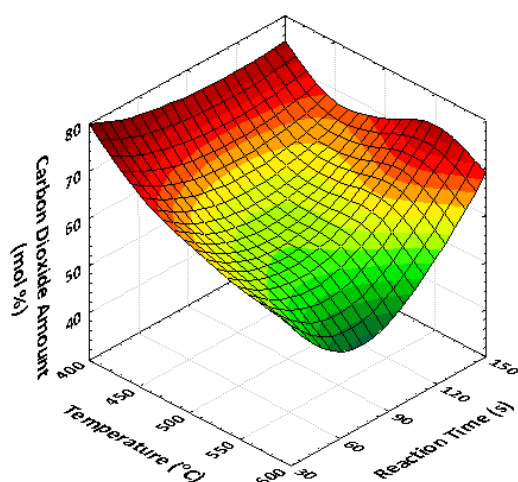


Fig. 10 The change of carbon dioxide amount with temperature and reaction time

IV. CONCLUSION

The experimental results regarding the gasification OMW with the use of Ru/Al₂O₃ catalyst show that the process can be employed both as a treatment process and as a way of energy recovery, in very short reaction times. The gaseous products were mainly composed of methane, hydrogen, carbon dioxide and C₂-C₄ hydrocarbons. Gas product yields up to 9.3L/kg OMW were obtained. What is more, at high temperatures and reaction times, treatment efficiencies up to 98% were obtained during the catalytic gasification of OMW in supercritical water conditions.

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