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Application of a Hydrothermal Gasification Method in the Treatment of Wastewater Generated from the Afyonkarahisar-Alkaloid Plant

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Abstract: The wastewater coming from the alkaloid production plant, located in the province of Afyon, must satisfy the discharge limits specified in the "Water Pollution Control Regulations, 2004" to be safely discharged into the environment. Treatment of the alkaloid plant wastewater with the existing treatment method, which is a combination of the biological (aerobic / anaerobic) and chemical treatment, is not sufficient. In this study, hydrothermal gasification (or supercritical water gasification, SCWG) is proposed as an alternative and advanced treatment technique. The other objectives of the study are to show the producibility of methane and hydrogen as a renewable energy source and to investigate, as to what extent was the removal of chemical oxygen demand and polluting compounds as a spontaneous result of gasification. The effect of a catalyst in the highest conversion of an organic carbon content in wastewater, to a gaseous product rich in H_2 and CH_4, and the maximum efficiencies in total organic carbon (TOC) and chemical oxygen demand (COD) removals. Hydrothermal gasification studies of alkaloid wastewater were carried out without a catalyst and with Na_2CO_3 (N). The experiments were performed at the reaction temperatures of 400, 500, and 600 °C with and without 0.12 g of catalyst and 15 mL of wastewater. The gaseous products were analyzed using gas chromatography, and the TOC and COD content of the aqueous products and raw wastewater were analyzed using a TOC analyzer and COD analysis set. The variation of the product distribution and yields, TOC and COD removal by temperature and catalysis were examined. The initial TOC, and COD values of the wastewater studied were 15,000 mg/L and 35,000 mg/L, respectively.

Keywords: Supercritical water gasification; methane; hydrogen; hydrothermal gasification; alkaloid wastewater.

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INTRODUCTION

In recent years, the gasification of biomass in supercritical wastewater is investigated with a growing interest. The choice of materials to be used as raw material [1-3], selection of the catalyst, [4-6], optimization of the operating conditions [7, 8], investigation in the behavior of the model compounds during the hydrothermal gasification period [9, 10], and thermodynamic calculations [11, 12] are the most investigated topics in this field. This new technique is also used in wastewater gasification and the production of valuable chemicals. The wastewater used in energy production and evaluated using the supercritical water gasification method has become one of the new types of raw materials [13-15]. There are two studies with black liquor which is generated from cellulose production by the sulfate method [15-16], a study with olive mill wastewater [13], and another study with wood gasification wastewater [17]. Besides wastewater coming from the amino acid production process [18], acrylonitrile plant wastewater [19], and coking plant wastewater [20] are also used as raw materials in hydrothermal gasification studies.

The wastewater generated by an Opium Alkaloid Factory is 840 m^3 per day and is discharged into Eber Lake by way of the river Akarcay after successive treatment processes. According to literature data, the COD value of this wastewater varies between 18.3 - 42.5 O_2/ liters [21]. This wastewater contains toxins and poisons, inhibiting microorganism activity, and biodegradation-resistant materials. Therefore, it must be treated to below 1500 mg O_2/liter before being discharged into the environment due to the Water Pollution Control Regulations published in 2004.

There are many studies on the treatment of this wastewater using chemical, biological, (aerobic and anaerobic medium), and wet air oxidation (oxidation with air in the liquid phase) [22-25]. It has been reported that the COD value of the wastewater could be reduced by approximately 33 to 80%. According to this ratio, the COD of the treated wastewater is at least 6000 mg. This is more than four times the discharge limit. The reason to choose this wastewater as a raw material is the high organic carbon content and to propose this method as a solution to the environmental problems caused by this wastewater in and around Lake Eber.

All these studies indicate that the Opium Alkaloids Plant wastewater shows a high resistance to treatment because of its complex structure, and has revealed that it is difficult to treat adequately.

The Opium Alkaloids Plant wastewater, which is a waste of a specific industry, has not been considered for the evaluation of hydrogen and methane production as an energy source using hydrothermal gasification in literature so far. This wastewater was not studied using this technique as a treatment alternative in any research.

RESULTS AND DISCUSSION

Hydrothermal gasification studies were carried out in a batch autoclave reactor system shown in Figure 1 in the absence of a catalyst and in the presence of Na_2CO_3 at various reaction temperatures. The pressures reached at studied runs changed within the range of 235-440 bar. The experiments were performed at the reaction temperatures of 400, 500 and 600 °C with and without 0.12 g of catalyst and 15 mL of wastewater. The effects of reaction temperature and the catalyst addition on the product yields and COD, TOC removals were investigated. The reactor was sealed tightly and the air inside it was purged with nitrogen then heated at a rate of 8 - 10 K/min to the reaction temperature. It is maintained constant during the reaction time of 1 h with a PID controller. Table 1 contains the studied experimental conditions. The selection of the alkali catalyst is based on enhancing the gasification efficiencies and providing high COD and TOC removal efficiencies.

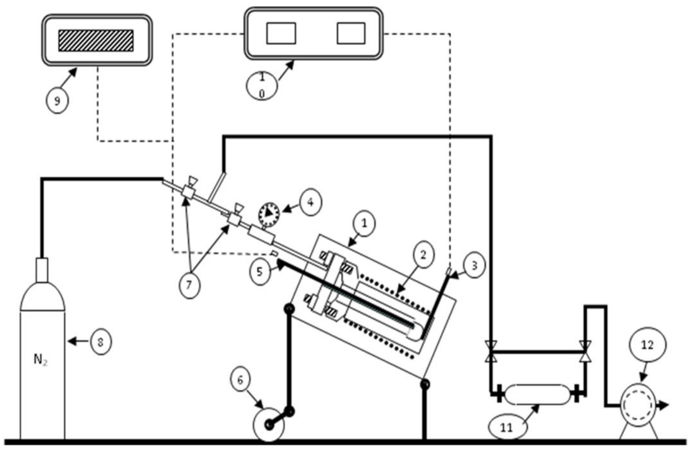

Figure 1: Schematic of the autoclave reactor.

Table 1: Hydrothermal gasification conditions (T:temperature, 4:400°C, 5:500°C, 6:600°C, and N: Na_2CO_3)

Exp Code	*T,°C*	*P, bar*	*Catalyst*	*Catalyst amount, g*
AF-T4	400	240	-	-
AF-T5	500	365	-	-
AF-T6	600	440	-	-
AF-T4N	400	235	Na_2CO_3	0.12
AF-T5N	400	355	Na_2CO_3	0.12
AF-T6N	400	415	Na_2CO_3	0.12

The other criterion for catalyst selection is the increasing effect on the percentage of H_2 and CH_4 in the gaseous product mixture.

The gaseous products were analyzed using gas chromatography (Agilent Technologies HP 7890A, USA). It is equipped with serially arranged 7 columns (Hayesep Q 80/100 mesh (0.5 m long × 2 mm i.d.), a Hayesep Q 80/100 mesh (1.8 m long × 2 mm i.d.), a Molsieve 5A 60/80 mesh (2.4 m long × 2 mm i.d.), a Hayesep Q 80/100 mesh (0.9 m long × 2 mm i.d.), a Molsieve 5A 60/80 mesh (2.4 m long × 2 mm i.d.), a DB-1 (pre-column), and HP-Plot Al_2O_3 S (25 m long × 0.32 mm i.d.). 3 detectors were serially connected with a special adapter (2 thermal conductivity detectors (TCD), and a flame ionization detector (FID)), and the TOC and COD content of the aqueous products and raw wastewater were analyzed using a TOC analyzer (Shimadzu TOC-VCPH, Japan). Chemical Oxygen Demand (COD) of the raw wastewater and aqueous products were determined with COD analysis equipment formed of thermo-reactor (MERCK, Spectroquant TR320) and spectrophotometer (MERCK, Spectroquant Nova 60), and kits (500-10,000 ppm and 150-1,000 ppm) depending on the COD level of the aqueous product. The distribution (molar percentage, %) and the yields (mol/kg C) of the compounds in the gaseous product are given in Figs. 2 and 3. The COD and TOC values and removal efficiencies are shown in Figs. 4 and 5.

Total Organic Carbon Removal Efficiency (TOC_{RE}, %) and Chemical Oxygen Demand Removal Efficiency (COD_{RE}, %) were expressed by using the following formulas;

Total Organic Carbon Removal Efficiency:

$$(TOC_{RE}, \%) = \frac{TOC_{ww} - TOC_{aq}}{TOC_{ww}} x100$$

Chemical Oxygen Demand Removal Efficiency:

$$(COD_{RE}, \%) = \frac{COD_{ww} - COD_{aq}}{COD_{ww}} x100$$

The effect of parameters on product distribution and yields were determined.

Table 2: Experimental results of catalytic and non-catalytic runs at studied reaction temperatures.

Exp Code	***TOC RE, %***	***COD RE, %***	***H_2 yield (mmol/kg C)***	***CH_4 yield (mmol/kg C)***
AFALT4	40.9	42.6	11.3	3.5
AFALT5	74.5	80.0	20.4	16.8
AFALT6	85.6	91.2	33.3	25.1
AFALT4N	52.7	45.4	16.1	5.9
AFALT5N	89.2	87.4	26.8	20.9
AFALT6N	90.3	93.3	37.2	29.8

The effect of the parameters on product distribution and yields were determined.

The proposed reactions associated with hydrothermal decomposition of organic carbon containing biomass in water are given below. Considering these reactions, for the carbon-containing organic pollutants and biomass in wastewater, assessing the results will be useful.

$$C_6H_{12}O_6 + 6H_2O \leftrightarrow 6CO_2 + 12H_2 \quad \text{(Eq. 1)}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \text{(Eq. 2)}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \text{(Eq. 3)}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \text{(Eq. 4)}$$

The gaseous product is composed of H_2, CO_2, CO, CH_4, C_2H_6, C_2H_4, C_3H_8, and C_4H_{10}. Smaller amounts were determined for C_2H_6, C_2H_4, C_3H_8, and C_4H_{10}, so the total amounts of these compounds were given as the C_2 - C_4 group in the plots for easier evaluation. The major products were detected as H_2, CO_2, CH_4, and CO. Hydrogen and carbon dioxide were formed by degradation of the organic compounds in the wastewater and the water gas shift reaction via reactions 1 and 4 dominantly. Methane is formed by the further reactions of the degradation products in reactions 2 and 3. As it is seen in Figure 2, the catalyst and reaction temperature has significant effects on the gas product distributions.

While the gaseous product distribution is considered in terms of molar percentage of H_2, in the absence of a catalyst, it is seen that there is no significant change with temperature and is partially reduced in the presence of Na_2CO_3. The yields were increased with increasing both the temperature and adding a catalyst as expected. The molar percentage and yields of CH_4 were promoted and clearly seen in Figures 2 and 3 from 400 to 600 °C with the increasing temperature in both the catalytic and non-catalytic cases. There is a significant reduction in the CO_2 percentage in the gas product related to the effect of the catalyst. The effect of temperature, on the molar percentage of CO_2 in the gaseous product varies according to the catalyst usage. It decreases as the temperature increases in the studies without a catalyst while an ordered decrease or increased is not mentioned in the studies with Na_2CO_3.

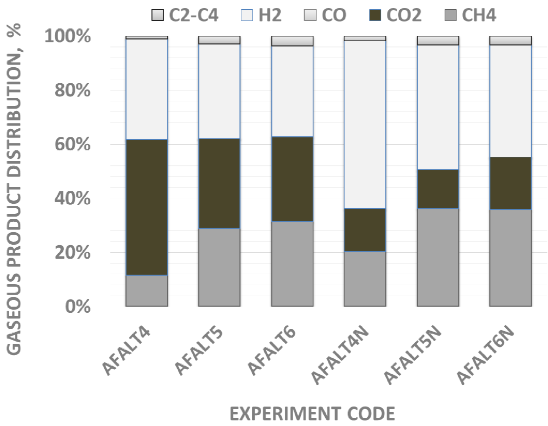

Figure 2: The effect of a catalyst and temperature on the gaseous product distribution.

Figure 3 shows the change in the number of gaseous products and the first noticeable inference is that the increasing temperature dramatically increases the total amount of product.

It is clearly seen that the yields of CH_4 and H_2 which were targeted to produce in this study reached the maximum yield at 600°C. While temperature is increasing from 400 to 600 °C, the yields of CH_4 and H_2 increased from 3.51 to 25.11 mmol / kg C and from 11.33 to 33.30 mmol / kg C, respectively.

At a specified reaction temperature, a significant decrease in the amount of CO_2 was seen by the effect of the alkaline catalyst. However, the amount of CH_4 and H_2 were promoted. In the presence of a catalyst, the CO_2 was converted to CH_4 via the 3rd reaction given above. It can be said that more organic compounds degraded with regards to the effect of the catalyst and converted to H_2 via reaction (1).

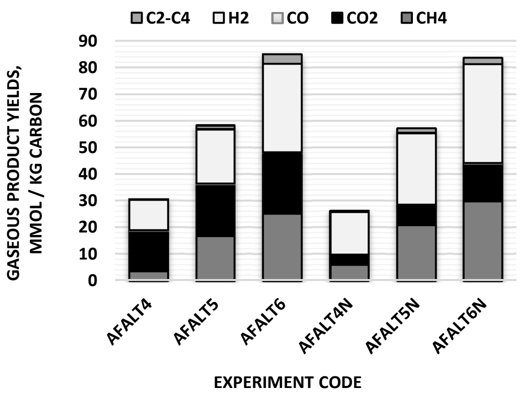

Figure 3: The effect of a catalyst on the gaseous product distribution and yields (mmol/kg C).

The TOC and COD content of the aqueous product decreases with the effect of the rising temperature dramatically in both the absence and presence of a catalyst. Temperature is the dominant factor in the removal COD and TOC. From 500 °C to 600 °C, the change in TOC and COD has a downward acceleration magnitude. So, the operating temperature should be selected as 500 °C as the optimum. The maximum TOC removal efficiencies were obtained as 85% without a catalyst and 90% with Na_2CO_3.

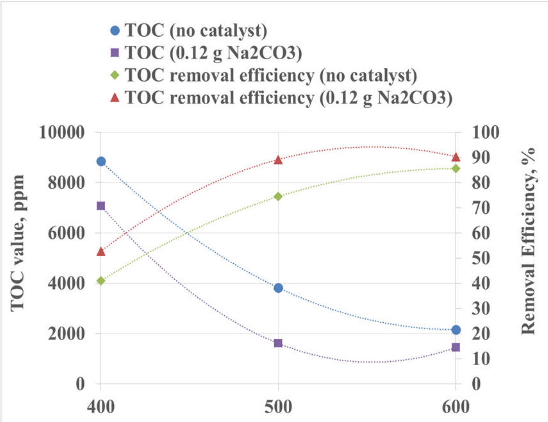

Figure 4: The variation of total organic carbon (TOC) in the aqueous product and TOC removal efficiencies with a catalyst and temperature.

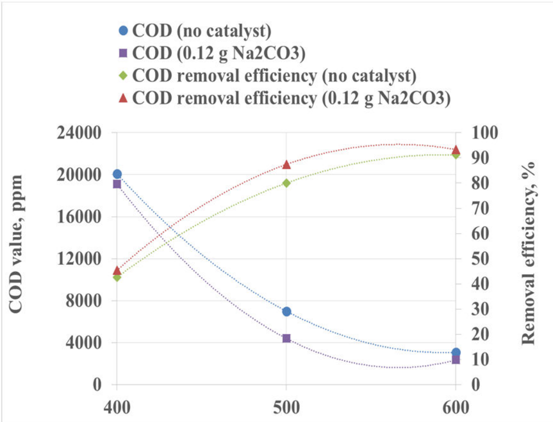

Figure 5: The variation of chemical oxygen demand (COD) in the aqueous product and COD removal efficiencies with a catalyst and temperature.

The highest COD removal efficiencies obtained were 91% without a catalyst and 93% with Na_2CO_3 as seen in Figure 5 at 600 °C. The economy of the process is taken into consideration to determine the most appropriate condition which is 500 °C as the reaction temperature. The catalyst should be added to improve efficiencies and yields.

CONCLUSION

Hydrothermal gasification of opium alkaloid wastewater in supercritical water was investigated at a temperature range of 400 °C – 600 °C. The effect of reaction temperature and the catalyst (Na_2CO_3, 0.12 g) added were represented in a batch autoclave reactor system for a reaction time of 1 h. The yields of CH_4 and H_2 promoted by increasing temperature from 3.5 to 25.1 mmol / kg C and from 11.3 to 33.3 mmol / kg C, respectively. Na_2CO_3 enhance the CH_4 and H_2 yields, while decreasing yields of CO_2. TOC removal increased by catalyst addition significantly but COD removal was not affected by catalyst remarkably. Treatment of alkaloid wastewater by the proposed method is accomplished due to high COD and TOC removal results obtained at 500 °C and above it.

It can be emphasized that hydrogen and methane production was succeeded by supercritical water gasification method providing also good treatment characteristics.

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Türkçe Öz ve Anahtar Kelimeler

Afyonkarahisar Alkaloid Tesisinden Üretilen Atıksuyun Terbiyesine Hidrotermal Gazlaştırma Yönteminin Uygulanması

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Öz: Afyon ilinde bulunan alkaloid üretim tesisinden gelen atıksu 2004 yılında yürürlüğe girmiş olan "Su Kirliliği Kontrol Yönetmeliği" kapsamında belirlenen deşarj sınırlamalarını karşılamalıdır. Biyolojik (aerobik / anaerobik) ve kimyasal terbiye yöntemlerinin bir karışımı olan mevcut terbiye yönteminde alkaloid tesisinin atıksuyunu terbiye etme yöntemi yeterli değildir. Bu çalışmada, hidrotermal gazlaştırma (ya da süperkritik su gazlaştırması, SCWG) bir alternatif ve ileri terbiye tekniği olarak önerilmektedir. Çalışmanın diğer amaçları, yenilenebilir bir enerji kaynağı olarak metan ve hidrojenin üretilebilirliğini göstermek ve gazlaştırmanın kendiliğinden olan bir sonucu olarak kirletici bileşiklerin ve kimyasal oksijen ihtiyacının ne kadar giderildiğini incelemektir. Atıksudaki organik karbon içeriğinin H_2 ve CH_4 açısından zengin gaz ürününe en yüksek mertebede dönüşümü için katalizör etkisi ve toplam organik karbon (TOC) ve kimyasal oksijen ihtiyacı (COD) giderimi için en yüksek etkinliklerin bulunması da amaçlanmıştır. Alkaloid atıksuyunun hidrotermal gazlaştırma çalışmaları katalizör olmadan ve katalizör olarak Na_2CO_3 (N) kullanarak yürütülmüştür. Deneyler 400, 500 ve 600 °C'de yürütülmüştür, katalizör kullanılacağı zaman, miktarı 0,12 g olarak belirlenmiştir ve atıksudan 15 mL alınmıştır. Gaz ürünler gaz kromatografisi ile analiz edilmiştir ve sulu ürünler ile ham atıksuyun TOC ile COD içeriği TOC analizörü ve COD analiz seti kullanılarak belirlenmiştir. Ürün dağılımı ve verimlerin değişmesi, sıcaklık ve katalizör ile TOC ve COD giderimi incelenmiştir. Atıksuya ait ilk TOC ve COD değerleri sırasıyla 15.000 mg/L ve 35.000 mg/L olarak bulunmuştur.

Anahtar kelimeler: Süperkritik su gazlaştırması; metan; hidrojen; hidrotermal gazlaştırma; alkaloid atıksuyu.

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