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Treatment of high-strength opium alkaloid wastewater using hydrothermal gasification

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A B S T R A C T

The hydrothermal gasification of opium alkaloid wastewater was investigated in a batch autoclave at 400, 500, and 600 °C at a pressure range of 23.0–45.5 MPa without and with various amount of K_2CO_3 catalyst. The maximum gas yields, hydrogen and methane, were obtained at 600 °C using K_2CO_3 at amounts higher than 0.375 g. TOC and COD contents of the aqueous products and raw wastewater were analyzed, the compounds existing in the raw wastewater and the aqueous products were identified and compared. The wastewater used in this work has a COD content of 35,000 mg O_2/L and a TOC content of 15,000 mg/L and the highest COD removal efficiencies acquired was 95% at 600 °C and in the presence of K_2CO_3 (varying from 0.375–0.625 g). The H_2 and CH_4 yields were maximized at 47.7 and 34.3 mol/kg OC in wastewater using 0.5 g of K_2CO_3 and at 600 °C, respectively.

1. Introduction

An Opium Alkaloids Plant is located in the city of Afyon, Turkey, producing alkaloids, using the opium poppy capsule, such as: morphine, codeine, thebaine, etc. for pharmaceutical purposes. The statistical data shows that the global demand for alkaloids are as high in 2013 as in the past two decades. The global consumption of morphine as pain reliever has increased fourfold, particularly in high-income countries in recent years. Turkey is one of twelve licensed countries for opium poppy cultivation worldwide and together with Australia, Spain, France, Hungary, and India one of the largest producer of poppy straw rich in morphine. According to the International Narcotics Control Board (INCB) reports [1], these six countries have met about 93 per cent of the global needs of poppy straw rich in morphine (in morphine equivalent) in 2014.

The wastewater generated from the Opium Alkaloids Plant in Afyon contains some alkaloids (codeine, morphine, and thebaine), aniline, phytin, toluol, acetic acid [2], wax type compounds, soluble components of cellulose, lignin, and hemicellulose [2,3]. This high strength wastewater has a dark-brown color originating from materials resistant to biodegradation [4] and is discharged into Eber Lake via the Akarçay River around the city of Afyon. The existing treatment plant is a two-stage system formed of biological (aerobic/anaerobic) treatment and chemical precipitation. Since there are some operating problems, the treatment plant does not work properly [4,5] and causes an environmental problem in this region.

The studies reported on the treatment of opium alkaloid wastewater by various treatment methods consist of characterization [2,6], biological and/or chemical treatment [7–9], long-term anaerobic treatment [2] and simulation of it using the Anaerobic Digestion Model No. 1 (ADM1) [10], pretreatment by wet air oxidation [3], gamma irradiation as pre-treatment [11], Fenton oxidation of pretreated opium alkaloid wastewater [12], anaerobic pretreatment and post treatment with lime and ozone [5], and membrane technology for advanced treatment [4]. The treated wastewater should meet the standards outlined in the Turkish Water Pollution Control Regulation (WPCR, 2004) shown in Table 1 [13]. The COD removal from the wastewater is between 33% and 88% of the initial COD value in these researches as seen in Table 6 . There are some treatment researches performed with diluted or pretreated forms of this wastewater and have low influent COD concentrations. The removal efficiencies reached > 90% in these studies, but, they cannot be considered for comparison of the treatment methods applied to the original wastewater. The results obtained in the treatment studies of the original wastewater, show that the COD content of the treated effluent is way above the discharge limits specified in the WPCR (2004) (Table 2).

The water gains high diffusivity avoiding mass transfer limitation and strong solvent properties hindering coke formation and poisoning of the catalyst in the critical region. Supercritical water (SCW) provides a homogeneous medium at near-critical and supercritical conditions due to great miscible characteristics with organic and inorganic compounds [14]. A superior side of the hydrothermal gasification processes

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Nomenclature

Ci	Concentration of component 'i' in the gas product (vol.%)
HTG	Hydrothermal gasification
ni	Number of carbon atoms of component 'i' in the gas product
m	Weight of biomass in feed (g)
M	Molar mass of carbon (g mol − 1)
P	Pressure (Pa)
R	Universal gas constant. 8.3143 J mol − 1 K − 1
T	Temperature (K)
Vgas	Volume of gas product under ambient conditions (L)
TOCaq	Total organic carbon content of the aqueous product (g L − 1)
TOCww	Total organic carbon content of raw alkaloid wastewater (g L − 1)
CODww	Chemical oxygen demand raw alkaloid wastewater (g L − 1)
TOCaq	Chemical oxygen demand of the aqueous product (g L − 1)

Table 1
Discharge limits for opium alkaloid production plants (WPCR, 2004).

Parameter	Unit	Composite Sample (24 h)
COD	mg/L	1.500
TKN	mg/L	15
TSS	mg/L	200
pH	–	6–9

Table 2
Opium Alkaloid Wastewater characteristics.

Parameter	Unit	In this study	Aydın 2002 [1]
COD	mg/L	35.000	18300–42500
TOC	mg/L	15.000	7335–14000
pH	–	6.5	4.9–6.3

(HTG) is that there is no necessity for the drying the biomass as opposed to classical gasification. The HTG processes are extensively investigated as the conversion of the organic content of biomass to biofuel products [15,16], oxidation of specific compounds or sludge [17], and the extraction of various waste materials [18,19]. Supercritical water gasification (SCWG) and supercritical water oxidation (SCWO) are both being studied as a waste treatment alternative for industrial wastewaters. In the gasification case the main objective is to produce a high-energy content gaseous product using a hydrolysis mechanism while in the oxidation case it is to destroy the organics using oxidation reaction by means of an oxidant agent. The effluent of SCWG is mainly composed of H_2, CH_4, CO_2, as H_2O, CO_2, and the inorganic salts are principally produced in the SCWO process.

Comprehensive researches have been conducted on the HTG of real biomass samples [20–22], and model compounds of biomass in the last decades [23–26]. Residues of the unused parts of the plants have a moisture content up to 80%, animal wastes, municipal wastes [27], agriculture based industrial wastes [28], and other wastes containing organic carbon such as activated sludge [29] formed in the wastewater treatment used in HTG studies in recent years. Industrial wastewaters have started to take place as feedstock in literature used in hydrothermal gasification studies. There are two studies with black liquor that is formed during cellulose production using a sulfate method [30,31], olive mill wastewater [32], wood gasification process wastewater [33], coking wastewater [34] and with various wastewaters [35–39], etc. A wide range of wastewaters having different compositions and components in crude forms have been used in the HTG processes. The chemical oxygen demand (COD) removal efficiencies varied from 45 to 99% depending on the chemical composition of the wastewater and the operated hydrothermal gasification conditions.

Opium capsules are processed with a water-lime solution and morphine is extracted, then a second stage extraction step is conducted with organic solvents and acid. Wastewater is generated during the recovery operation of the organic solvents and alcohol groups as a by-product. The amount of wastewater produced is reported as 27.5 m^3/h. In this study, the HTG of opium alkaloid wastewater was carried out in a batch autoclave system with a temperature range of 400–600 °C with and without a catalyst during a reaction time of 1 h. The main objective is to determine the optimum reaction conditions and the appropriate catalyst in gasifying the organic part, which causes environmental pollution, with a high product efficiency. The organic carbon in the wastewater reacts with the supercritical water to produce an H_2 and CH_4 rich gas. The chemical oxygen demand (COD) value of the wastewater is the most important indicator for the success of the study and

Table 3
Reaction conditions and experimental results.

Exp Code	T, °C	P, bar	Catalyst	Catalyst Amount, g	Gas product yield (mol gas/kg C in ww)	CGE, %	TOC RE, %	COD RE, %
AF-T4	400	240	–	–	30.5	23.7	41.0	37.1
AF-T5	500	365	–	–	58.2	47.9	74.5	75.8
AF-T6	600	440	–	–	85.2	68.5	85.6	88.7
AF-T4-K1	400	255	K_2CO_3	0.125	39.7	27.8	47.4	40.8
AF-T4-K2	400	260	K_2CO_3	0.250	42.4	28.8	49.8	45.9
AF-T4-K3	400	240	K_2CO_3	0.375	45.2	29.4	55.2	43.7
AF-T4-K4	400	235	K_2CO_3	0.500	48.4	29.9	58.3	47.3
AF-T4-K5	400	230	K_2CO_3	0.625	51.7	28.7	57.0	51.4
AF-T5-K1	500	360	K_2CO_3	0.125	77.7	64.0	84.9	87.3
AF-T5-K2	500	355	K_2CO_3	0.250	82.3	65.2	87.1	88.0
AF-T5-K3	500	350	K_2CO_3	0.375	83.9	65.4	88.3	85.2
AF-T5-K4	500	355	K_2CO_3	0.500	85.9	65.6	89.3	88.9
AF-T5-K5	500	322	K_2CO_3	0.625	87.6	65.3	92.0	89.4
AF-T6-K1	600	425	K_2CO_3	0.125	90.5	72.8	90.7	91.8
AF-T6-K2	600	445	K_2CO_3	0.250	92.6	73.0	91.6	92.4
AF-T6-K3	600	450	K_2CO_3	0.375	97.9	73.6	92.2	95.5
AF-T6-K4	600	455	K_2CO_3	0.500	106.3	74.0	92.8	94.8
AF-T6-K5	600	442	K_2CO_3	0.625	98.9	72.8	96.6	95.1