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Combustion as a Possible Solution to Pyrolytic Wastewater Utilization

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Treatment of hazardous liquid wastes can never be considered as economically beneficial process. It often involves many different treatment steps, especially in the case of highly polluted industrial wastewaters like pyrolytic wastewater (WW) from shale oil production. Currently in Estonia approximately 0.15 million tonnes of this pyrolytic water is generated annually. In the future according to the Estonian National Development Plan for the Use of oil shale this amount is expected to increase by 5 to 6 times (Anon 2016).

The current paper presents the experimental results of wastewater incineration as an alternative approach to water purification. Combustion of this pyrolytic WW was carried out in a pilot-scale 60 kW_{th} circulating fluidized bed (CFB) combustor firing oil shale or with propane. The influence of the flow rate of pyrolytic water (up to 0.36 kg_{water}/kg_{os}) on gaseous emissions was studied.

The results show that incineration of this highly polluted pyrolytic water under studied conditions in CFB combustor fed with oil shale does not pose environmental risks as intensive heat and mass transfer allows almost complete combustion of VOC's. Due to the chemical composition of oil shale ash, SO_2 formed during WW incineration was bound to the oil shale ash resulting zero SO_2 emissions. Only NOx emissions were increased by up to 1.8 times at highest pyrolytic water loading.

1. Introduction

Oil shale is a natural resource with potentially usable large reserves available around the world. Estonia is one of the few countries in the world that is utilizing oil shale in significant amounts for both electricity and shale oil production. It provides approximately 80 % of Estonian electricity needs, making Estonia one of the least energy dependent countries of Europe (IEA, 2013). Oil shale sector is known for wider publicity by its large environmental footprint. However, it is not widely recognized that during the last 25 years there have been significant improvements in reducing the environmental impact of oil shale related industries (both power and shale oil production). This has been achieved mainly by utilizing CFB combustion technology and in case of pulverized combustion the flue gas purification (deNOx and deSOx) technologies. More efficient CFB technology has also helped to reduce the carbon footprint of oil shale power sector which is an important goal for the energy sector in general (Jaromír Klemeš et al., 2017).

Shale oil, which is produced from oil shale by pyrolysis process, is used to fulfil energy requirements, as well as to serve as a source of fine chemicals for the chemical industry. Annual shale oil production in Estonia is about 0.8 Mt. As a waste stream about 0.15 million tonnes of pyrolytic water is obtained (at the rate of approximately 16 t/h) that needs to be treated for safe disposal. Its treatment, however, because of its composition (Kamenev et al., 2003; Maaten et al., 2017), is not a simple task. High concentrations of volatile and recalcitrant organic compounds (VOCs and ROCs), including phenols, polycyclic aromatic hydrocarbons (PAHs), carboxylic acids, ketones, and also inorganic compounds (like ammonium and sulphates) has been measured in this pyrolytic water (Klein et al., 2017). So far the pyrolytic water has either been mixed with municipal wastewater followed by biochemical wastewater purification (Kamenev et al., 2003) or utilized in oil shale pulverized combustion boilers to minimize gaseous SO_2 emissions. Since these old pulverized combustion boilers are inefficient and unreliable, new solutions for utilization of shale oil pyrolytic wastewater is needed.

Shale oil producing companies are interested in combusting this pyrolytic water in the newer CFB boilers in the local oil shale power plant (Eesti Power Plant) situated next to shale oil production facility. Therefore, the focus

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of the current study was to carry out pyrolytic wastewater combustion studies in 60 kW_{th} CFB test facility to determine if wastewater has any major influence on the flue gas composition and gaseous pollutants emissions (NOx, SO_2, VOC). Experiments were performed using different pyrolytic wastewater flow rates and thereby at different furnace temperature conditions. These results will serve as a basis for deciding of moving to industrial tests on the CFB units.

2. Materials and methods

2.1 Test plan

The tests included combustion of pyrolytic wastewater in CFB combustor in propane flame and in CFB combustor fed with oil shale. The flow rate of wastewater was varied while the propane and oil shale input was kept constant as shown in Table 1.

Table 1: Fuel thermal inputs and pyrolytic water flow rates used in tests

Fuel	Fuel thermal input, kW_{th}	Pyrolytic water flow rate, kg/h
Propane	16	0
	16	2.4
	16	6.5
Oil shale	34	0
	34	2
	34	4.6

2.2 Wastewater and oil shale

The pyrolytic wastewater was obtained from the Enefit-140 shale oil plant utilizing solid heat carrier process. A description of this oil shale retorting process is given elsewhere (Golubev, 2003). The wastewater was analysed to determine its main parameters (given in Table 2 and Table 3). The experiments were carried out with Estonian oil shale from Ojamaa underground mine. The results of the ultimate and proximate analysis of oil shale are presented in Table 3 and Table 4, respectively.

Table 2: Characteristics of pyrolytic wastewater

Parameter	Value
Chemical Oxygen Demand, mgO_2/L	26,000
Biochemical Oxygen Demand, mgO_2/L	19,000
Total Organic Carbon, mg/L	8,600
Phenols, mg/L	730
Petrochemicals (C10-C40), mg/L	56
Totals sulphur, mg/L	3050
Total Kjeldhal Nitrogen, mg/L	1900
pH	9

Table 3: Ultimate analysis of pyrolytic wastewater and oil shale

	C, wt. %	H, wt. %	N, wt. %	S, wt. %
Pyrolytic WW	0.95	10.09	0.24	0.30
Oil shale	28.60	2.80	0.07	1.60

Table 4: Proximate analysis of oil shale

LHV, MJ/kg	W^{ar}, wt. %	VM^{ar},wt. %	FC^{ar}, wt. %	A^{ar}, wt. %
9.83	0.20	49.20	1.80	49.00

2.3 CFB test facility

For the studies the 60 kW_{th} CFB combustor in the Department of Energy Technology of Tallinn University of Technology was used. The combustor contains a ceramic riser with a 0.120 m of inner diameter and a length of 4.9 m. The combustor is equipped with fuel/bed material feed silos, water dosing system and gas input. The fuel is fed with a screw conveyer at the height of 0.49 m. The secondary and tertiary air inlet ports are located at the heights of 0.49 m and 0.86 m. Circulated solid particles are separated in refractory lined cyclone and returned to the bed base through return leg at the height of 0.86 m after passing external heat exchanger (EHE). The cyclone flue gas enters to the two-stage cooling system consisting of two shell-and-tube heat exchangers in series. The cooled flue gases are cleaned from remaining fly ash with the fabric filter. The cleaned flue gases leave the system by means of an induced high pressure fan to the stack. The combustion air flow is controlled with mass flow controller as also bottled CO_2 that is used for simulation of recycle flue gas. Mass flow controllers are also used to precisely control primary air and secondary air entering to the system. The primary line as well as wind box shell contains the electrical heaters maintaining the temperature of primary air. The temperatures in the furnace are monitored at six different heights (points A to F in Figure 1). The control of the test facility and data acquisition is achieved by implementing National Instrument CompactDAQ operated by Labview system.

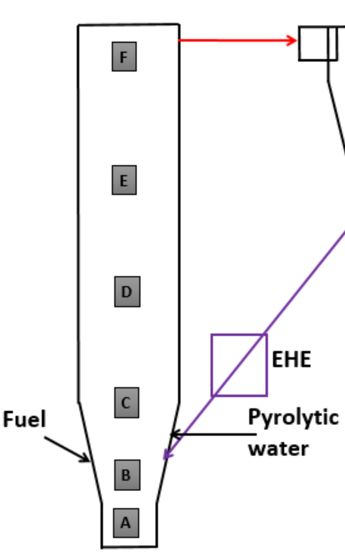

Figure 1: Temperature measurement points (marked as A, B, C, D, E, and F) in the furnace

2.4 Flue gas analysis

Flue gas composition was measured after the fan in the vertical stack with an inner diameter of 0.20 m. Flue gas analyses were performed using Gasmet DX4000 FTIR analyzer controlled through Calcmet software. Total organic carbon content in flue gas was monitored by Siemens Fidamat 6 flame ionization detector total organic carbon analyser.

3. Results and Discussion

As shown in Table 1, the tests were carried out using propane and oil shale as fuels. Combustion of pyrolytic wastewater in propane flame was performed as a baseline test. In that case no bed material was used to mimic the WW combustion in gas flame. The tests with oil shale as a fuel with solids circulation were started after the desired furnace temperature and the proper ash circulation was reached.

3.1 Combustion with propane

The temperatures in active zone (lower part of furnace) were maintained between 800 to 1000 °C, and in upper part of furnace between 300 to 500 °C (Figure 2) indicating large temperature gradient in the furnace. The temperatures were lower during combustion of pyrolytic water. Concentration of gaseous pollutants (NOx, SO_2 and VOC) was continuously measured. The measured values in ppm were converted to mg/Nm^3 in dry gases at 6 % oxygen content using Eq(1) although usually in accordance with the Estonian legislation the emissions from combustion of gaseous fuels are presented at 3 % oxygen content. In this equation MW is molecular weight of specific compound and $O_{2,dry}$ is the oxygen concentration in dry flue gases expressed as volume percent.

$$C_{dry}\left[\frac{mg}{Nm^3}\right] = C_{dry}[ppm]\cdot\frac{MW}{22.4}\cdot\frac{20.9-6}{20.9-O_{2,dry}} \tag{1}$$

The changes in the concentrations of measured gaseous pollutants are presented in Figure 3. It is clear that the pyrolytic water has strong influence on the gaseous emissions. On one hand, water due to its high enthalpy of vaporization when pumped to the combustion zone causes temperature reduction which has positive effect on NOx emissions as ionization of nitrogen is reduced. On the other hand, SO_2 and VOC emissions are greatly increased due to relatively high sulphur content (approximately 3,050 mg/L) in pyrolytic water and incomplete combustion of organics at lowered temperatures and under applied conditions. The average NOx, SO_2 and VOC concentrations during different test conditions are summarised in Table 5.

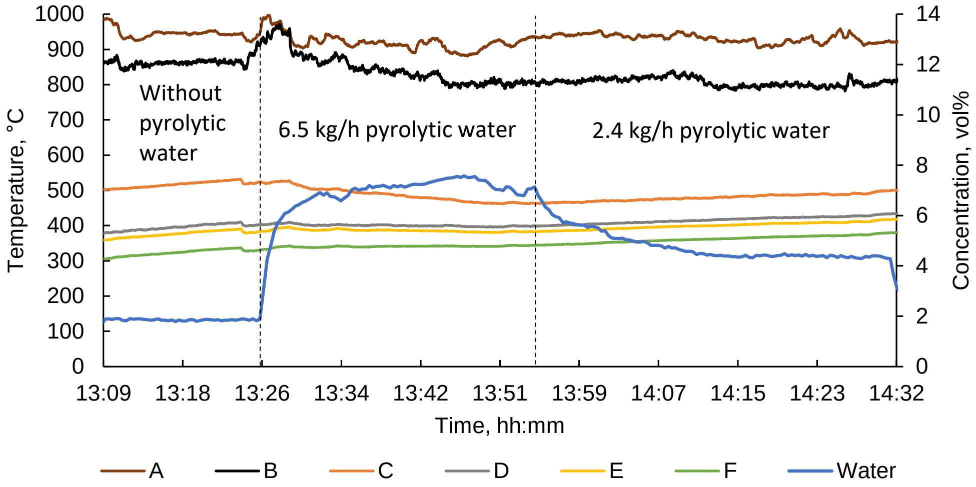

Figure 2: Changes in temperatures in the measurement points in the furnace and water vapour concentration (indicating wastewater injection) during pyrolytic water combustion in propane flame

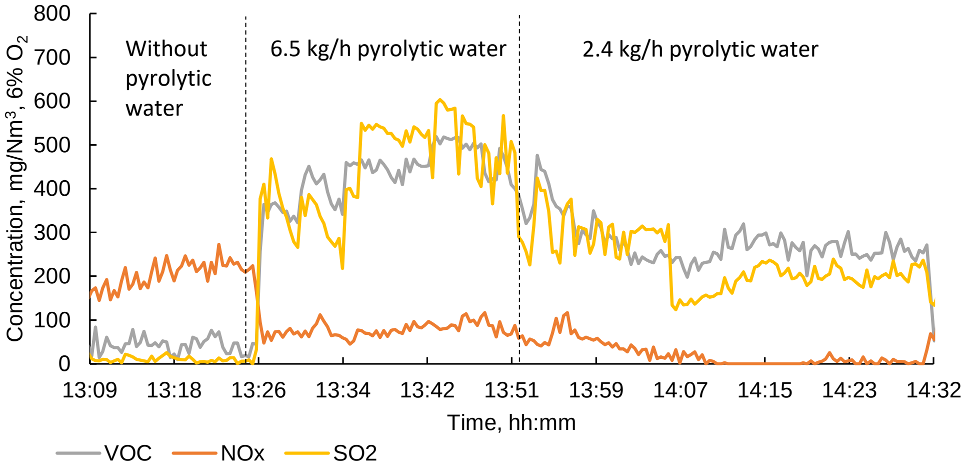

Figure 3: Changes in concentrations of gaseous pollutants during pyrolytic water combustion in propane flame

3.2 Combustion with oil shale

Combustion of pyrolytic water with oil shale was carried out at two pyrolytic water flow rates in oxidizing environment. Pyrolytic water flow rates are given in Table 1 and Figure 4. The highest flow rate of 4.6 kg/h corresponds to 0.36 kg_{water}/kg_{os}. Compared to combustion with propane, the temperature differences between the upper and bottom part of the furnace was much smaller as temperatures varied in between 600 and 900 °C (Figure 4).

The results of the evolution of the concentrations of measured gaseous pollutants during different test conditions are presented in Figure 5. During oil shale combustion (without pyrolytic water) in CFB measured average NOx, SO_2 and VOC concentrations in dry gases at 6 % O_2 were 265, 64, and 30 mg/Nm^3, respectively. NOx in flue gases originates mainly from organic matter. SO_2 originates from the combustion of oil shale organic matter as it contains remarkable amount of sulphur. However, due to the large amount of free CaO in the oil shale ash (formed during decomposition $CaCO_3$), large amount of this SO_2 is bound to the CaO forming $CaSO_4$ anhydrite. This is achieved because of relatively long contact time between CaO and flue gases in CFB and appropriate temperature range (700 - 800°C). Because of these reasons also SO_2 emissions from large industrial power plants utilising oil shale in CFB combustion boilers are similarly close to zero, whereas SO_2 emissions from pulverized oil shale combustion boilers (higher temperature in the furnace 1,300-1,400°C) without flue gas desulphurization would be in the range of 2,500 mg/Nm^3.

Table 5: Average concentrations of gaseous pollutants in dry flue gases

Fuel	Pyrolytic water flow rate, kg/h	NOx, mg/Nm^3, 6% O_2	SO_2, mg/Nm^3, 6% O_2	VOC, mg/Nm^3, 6% O_2
Propane	0	203	11	42
	2.4	77	192	229
	6.5	35	426	427
Oil Shale	0	265	64	30
	2	381	1	18
	4.6	475	0	17

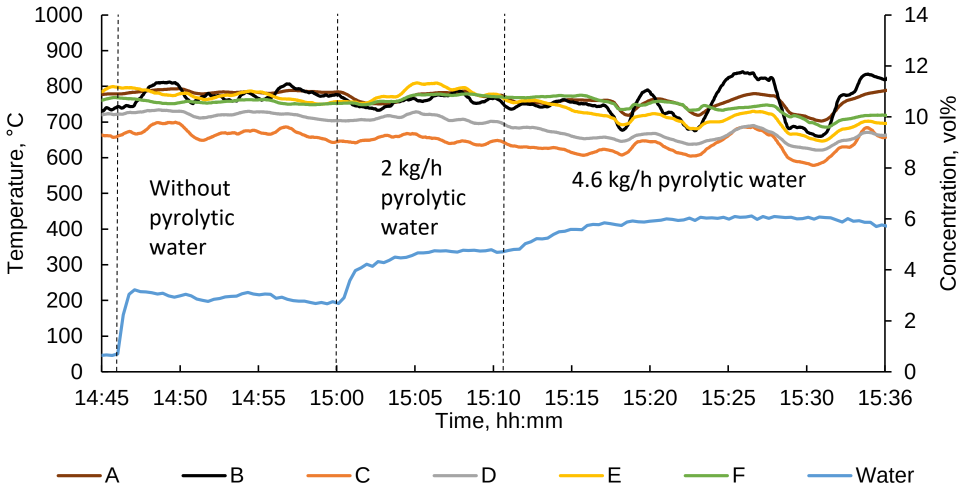

Figure 4: Changes in temperatures in the measurement points in the furnace and water vapour concentration (indicating wastewater injection) during pyrolytic water combustion with oil shale

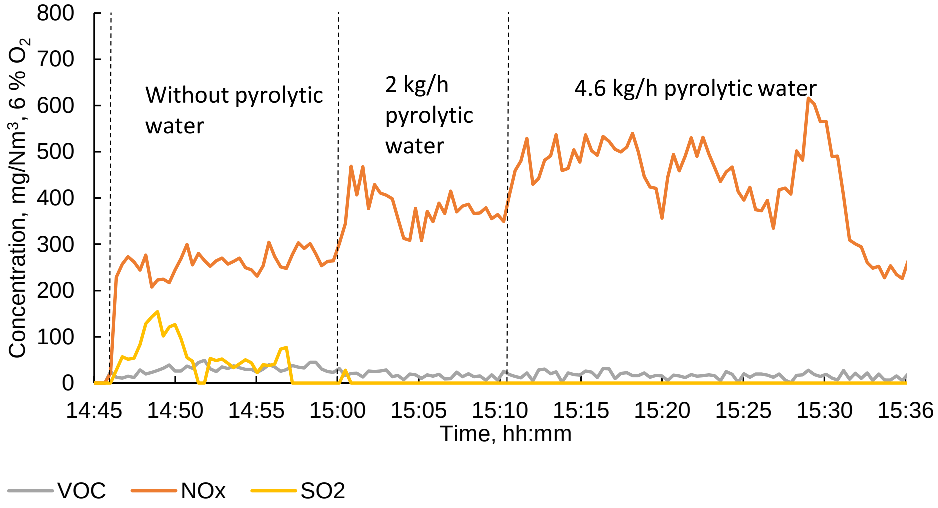

Figure 5: Changes in concentrations of gaseous pollutants during pyrolytic water combustion with oil shale

Measured VOC concentrations show minor changes after addition of pyrolytic water. This indicates that the combustion process is complete.

Compared to the combustion of pyrolytic water in propane flame, there are significant differences when pyrolytic water is added. As the humidity is increased, complete SO_2 removal is achieved because CaO activity toward SO_2 is increased. As opposed to the SO_2 concentration, NOx concentration is increased. After adding pyrolytic water to the combustion process, the temperatures in the furnace are slightly lowered, reducing the amount of air nitrogen oxidation. Therefore, this increase in NOx concentrations comes from the oxidation of nitrogen compounds in pyrolytic water (total nitrogen in pyrolytic water was 0.24 wt. %). Compared to the sulphur the formed NOx can’t be bound to the solid particles under furnace conditions, meaning other measures have to be taken for the reduction of NOx emissions.

4. Conclusions

Pyrolytic water formed in shale oil production process was combusted in the pilot scale 60 kW_{th} CFB combustor. For comparison, pyrolytic water was also added to the propane flame in the same combustor. The results showed that the chemical composition of circulating oil shale ash and increased humidity, as a result of pyrolytic water addition, resulted in zero SO_2 emissions, while adding pyrolytic water to a propane flame resulted in SO_2 concentrations, which increased from trace amounts to of 426 mg/Nm^3 in dry gases at 6 % O2. Also, according to the test results, VOC emissions is not an issue due to high heat and mass transfer in CFB furnace fed with oil shale.

There is a more than 5,000 fold difference in thermal output between the test facility and an industrial CFB boiler. This large difference makes exact modelling, based on the presented results, impossible. However, as the temperature and pressure-dependent processes and mechanisms in the test facility and in industrial boiler are similar, it may be concluded that the addition of pyrolytic water to oil shale combustion process in CFB combustor doesn’t increased the environmental impact of the process as long as NOx emission are controlled using secondary measures. Nevertheless, utilization of WW in CFB will decrease the combustion process fuel efficiency.

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