

# HYDROTHERMAL GASIFICATION OF WET SLUDGE PRODUCED FROM BIOLOGICAL TREATMENT OF TEXTILE AND LEATHER INDUSTRIAL WASTEWATER

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REFERENCE NO	ABSTRACT
GASF-01	Hydrothermal gasification of wet sludge was investigated in order to produce fuel gas with high calorific value. The gasification experiments were performed between 450 and 550°C, KOH and dolomite were used as additives to increase gasification efficiency. Hydrogen and methane compositions in the gas was between 42 to 57 vol%, while CO <sub>2</sub> was between 30 and 40 vol%. The effect of time on the gas product distribution was studied at 0, 30 and 60 minutes reaction times. The calorific value of the sludge was determined as around 16 MJ/kg, while after gasification the calorific value of the gas fuel produced was found to be 24.7 MJ/kg (24.3 MJ/Nm <sup>3</sup> ) after 30 min. reaction time in the presence of KOH. Around 70 wt. % of the sludge was converted into either gas or liquid with hydrothermal treatment.

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*Keywords:*  
Activated Sludge, Hydrothermal Gasification, Supercritical Water, Hydrogen,

## 1. INTRODUCTION

Establishing environmentally friendly processes to produce energy is vital as concerns over global warming increasing recently. Especially utilizing a process to convert waste into clean energy has gaining much attention. One of the promising processes is hydrothermal gasification of wastes and/or biomass to produce gas fuel. Among the many type of wastes and biomass, activated sludge has great potential as it is produced in large amounts. Activated sludge is a by-product of biological treatment of wastewater and it has high water content (around 70-95 wt %) [1, 2]. Depending on the type of the wastewater processed, it may contain hazardous and toxic compounds.

Current conventional treatment and disposal methods of sludge contain landfilling and incineration. However, these methods create risk to the environment as landfilling would result in contamination and incineration yields to increase in CO<sub>2</sub> and other greenhouse gas emissions. Also for incineration, drying the sludge is another drawback which increases the cost of the process. Gasification of wet sludge via hydrothermal method is

considered as a promising solution as no drying process is necessary [3].

As a thermochemical method, in hydrothermal processing water reacts with biomass and/or organic wastes to yield smaller chain hydrocarbons due to phenomenal changes in its properties at critical conditions (374°C, 22.1 MPa). Water becomes an ideal reactant, solvent and catalyst for hydrothermal treatment of hydrocarbons since its properties such as reactivity, ionic product, dipole moment and density undergo unique changes [4].

Recent studies on hydrothermal processing of activated sludge produced from biological treatment of sewage have shown promising results [5, 6]. Xu et. al. reported 100% carbon gasification efficiency after hydrothermal gasification of sewage sludge mixed with corn starch paste at 650°C and 28 MPa in a continuous flow reactor packed with coconut shell activated carbon as catalyst. The liquid product was clean water and the gas product was hydrogen rich fuel gas containing 42 vol% H<sub>2</sub> [7]. The carbon gasification efficiency was decreased with the decreasing temperature, according to the research conducted by Schmieder et. al. They used

batch reactor for the gasification of sewage sludge at 450 °C and after 2 hours of residence time, 55% carbon gasification efficiency was achieved. The addition of K<sub>2</sub>CO<sub>3</sub> enhanced the gasification efficiency up to 85% by promoting the water-gas shift reaction [8]. Gong et. al. investigated the hydrothermal gasification of ten different type of sewage sludge. The organic matter in the samples varied from 29 wt% to 73 wt% and pH from 3.7 to 8.1. The gasification experiments were performed at 400°C and 23 MPa, and it was concluded that the hydrogen yield in the gas products depended on the water content, pH and the inorganic content of the sample [2]. Also effects of Ni as catalyst together with NaOH addition was tested and results showed that the hydrogen yield increased twelve times comparing to that of without catalyst [9]. Acelas et. al. used hydrothermal process to recover phosphorus from sewage sludge in the solid residue. The effect of reaction temperature and time was investigated in a batch autoclave reactor. 95 wt% of phosphorus was recovered from the solid residue by acid leaching, after 60 min reaction at 600°C [3]. The catalytic effect of Raney nickel was tested at 380°C and 15 min reaction time. It was found that up to 69% carbon gasification efficiency was reached after hydrothermal treatment of activated sludge. In the absence of catalyst, the efficiency was 10%, concluding that Raney nickel catalyst enhanced the gas yield. Also hydrogen yield increased from 16 vol% to 46 vol% [1].

Although there are numerous reports on hydrothermal gasification of sewage sludge in the literature, there is not much studies conducted on industrial sludge. In the present work, hydrothermal gasification of activated sludge produced from the biological treatment of textile and leather industrial wastewater was investigated. The effects of temperature, reaction time and the additives of KOH and dolomite were tested in order to determine the optimum conditions for the production of fuel gas having high calorific value.

## 2. EXPERIMENTAL

### 2.1 Samples

The sludge sample was collected from Leather and Textile Organized Industry – Wastewater Treatment Plant, Uşak. The sludge contains around 70 wt% moisture, 21.09 wt% organic matter and 9.35 wt% inorganics. The pH was determined as 7.24 and the dissolved oxygen content was 1.50 mg/l. The higher heating value of the dried sludge was found to be 16 MJ/kg (ASTM D 5865) [10]. The XRD analysis were carried out using PANalytical X'Pert Pro MPD model XRD with Cu X-light ( $\lambda=1.5404 \text{ \AA}$ ) and ICP/MS analysis were conducted according to EPA 6020A method and the results are summarized in Table 1 & 2 respectively [11].

Table 1 XRD analysis of the sludge

Compound	Inorganic phase [wt.%]	Sludge [wt.%]
Chlorapatite [Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl]	31.1	2.9
Feldspar (KAlSi <sub>3</sub> O <sub>8</sub> – NaAlSi <sub>3</sub> O <sub>8</sub> – CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> )	28.0	2.6
Quartz [SiO <sub>2</sub> ]	14.5	1.4
Illite [(K,H <sub>3</sub> O)Al <sub>2</sub> Si <sub>3</sub> Al O <sub>10</sub> (OH) <sub>2</sub> ]	13.6	1.3
Chromatite [Ca(CrO <sub>4</sub> )]	5.1	0.5
Enstatite [MgFeSi <sub>2</sub> O <sub>6</sub> ]	4.7	0.4

Dolomite [CaMg(CO<sub>3</sub>)<sub>2</sub>] was used as received, mined in Eskişehir, Turkey. KOH was purchased from Sigma-Aldrich.

Table 2 ICP/MS analysis of the sludge

Metal detected	Composition [wt%]
Na	0.95
Mg	0.66
Al	3.26
K	0.27
Ca	0.58
Cr	1.38
Mn	0.015
Fe	0.52
Zn	0.012
Sr	0.019
Ba	0.016

## 2.2 Reactor System

The gasification experiments were conducted in a stainless-steel batch reactor having 50 ml volume. The maximum pressure and temperature that the reactor could handle was 50 MPa and 650°C. An electrical furnace was used to supply heat to the reactor and the temperature was controlled with the help of a PID controller. The details of the batch reactor system is explained in elsewhere [12].

## 2.3 Procedure and Analysis of Reaction Products

The wet activated sludge sample was sundried for 15 days. During drying, the sludge sample agglomerated to form some rock-shaped rough particles. Therefore, the samples underwent a size reduction process to produce 1.7<x<2.36 mm size particles. 1 g of dry sludge was fed to the reactor along with 10 ml of water for each run. When additives were used, 0.1 g (10 wt%) of KOH or dolomite was added to the sludge. The reactor was sealed and purged with N<sub>2</sub>, and then heated with a heating rate of 12°C/min to the designated temperature. The reaction time was defined as the time after reaching to the designated temperature.

After the reaction completed, the reactor and its contents cooled with the help of a fan. The volume of the gas was measured with a gasometer and the gas sample was collected with the help of a gas-tight syringe. The remaining products in the reactor was washed with de-ionized water, then filtered to separate the solid residue. The liquid was analysed for the organic content via TOC device. The solid residue was dried at 105°C and its weight was recorded after the moisture was removed.

Analysis of gas products were performed via HP 7890A gas chromatography, which is equipped with detectors; TCD, FID, TCD connected in series. The liquid products were analysed to measure organic carbon content by using a TOC analyser (Shimadzu TOC-V<sub>CPH</sub>, JAPAN). Thermogravimetric analyses were carried out using a NETZSCH STA 449 F3 thermal analyser.

The gross calorific values of the product gas mixtures after hydrothermal gasification of sludge were calculated based on equation (1).

$$HHV = \sum_{i=1}^n X_i \cdot HHV_i \quad (1)$$

Where  $i, \dots, n$  = each combustible gas in the product mixture and  $X_i$  denotes for mass fraction of each gas in the product mixture.  $HHV_i$  is the higher heating value of each gas [MJ/kg].

## 3. RESULTS

### 3.1 Thermal Decomposition of Activated Sludge

The thermal degradation behaviour of the dried sludge sample was investigated to determine the thermal stability and the fraction of the volatile components. Around 40 mg of sample was placed into alumina crucible and heated with a rate of 10°C/min under N<sub>2</sub> atmosphere until reaching 900°C.

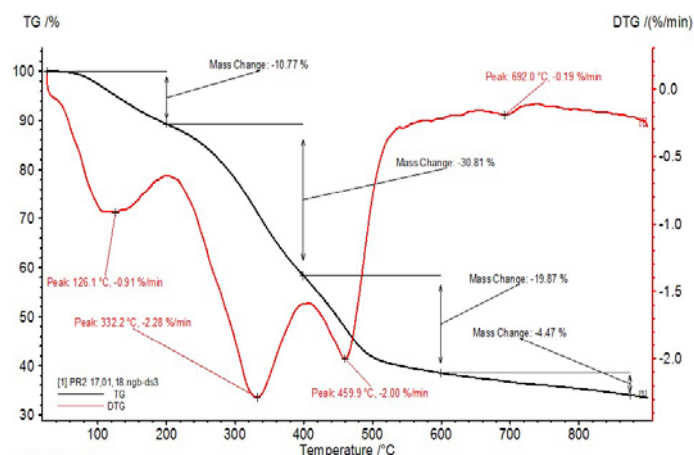


Fig. 1. TGA and DTG curves of sludge sample

The resulting thermograph is shown in Figure 1. The thermal decomposition of the sludge is continuous which is the case in the thermal degradation of sewage sludge as well [13]. The first decomposition part was between 80 and 200°C, mostly due to moisture content of the sludge. After reaching 200°C, the degradation of hydrocarbons started and created two major peaks in the DTG curve, which is due to the complex organic structure of the sludge. The mass loss was recorded to be around 50 % between the temperatures 200 and 600°C whereas all the volatile

hydrocarbons degraded. The final mass loss starting at 600°C represents the decomposition of the inorganic content of the sludge sample. The total weight loss was determined to be 65% during the thermal decomposition of the sludge.

The ash content of the sludge was determined as 27 wt.% by oxidizing around 30 mg of sample at 900°C.

### 3.2 Hydrothermal Gasification of Activated Sludge

Activated wet sludge initially containing 70 wt% water and 21.1 wt % organic matters, produced from biological treatment of textile and leather industrial wastewater was processed by means of hydrothermal treatment to produce clean gas fuel. The dried sludge fed to the reactor with a concentration of 10 wt%. The effects of reaction time, temperature and the additives KOH and dolomite was investigated.

In all experiments, around 70 wt% of the sludge was converted to either gas or liquid. The TOC analyses of the liquid products suggested that most of the organics in the feed degraded to yield gas products as shown in Table 3.

Table 3. Weight of solid residues and TOC of liquid products after hydrothermal gasification of sludge

T [°C]	Additive	Time [min]	TOC [g]	Weight of Solid* [g]
400	-	30	0.08	0.34
450	-	30	0.07	0.28
500	-	30	0.05	0.25
550	-	30	0.02	0.25
500	-	0	0.07	0.27
500	KOH	0	0.06	0.27
500	Dolomite	0	0.06	0.37
500	KOH	30	0.04	0.27
500	Dolomite	30	0.03	0.32
500	-	60	0.04	0.25
500	KOH	60	0.05	0.27
500	Dolomite	60	0.05	0.34

\*The dried solid remained after the filtration

#### 3.2.1 Effect of Temperature

The hydrothermal gasification of activated sludge was carried out at temperatures 400, 450, 500, 550°C and corresponding pressures 19, 23, 27 and 30 MPa respectively. The Figures 2 and 3 represent the moles of gas produced per kg sludge processed and gas products distribution in volume percentage. C<sub>2-4</sub> denotes for the light hydrocarbons, ethylene (C<sub>2</sub>H<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), propane (C<sub>3</sub>H<sub>8</sub>) and butane (C<sub>4</sub>H<sub>10</sub>).

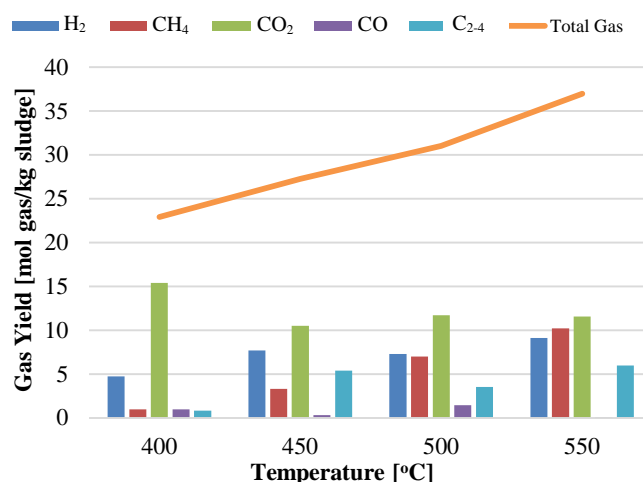


Fig 2. Gas Yield after hydrothermal gasification of the sludge at different temperatures

The state of the reaction medium was sub- and near-critical at temperatures 400 and 450°C, while at 500 and 550°C supercritical water medium was achieved. The increase in the temperature effected the gasification yield as it was risen up from 23 to 38 mol/kg sludge when the temperature increased from 400 to 550°C. This was expected, as temperature is one of the most influential variable during the hydrothermal gasification of biomass and organic wastes [8, 14].

While at subcritical conditions hydrogen yield was 4.7 mol/kg, it was increased to 9.1 mol/kg when the supercritical water conditions were met. It is well known that above critical point, free-radical reactions are more favourable yielding more hydrogen to be produced [15].

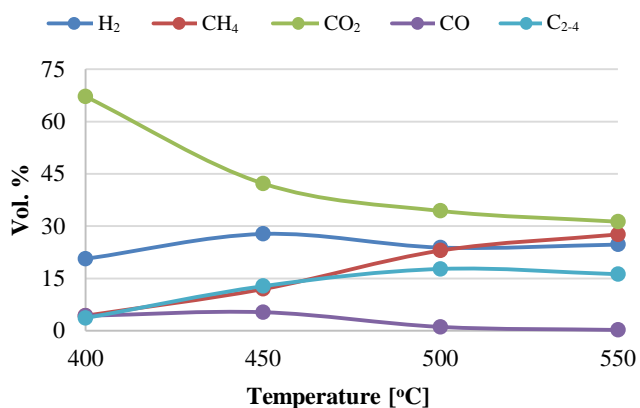
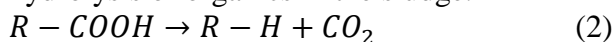
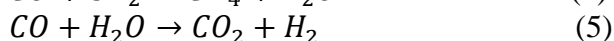
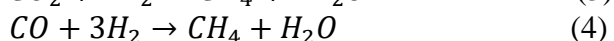
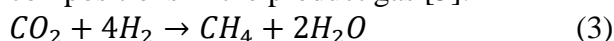


Fig. 3. Product gas distribution after hydrothermal gasification of the sludge at different temperatures

The product gas distribution was also changed with the temperature. At 400°C, carbon dioxide was the main component in the gas with a composition around 70 vol.%, however it decreased to 31 vol.% when the temperature reached 550°C. The high CO<sub>2</sub> composition could be due to decarboxylation (2) of the intermediates produced by hydrolysis of organics in the sludge.

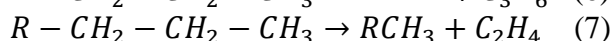
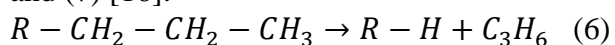


As the temperature increased, the methanation of CO<sub>2</sub> and CO (3-4), and water-gas shift (5) reactions became dominant, causing an increase in hydrogen and methane compositions in the product gas [5].



The dramatic change in methane composition from 4.3 to 27.6 vol% at temperatures 400 and 550°C also suggested that the selectivity of methanation reactions were higher than water-gas shift reaction in supercritical water.

At high temperatures, the composition of C<sub>2-4</sub> hydrocarbons were around 15 vol% in the product gas mixture. This might be due to the cracking of longer chain hydrocarbons or liquid products at these temperatures. The suggested reaction is given in equations (6) and (7) [16].



There is not enough data available in the studies with sewage sludge, while in the

reports on hydrothermal gasification of biomass the composition of C<sub>2-4</sub> hydrocarbons is around 5 vol% in general. It can be said that the production of high amount of C<sub>2-4</sub> might be due to complex nature of the activated sludge containing long chain hydrocarbons [1, 14, 17].

### 3.2.2 Effect of Reaction Time

The effect of reaction time on hydrothermal gasification of sludge was investigated at 500°C. In the absence of additives, the increasing time slightly increased the total gas produced as shown in Figure 4 and 5.

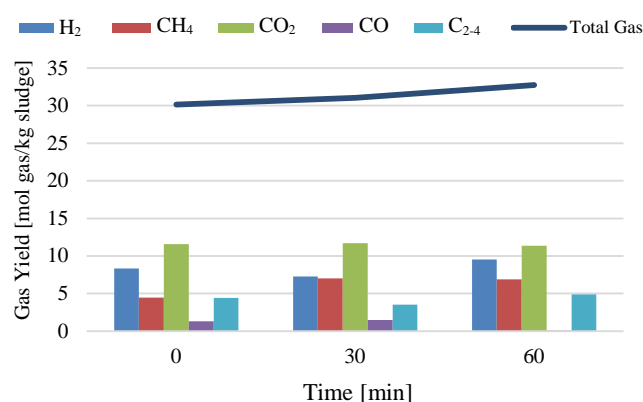


Fig. 4. The Effect of Reaction time on gas yield after hydrothermal gasification of sludge at 500°C without any additives

Methane yield was increased with the increasing reaction time as it was 4.5 mol/kg at 0 min while it went up to 7 after 60 min reaction time in hydrothermal medium at 500°C. Carbon dioxide yield remained same when the reaction time changed.

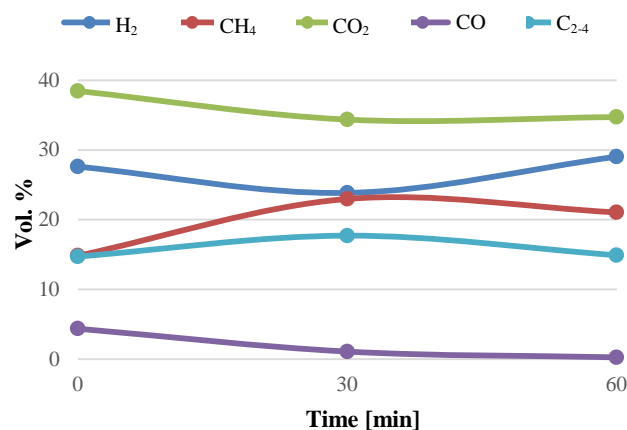


Fig. 5. Product gas distribution after hydrothermal gasification of the sludge at different reaction times

The gas composition was also changed with the changing time during hydrothermal gasification of the sludge. Carbon monoxide composition was 4.4 vol.% at 0 minute reaction time, while it decreased to a value of 0.3 vol% after 60 min reaction time. This could be the result of the water gas shift reaction (equation 5) since hydrogen composition was increased from 24 to 29 vol% after 60 min reaction time. The increasing H<sub>2</sub> and CH<sub>4</sub> yields with the increasing time also suggested that the methanation reaction (eq. 3) became dominant as there was no major change in CO<sub>2</sub> composition with the increasing time.

### 3.2.3 Effect of Additives

KOH as an alkali and dolomite as a natural mineral catalyst were used as additives in order to enhance the hydrothermal gasification of the sludge. Figure 6 and 7 represent the moles of gas produced per kg sludge processed and gas products distribution in volume percentage. At 500°C and 30 min reaction time, 31 mmol of gas was produced from hydrothermal gasification of 1 g dry sludge in the absence of any additives. While the addition of dolomite slightly decreased this to 29.7, it was increased to 32.7 mol/kg with the addition of KOH.

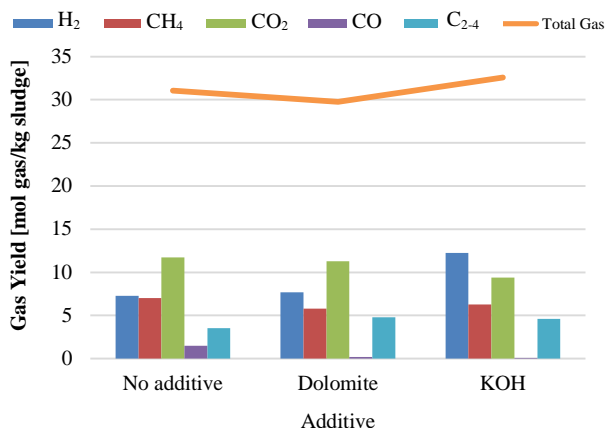
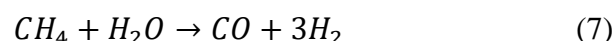


Fig. 6. Gas Yield after hydrothermal gasification of sludge at 500°C and 30 min reaction time

The major change was observed in the H<sub>2</sub> yield, as it was increased from 7.3 mol/kg to 12.2 mol/kg when KOH was introduced to the reaction medium. The water-gas shift reaction is promoted when KOH present in the

hydrothermal gasification of biomass [18]. This increases the yields of both H<sub>2</sub> and CO<sub>2</sub>, however during the hydrothermal gasification of the sludge, CO<sub>2</sub> yield decreased as well.

Although CO<sub>2</sub> could be consumed via methanation reaction to produce methane, there was also no significant change in the CH<sub>4</sub> yield. This situation might be well explained by enhanced steam-methane reforming reaction (eq. 7) since methane and water react to form hydrogen and carbon monoxide.



Therefore, it could be summarized as the produced CO<sub>2</sub> from water-gas shift reaction was consumed through methanation reaction, while the methane was also consumed with steam-methane reforming reaction resulting in a decrease in carbon dioxide yield.

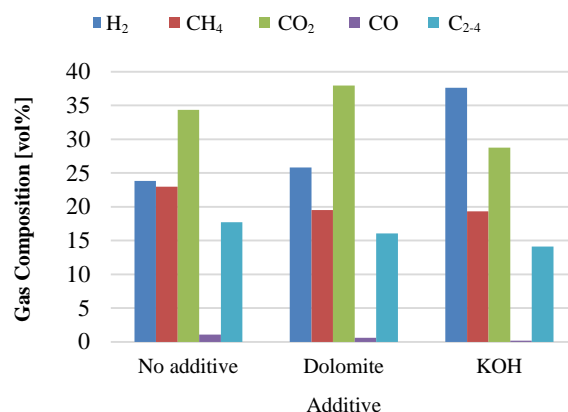


Fig. 7 Product gas distribution after hydrothermal gasification of sludge at 500°C and 30 min reaction time

The presence of dolomite [CaMg(CO<sub>3</sub>)<sub>2</sub>] did not affected the major gas compositions. Probably since there have already been Ca and Mg (0.58 and 0.66 wt%) in the sludge sample due to its nature, dolomite addition did not create a difference in the gas product distribution. Only carbon monoxide yield was decreased, while C<sub>2-4</sub> hydrocarbon gases yield was increased slightly comparing when there was no additive present.

Figure 8 shows the calculated calorific values of the product gases. The dried sludge had a calorific value of 16 MJ/kg and after hydrothermal gasification, clean fuel gas with higher calorific values which were in a range

of 18.0 - 24.7 MJ/kg was obtained. When the sludge underwent hydrothermal gasification with the addition of KOH at 500°C and 30 min reaction time, the product gas with a heating value of 24.7 MJ/kg (24.3 MJ/Nm<sup>3</sup>) was produced.

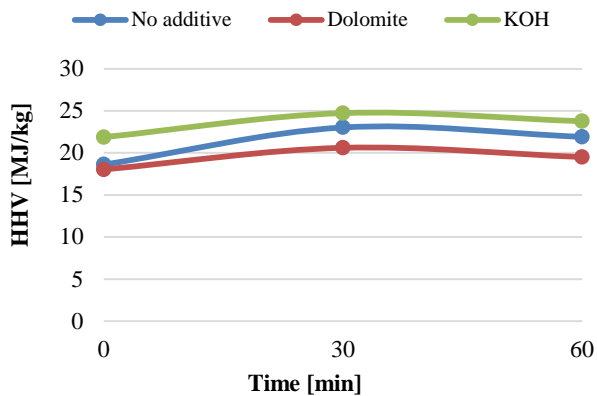


Fig. 8. The calorific values of the product gases obtained after hydrothermal gasification of the sludge

In a previous work, refused derive fuel as a representative of municipal solid waste was processed by means of hydrothermal treatment in the presence of Ru catalyst and obtained fuel gas had a calorific value in the range of 18-22.5 MJ/Nm<sup>3</sup> [19]. In this study, even in the absence of any additives, sludge was converted successfully to fuel gas having a calorific value of 22 MJ/Nm<sup>3</sup> proving that hydrothermal method could be utilized in order to produce energy from wet sludge.

#### 4. CONCLUSION

Activated sludge produced during biological treatment of textile and leather industrial wastewater was processed by hydrothermal treatment to obtain clean fuel gas. The gas yield was increased with the increasing temperature. At supercritical conditions, high yields of hydrogen was obtained and this even improved with the addition of KOH as an additive by promoting water-gas shift reactions. The addition of dolomite did not affect the gas yield and composition.

Around 70 wt.% of the sludge was converted to either gas or liquid. Hydrogen and methane compositions in the product gas were in the range of 42 to 57 vol% while CO<sub>2</sub> was between 30 and 40 vol% at supercritical

conditions. The calorific value of the sludge on a dry basis was determined around 16 MJ/kg, while after gasification clean fuel gas produced with the calorific value of 24.7 MJ/kg (24.3 MJ/Nm<sup>3</sup>) after 30 min. reaction time in the presence of KOH.

These results suggest that the hydrothermal gasification can be utilized to convert wet activated sludge into clean fuel gas, without any drying process.

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