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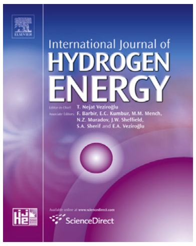

Gasification of biomass and treatment sludge in a fixed bed gasifier

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ABSTRACT

This study aims to compare synthetic gas (syngas) production efficiencies of a specific forest residue (chamaecyparis lawsoniana) and treatment sludge from a textile industry. The experiments were carried out in a lab-scale fixed bed steel reactor with cyclone separator. Gasification process was assisted by pre-pyrolysis of the samples at 300 °C in an inert media via N_2 gas. Internal temperature of the reactor during gasification was 750 °C. Dried air was used as an oxidizing agent with the varying flow rates of 0.05, 0.1 and 0.2 L min^{-1} in order to determine optimum flow rate. The highest syngas calorific values was calculated around 2500–2677 kcal m^{-3} for chamaecyparis and 2500–2680 kcal m^{-3} for the treatment sludge when the flow rate was 0.05 L min^{-1}. Solid residues and liquid products were weighed after each experiment. 55 wt% of chamaecyparis and 30 wt% of treatment sludge were converted in to medium calorific syngas.

Introduction

Integrated waste management can be defined as selecting and applying the required suitable method, technology and management programs towards a specific waste management. Today, integrated waste management composes of waste prevention, reduction, reuse/recycle/recovery and disposal steps. According to the EU Environment Directives, Waste Management has also been determined as a sub-heading in order to prevent environmental risks and to provide a sustainable environment management. Thermochemical methods are among the alternatives having a wide application area within the scope of waste management [1–3]. Organic substances or waste forms containing organic content can be reintegrated to economy both with industrial raw material and energy recycling by utilizing them through thermochemical methods such as pyrolysis and gasification which are the alternatives for burning.

Although there are lots of studies regarding not only biomass but also mostly domestic waste water treatment sludge in the literature, studies regarding industrial treatment sludge are more limited. Systems designed to benefit from biomass offer quite reliable results. Fixed bed gasifiers are the most widely used technology in small-scale applications [4,5]. They are not complex, and also they offer syngas efficiency in satisfactory levels in order to obtain energy from biomass. It is possible to produce syngas that is rich in CO and H_2 and which contains a small amount of CH_4. Drying, pyrolysis, oxidation, gasification processes are basic steps undergoing during decomposition of organic matter in a gasifier. There are also some review studies explaining chemical processes in a gasifier in detail [6]. The drying process occurs at around 100 °C. Steam is involved with water–gas reaction due to high temperature. When the temperature reaches up to

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200–300 °C, pyrolysis starts and volatiles are released as char is produced [7]. Volatiles and char reacts with oxygen in the air and carbon monoxide and carbon dioxide are produced by combustion process. Since combustion and/or partial combustion (R1–R4) are exothermic reactions, it supplies heat for gasification reactions in reduction zone. At this point, parameters such as character of the fuel, reactor size, operation temperature, enthalpy need, reactivity and waiting period are of a great significance in order for the system to reach thermodynamic balance [8]. Within the “reduction zone” where CO and H_2 production forms a basis, system produces syngas, the energy value of which is high while Boudouard (R5) and Water–gas (R6) reactions are proceeding. Proceeding reactions for these processes are given below [9,10].

$$C + O_2 \rightarrow CO_2 \quad \Delta H = -394\ kj\ mol^{-1} \tag{R1}$$

$$C + \frac{1}{2}O_2 \rightarrow CO \quad \Delta H = -111.1\ kj\ mol^{-1} \tag{R2}$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \Delta H = -242\ kj\ mol^{-1} \tag{R3}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \quad \Delta H = -283\ kj\ mol^{-1} \tag{R4}$$

$$C + CO_2 \rightarrow 2CO \quad \Delta H = +172\ kj\ mol^{-1} \tag{R5}$$

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H = +131\ kj\ mol^{-1} \tag{R6}$$

Rollinson and Karmakar (2015) [9] conducted a study to understand the behavior of the fuel fed by gasification of 7 different biomass samples (Eucalyptus, Silver Birch, Corsican Pine, European Larch, Coconut Coir, Jute, and Sugar Bagasse) that had been collected from Europe and Asia. At the end of the trials performed in slow heating speeds and at 800–950 °C isothermal temperatures, similar behaviors were determined for all samples between 900 and 950 °C interval and it was specified that these temperatures might be the optimum temperatures for the gasification design. Process temperature, equivalence ratio (ER) and biomass feeding rate in permanent systems are the main parameters having impact on system performance and efficiency [11–14]. In oxidation and reduction areas, it is observed that high and uniform temperature values lead to a rise in “tar cracking” efficiency. The rise of ER ($0.18 < ER < 0.37$) also increases reactor temperature along with the heat raising as a result of combustion reactions. Similarly, due to the fact that increase in feeding rate of feedstock also increases biomass consumption speed, it leads to rise in reactor temperature as well. However, it is stated that extreme feeding rate affects CO and H_2 formation adversely [12]. In studies in which performance parameters of thermochemical processes performed in fixed bed systems are examined, biomass type and the effect of their character on process have been explored [15–18]. Amounts of H_2, CO and CH_4 with the content of syngas, which is produced with similar processes, directly affect the calorific value of the produced syngas. Plis and Wilk (2011) [17] assessed biomass gasification both theoretically and experimentally. Although both samples used in experiments were similar in terms of carbon content, it was reported that wooden pellets (C 48 wt.%) provided much more efficiency for gasification compared to oats husk pellets (C 44 wt.%) and the increase of moisture within the fuel led to fall of combustive content within syngas. Luo et al. (2009) [19] performed biomass gasification in a lab-scale fixed bed reactor in order to evaluate the effects of temperature and gasifying agent to biomass ratio on the gasification performance. They studied at temperatures from 600 up to 900 °C and reported that increasing temperature from 600 to 900 °C, H_2 content increased from 25.2% to 51.5%. In another study gasification temperature was reported to be a very important parameter to produce H_2 via biomass gasification. They reported that H_2 content reached the maximum at the gasification temperature 850 °C for a given air flow [20].

Leather industry waste water treatment sludge was gasified by the researchers within the scope of waste management. Sludge collected from filter press were gasified in fixed bed reactor with dry air at 700 °C. Optimum dry air flow was determined within 0.05–0.1 L min^{-1} interval and it was determined that syngas produced under these conditions had calorific value between 1000 and 1500 kcal m^{-3} [21]. Ongen and Arayici (2014) [22] revealed the composition of syngas that can be acquired by the gasification of leather industry is based on fleshing residues and calorific value of this gas. In the study, dry air and O_2 with a purity percentage of 99% were used as gasification oxidizing. While optimum dry air flow was found as 0.1 L min^{-1}, syngas having roughly 2000 kcal m^{-3} calorific value (medium calorific value syngas) between 700 and 900 °C was produced. On the other hand, at the end of the studies conducted under the same conditions with pure oxygen, it was observed that calorific value reached up to 3000 kcal m^{-3}. This situation was explained by the absence of nitrogen diluting oxygen in the setting. Gil-Lalaguna et al. (2014) [23] studied air-steam gasification of pyrolyzed sewage sludge. It was found that pyrolyzed sludge had 70% more CO content compared to directly gasified sludge. This situation was interpreted as condensing fixed carbon with pyrolysis in the fuel led to rise in heterogenic reactions such as Boudard occurring in high temperatures. In a study comparing combustion, pyrolysis and gasification processes, it was reported that pyrolysis was a more convenient process thanks to its efficiency within the scope of economy, energy-saving, product gain and “zero waste”. In the study applying Strength, Weakness, Opportunity and Threat Analysis, it was specified that gasification was more convenient compared to combustion [24].

On the other hand, while Lenis et al. (2013) [25] conducted repeatability studies statistically, some researchers conducted studies on the applicability of Artificial Neural Network (ANN) model technique for gasification process. In a study, in which the researchers modeled gasification of treatment sludge caused by leather industry with artificial neural nets, Ongen et al. (2013) [21] reported that model estimations with experimental model were satisfactorily successful. Mikulandric et al. (2014) [26] also carried out evaluations in their study that artificial neural nets were usable in gasification modeling.

The objective of this work was to present the experimental results of a fixed bed gasification system using an updraft approach with cypress and a treatment sludge as two different feedstock. Treatment sludge was a real waste that gasification experiments reflected more realistic results when compared to synthetic sample gasification experiments. Thermal decomposition of feedstock and changes in the physical forms were monitored by mass differences. Energy potential of synthetic gases produced from both feedstocks were calculated. The acquired results were compared with the results in the literature.

Material and methods

Materials

Cypress was collected from Istanbul Province in Turkey. Wastewater treatment sludge was collected from a textile industry located in Istanbul/Turkey. Elemental analysis of the samples were carried out at central laboratory of Istanbul University. C, H and O are the elements containing the main content of cypress. On the other hand, nitrogen is in small levels as no sulfur is detected. Similarly, while C and H stand out as the main elements for treatment sludge, when it is particularly compared with cypress, it is seen that its carbon content is relatively low. Proximate analysis were carried out according to the Standard Methods [27]. The chemicals used were analytical reagent grade.

Apparatus and experimental procedure

Thermochemical experiments were carried out in a updraft fixed bed steel reactor having 40 cm height and 7 cm diameter with a cyclone separator. Reactor was equipped with two gas inlet lines allowing gasification gases (dried air and/or pure oxygen) to enter and one exhaust line allowing generated syngas to pass through the continuous gas analyzer. In order to prevent gas leakage from reactor intake, pure graphite or graphite-lead spiral seals were used. Fig. 1 shows the schematic diagram of gasification system.

In order to determine the optimal gas flow for gasification, oxidizer flow rate varying between 0.05 and 0.5 L min^{-1} dry air was used. Gas flow rate was adjusted by a HOSCO-brand flow meter in the range of 0–0.5 L min^{-1}. In the experiments, 20 g of sludge and 50 g of cypress were used. Gasification experiments were carried out at 750 °C and gas composition variance depending on process temperature was recorded. The condensable part of the syngas was collected by cooling columns with water jacket. Then, syngas was directed to the continuous gas analyzer. CO, CO_2, H_2, CH_4 and O_2 contents of syngas were monitored. Process temperature was followed up with two thermocouples extended into middle and upper internal zones of reactor. For pyrolysis experiments, oxygen inside the reactor was removed by pure N_2 (1 L min^{-1}) and pyrolysis temperature was arranged at 200 °C and 300 °C in turn. Effect of process temperature on gasification process was investigated. Table 1 shows the experiments carried out with their codes used in the manuscript.

Analysis

Chemical analyses of the used samples were performed in accordance with Standard Methods (21st edition, 2005) [27]. Thermo Finnigan FlashEA 1112 Series elemental analysis device was used to determine elemental composition of the samples. The elemental analyzer operates according to the dynamic flash combustion (modified Dumas method) of the sample for the determination of Carbon, Hydrogen, Nitrogen and Sulfur. When the sample enters the reactor, inserted in the special furnace heated at 900–1000 °C, a small volume of pure Oxygen is added to the system and helps to burn the organic or inorganic material, converting the sample into elemental (simple) gases. . For thermo-gravimetric analysis, Linseis branded STA PT 1750 model TGA equipment located was used. In the thermograms drawn the weight loss at temperature range was calculated in wt.%. The device determines calorific value through measurement of the heat

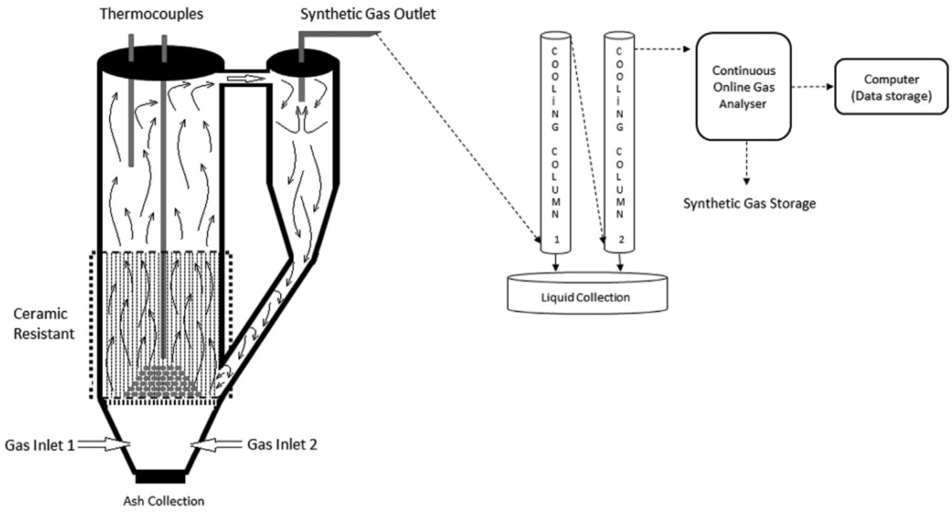

Fig. 1 – Schematic diagram of gasification reactor.

Table 1 – Codes used for the experiments.

Code	Feedstock	Process (°C/L min^{-1})
S2	Sludge	P 300/G 0.05
S3	Sludge	P 300/G 0.1
S4	Sludge	P 200/G 0.2
S5	Sludge	P 200/G 0.05
S6	Sludge	P 200/G 0.1
C7	Cypress	P 300/G 0.05
C8	Cypress	P 300/G 0.1
C9	Cypress	P 300/G 0.2

P: Pyrolysis, G: Gasification.

released after combustion of a sample. Some characteristics of fuels are presented in Table 2.

Syngas composition was determined by ABB-brand, The Advance Optima process gas analyzers equipped with thermo-magnetic and infrared photometers. Calorific value of syngas generated during gasification experiments was calculated. For calculations, values presented in Table 3 were used [28,29].

The elemental composition of cypress (Table 2) is in the range of values determined for cypress from the Henan Province (China) by Liu et al. (2013) [30]. "O" element was determined for cypress by taking differentiation from total mass. When two materials were assessed in terms of ash content, it is observed that cypress has rather low ash content depending on its organic content. High volatile substance content is also important in terms of gasification process.

At standard temperature and pressure, 2.5 m^{-3} syngas is produced from average 1 kg biomass. In this process, 1.5 m^{-3} air was used for combustion. On the other hand, the necessary air amount for a complete combustion was determined as approximately 4.5 m^{-3}. In that case, it was found out that 33% of the air consumed with combustion during gasification was used. It was established that energy recovery efficiency was 60–70% during the gasification of wooden, timber, etc. fuels. This situation was defined with the following equation. Energy recovery efficiency ($\dot{\eta}$) was calculated by the following equation [31];

$$\dot{\eta} = \frac{\text{Calorific value of gas, MJ/m}^3\text{/Fuel, kg}}{\text{Calorific value of fuel, MJ/kg}} \tag{7}$$

Table 2 – Cypress and sludge properties (Data are dry wt.% unless otherwise indicated).

Parameter	Cypress	Wastewater sludge
Initial moisture (Wet basis)	8.8	72 (Dewatered)
Volatile matter	77.2	39.7
Ash	4.3	53.2
Fixed carbon[a]	9.7	7.1
C	48.03	19.45
O[a]	45.01	–
H	6.68	5.12
N	0.28	1.85
S	–	–
HHV (kcal kg^{-1})	4200	1450
LHV (kcal kg^{-1})	3800	1280

[a] Calculated by difference.

Table 3 – Higher heating values of some common fuels.

HHV	Density	MJ m^{-3}	kcal m^{-3}
H_2	0.0899	12.77	3050
CO	1.25	12.64	3020
CH_4	0.717	39.82	9520

Results and discussion

Gasification experiments

Sludge gasification

Experiments were performed for enriching carbon within the fuel with pyrolysis at 200 and 300 °C and gasification experiments were carried out at 750 °C after the determination of favorable pyrolysis temperature. Results of the performed experiments are presented in Figs. 2 and 3.

It was decided that the effect of pyrolysis temperature increases the fuel carbon by observing calorific content of syngas acquired after gasification. Both alteration in gas composition and increase of calorific value had effect on the preference of 300 °C as optimum pyrolysis temperature and all pyrolysis studies were performed at 300 °C.

While gasification agent flow exceeded the level of 0.1 L min^{-1}, CO_2 increased over 30 vol.%. This situation was interpreted as increasing air flow directed environment stoichiometry to combustion. In experiments carried out with 0.05 and 0.1 L min^{-1} flows, H_2 increased over 30 vol.%. Following experiments were carried out with 0.05–0.1 L min^{-1} agent flows. In sludge gasification performed with 0.05 L min^{-1} dry air flow, production of 30% H_2 gas was achieved.

Cypress gasification

Figs. 4 and 5 show results of gasification experiments carried out with cypress. Although close measurements were made for H_2 gas in the studies in which two different flows were tested, differences were determined in CO formation.

In Fig. 4a., CO was determined as 25% and CH_4 was determined as 16% when H_2 was between 30 and 35% levels. On the other hand, when Fig. 4b. was examined, H_2, CO and CH_4 were calculated as 30%, 24% and 16%, respectively. Results showed that increasing agent flow rate from 0.05 to 0.1 L min^{-1} did not change the system performance. The optimum flow rate varied in the range of 0.05–0.1 L min^{-1}.

Hydrogen production

Hydrogen production performances for each experiment are given in Fig. 5.

Pyrolysis at 300 °C pre-treated gasification experiment with cypress achieved maximum H_2 production of 33 vol.%. Cypress gasification experiments with gasifying agent flow rate between 0.05 and 0.1 L min^{-1} resulted with highest H_2 production capacity between 30 and 33 vol.%. H_2 production rate decreased due to rising agent flow rate up to 0.2 L min^{-1}. Increasing air flow rate changed system from gasification to combustion which also decreased syngas calorific value. Similar behavior was also determined for sludge samples. Maximum H_2 value was 30 vol.% for S_2 coded experiment. The

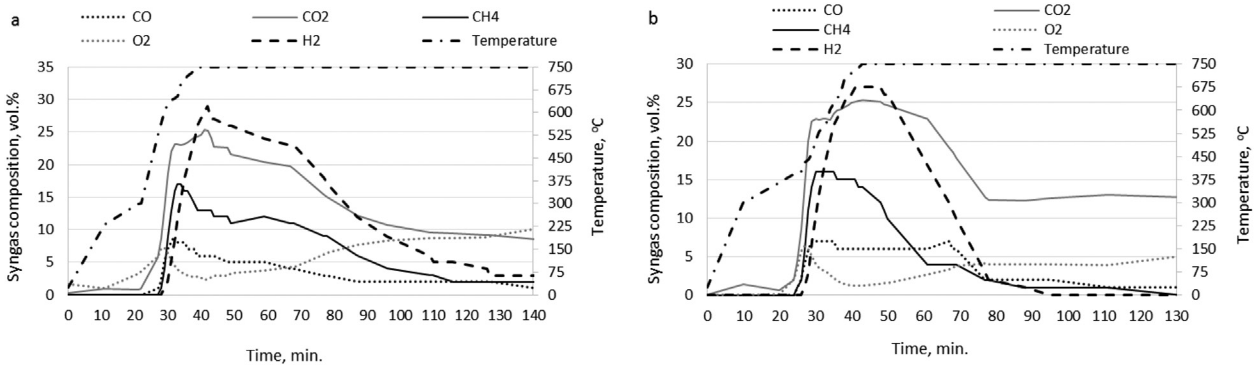

Fig. 2 – a) Sludge, 200 °C-pyrolysis + 0.05 L min^{-1} gasification, b) Sludge, 200 °C-pyrolysis + 0.1 L min^{-1} gasification.

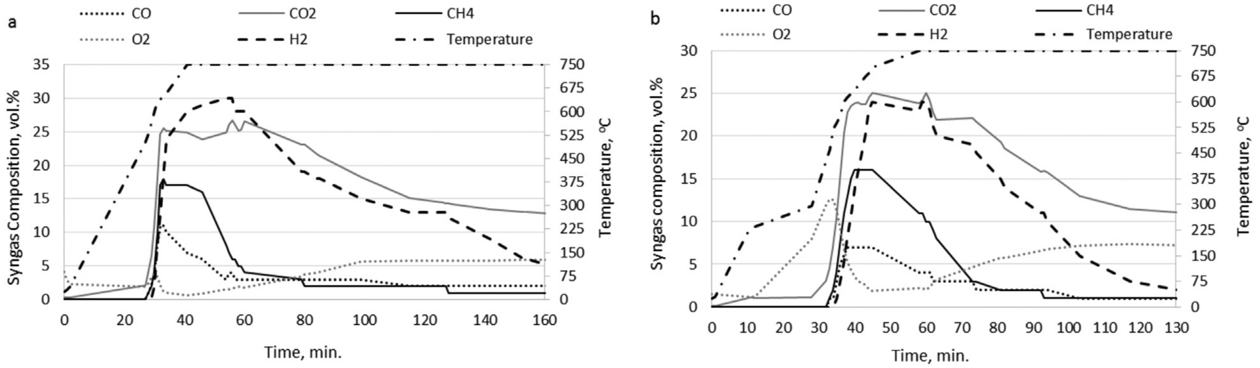

Fig. 3 – a) Sludge, 300 °C-pyrolysis + 0.05 L min^{-1} gasification, b) Sludge, 300 °C-pyrolysis + 0.1 L min^{-1} gasification.

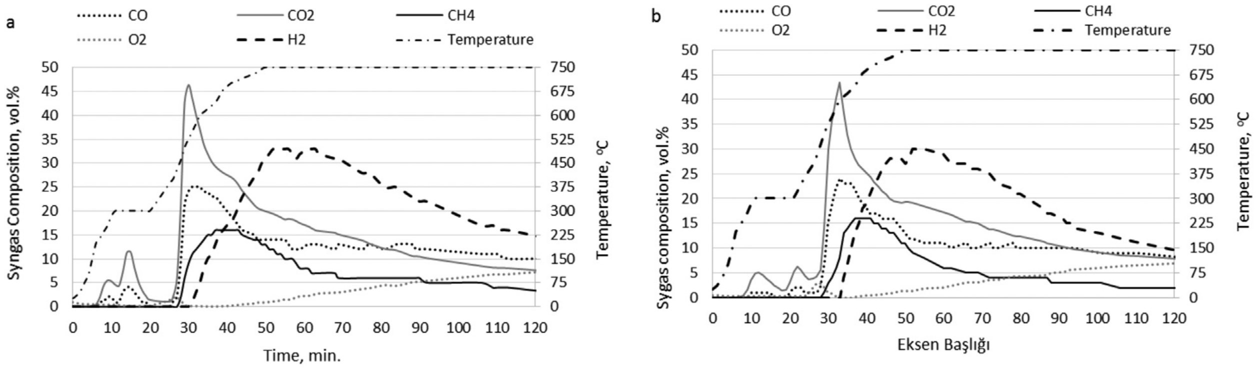

Fig. 4 – a) Cypress, 300 °C-pyrolysis + 0.05 L min^{-1} gasification, b) Cypress, 300 °C-pyrolysis + 0.1 L min^{-1} gasification.

significant difference between two feedstocks was the period of time that syngas with high calorific value could be produced. All cypress experiments resulted with longer period of time syngas production with calorific value.

Fuel/product conversion by weight

Mass changes at the end of the gasification applications are given in Table 4.

Solid residue amount of cypress sample depending on organic substance content is relatively low. When it is taken into consideration that its volatile part is 77%, the remaining part can depend on both its carbonization process with pyrolysis and limited performance of fixed bed reactor. The main technical challenges of fixed-bed reactors that have to be faced include: Long residence time; Non-uniform temperature distribution; Possible high char or/and tar contents in the fuel gas and low productivity [32].

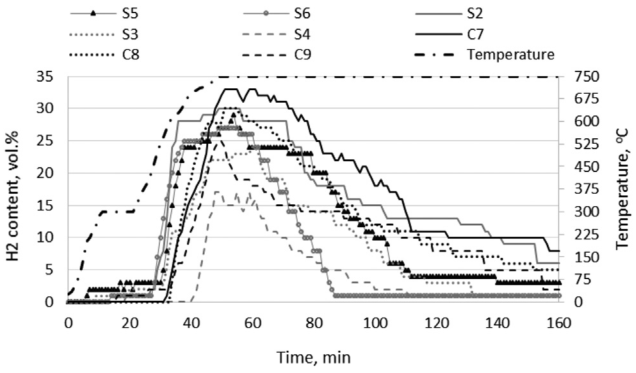

Fig. 5 – Hydrogen production performances of each experiment.

Table 4 – Products after process.

wt.%	Cypress	Sludge
Solid residue	32–35	60–63
Liquid product	8–10	8–10
Syngas product	55–60	27–30

Calorific value and energy recovery efficiency

Approximate calorific value comparison calculated by syngas compositions which were found as a result of the performed experiments are given in Fig. 6.

In the studies conducted with both examples, while CO_2 increased as vol.% after agent flow increased over 0.1 L min^{-1}, syngas calorific value started to decrease. The highest calorific values were determined at 0.05–0.1 L min^{-1} dry air flows. On the other hand, maximum calorific value was found as “medium calorific syngas” in S2 coded experiment with sludge sample and 0.05 L min^{-1} dry air flow at the levels of approximately 2680 kcal m^{-3}. It was determined that while maximum 2677 kcal m^{-3} of “medium calorific syngas” could be produced in the experiments performed with cypress sample, 0.05–0.1 L min^{-1} interval did not change efficiency. However, syngas production with longer period of time was achieved when compared to sludge experiments performed in this manuscript. Results were compared to the data in the literature in Table 5.

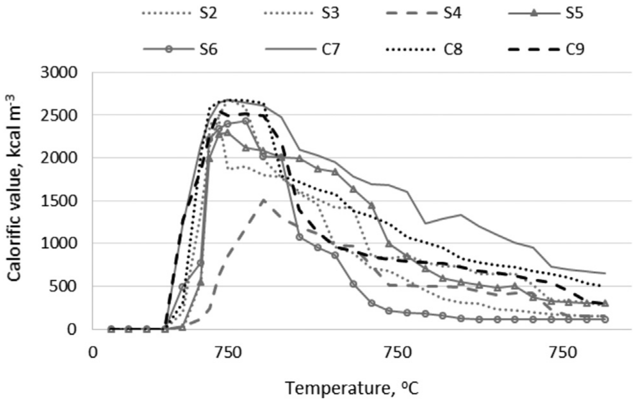

Fig. 6 – Comparison of calorific values.

Table 5 – Comparison of the results.

Syngas composition vol.%	Plis and Wilk, 2011 Wood pellets	Birch wood	Wood pellets	This study Cypress*	This study Sludge*
H_2	7.13	7.96	7.00	33.00	30.00
CO	27.47	25.53	28.60–30.00	25.00	11.00
CO_2	6.22	7.06	7.00–5.50	45.00	25.00
CH_4	1.88	1.44	1.80	16.00	18.00
O_2	1.44	3.49	–	0.76	0.94
HHV (MJ m^{-3})	–	–	–	11.21	11.22
HHV (kcal m^{-3})	–	–	–	2677	2680

* Maximum values are given.

In a study presented by Plis and Wilk (2011) [17], they gave gasification results performed with some organic substances and their calorific values. In the comparison made with the values given in this study, highly different values were determined. Although 800–1000 °C of reactor temperature and the used air flows have common features, it is assumed that these differences may be the result of the structural features of the used reactors. The alterations in H_2, CO and CO_2 percentages clearly reveal the effect of process differences on syngas composition.

According to Eq. (7), calculated energy recovery efficiency values were compared with literature data and presented in Table 6.

Average calorific value data was used in the calculation of gasification energy recovery coefficients. Experiment results were compared with the literature data. The remarkable matter at this point is the difference of occurring synthesis gas volumes. While low volume syngas was produced with sludge sample, higher volume syngas could be produced in biomasses. Experiment results show that recovery ratios of biomass is higher.

Another matter having impact on gasification efficiency is the difference between the calorific value of syngas produced in this study and data given in the literature. It was found that variation of CH_4 levels determined in syngas composition led to this result. Considering the fact that unit calorific value of CH_4 is roughly 39.82 MJ m^{-3}, 16 vol.% CH_4 (for cypress) difference would be reflected as approximately 6.37 MJ energy to syngas total calorific value.

Table 6 – Energy recovery efficiency ratios.

Feedstock	Reference	HHV_{syngas} MJ m^{-3}	HHV_{fuel} MJ kg^{-1}	Gas vol., m^3	η %
Textile sludge	this study	13.15	6.60	0.3	60
Cypress	this study	10.99	17.60	1.2	75
Wood	[27]	5.4	19.80	2.5	68
Rubber	[27]	–	32.60	–	50

Conclusions

Based on the information and data presented, the following findings are suggested:

- Thermo-chemical conversion of a specific forest residue (chamaecyparis lawsoniana - cypress) and treatment sludge from a textile industry was investigated. Considering the limited number of studies used for industrial waste management of gasification, it is evaluated that this laboratory scaled study has importance in terms of building database;
- Process temperature was 300 °C for pre-pyrolysis and 750 °C for gasification. Pyrolysis temperature and time need further studies to achieve more effective carbonization;
- 55–60 wt.% of cypress was converted into a synthesis gas (syngas). Although the cypress is an organic compound (77.2 wt.% - volatile), limited conversion was achieved during gasification. Limited performance of fixed-bed reactors may be one reason for that. For sludge samples, almost 30% syngas conversion was achieved;
- Solid and liquid phase analyses must be carried out regarding alternative use of thermo-chemical conversion derived products, such as; activated carbon, fuel, raw material or etc.;
- Medium calorific syngas was achieved during processes. Satisfactory higher heating values of 11.21 MJ m^{-3} and 11.22 MJ m^{-3} were achieved for cypress and treatment sludge, respectively. Results reported in the literature present varying syngas compositions with heating values of 4.67–10.15 MJ m^{-3} for organic compounds such as wood and cypress.
- Calorific value of the produced syngas is highly methane dependent. Methane was produced during each experiment with higher values than it was reported in the literature. Gas compositions also varied when compared to the literature. Operational conditions and reactor type are believed to be reasons for such variations.
- Energy recovery ratio was determined as 75% for biomass (cypress) while it was determined as 60% for sludge.

Thermochemical processes such as pyrolysis and gasification are rapidly developing technologies with great potential. Energy recovery from waste is a part of the waste management hierarchy and results showed that gasification is a promising technology for waste management.

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