Pyrolysis of biomass and refuse-derived fuel performance in laboratory scale batch reactor

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Abstract The results of pyrolysis of pine chips and refuse derived fuel fractions are presented. The experiments were carried out in a pilot pyrolysis reactor. The feedstock was analyzed by an elemental analyzer and the X-ray fluorescence spectrometer to determine the elemental composition. To find out optimum conditions for pyrolysis and mass loss as a function of temperature the thermogravimetric analysis was applied. Gases from the thermogravimetric analysis were directed to the infrared spectrometer using gas-flow cuvette to online analysis of gas composition. Chemical composition of the produced gas was measured using gas chromatography with a thermal conductivity detector and a flame ionization detector. The product analysis also took into account the mass balance of individual products.

Keywords: Slow pyrolysis; Fast pyrolysis; Oil; Refuse derived fuel

1 Introduction

Processing of biomass and wastes into liquid or gaseous fuel is a very interesting perspective for the agricultural industry, forestry and other industries using these raw materials. Studies on thermoconversion of biomass and refuse derived fuel (RDF) are very promising and develop very quickly, which may be an alternative in the fuel sector. For this reason, there are

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many studies on pyrolysis of biomass and refuse derived fuel (RDF) [1–4]. The composition of pyrolysis products depends on many factors including the process temperature, heating rate and the cooling rate of products. The most important factors for pyrolysis are heating rate and final temperature [5–7].

Fast pyrolysis presented in this paper means heating rate 80 °C/min and is directed on the liquid products receiving and reaction temperature within the range of 400–600 °C. Slow pyrolysis, defined also as conventional pyrolysis, because of low heating rate 3 °C/min results in the formation of char and gaseous products in the relatively low temperature (about 320–400 °C).

The aim of this study is to present the characteristics of conventional pyrolysis and due to the much higher heating rates fast pyrolysis of biomass and refuse derived fraction. The products distributions of conventional and fast pyrolysis were compared. Effect of temperature on gas composition was also studied. To determine thermal degradation characteristics and define optimum conditions for pyrolysis the ultimate, proximate and thermogravimetric analysis were performed.

2 Materials and methods

2.1 Materials

Two kinds of materials: refuse derived fuel fraction and pine chips were examined in this work. The RDF fraction had been prepared by separation of glass or metals. A sample was dried before and grinded to a size of maximum 0.01 m. As a result, a unified material consisting mainly of paper, textiles, wood and plastic was obtained and subsequently kept at ambient conditions. Pine chips which had a size similar to that of RDF samples were selected. The proximate and ultimate analysis of the pine chips and RDF are given in Tab. 1. The RDF fraction consist of 5.3% moisture, 77.2% volatile matter, 5.1 fixed carbon and 12.4% ash. This composition however may be varied depending on the origin of the fraction [4,8]. In comparison with the pine chips, RDF sample contains a large amount of ash. According to ultimate analysis presented derived fuel fraction contains 0.25% sulfur and 0.17% chlorine.

Table 1. Proximate and ultimate analysis of pine chips and RDF sample

Parameter	RDF	Pine chips
Higher Heating Value [MJ/kg]	23.8	19.21
Proximate analysis [%]		
Moisture	5.3	7.4
Volatile matter	72.2	68.4
Fixed carbon	10.1	21.9
Ash	12.4	2.3
Ultimate analysis [%]		
C	46.46	45
H	6.52	6.4
O	46.26	47.3
N	0.34	1.3
S	0.25	0.0
Cl	0.17	0.0

3   Apparatus and procedures

The pine chips and RDF pyrolysis were performed in a laboratory scale
pyrolyser with the capacity of 3 dm^3 and the maximum pressure of 3 MPa.
The schematic diagram of the pyrolysis system is shown in Fig. 1 for con-
ventional and fast pyrolysis. The reactor was heated by a 1000 W electric
furnace. Two thermocouples were attached to the wall and bed of the reac-
tor with the aim of controlling and monitoring the reactor temperature.

The produced pyrolitic gas was directed to the gas cooler, which was
coupled with a pressuremeter and a safety valve. Next, it was passed to the
cooling system represented by two washers (empty, or filled with charcoal or
clay). Gas samples were collected into a tedlar bag to measured by means
of chromatography. Liquid products obtained by the condensation of gases
within the washers in room temperature residues were weighted after the
process as well as the solid residues.

In the conventional pyrolysis 100 g of the RDF or pine chips sample
was placed inside the tubular reactor. The sample was heated from the
ambient temperature to 500 ℃ at a heating rate of 3 ℃/min. The reaction
time of about an hour was needed to complete the conversion of the RDF.
During the process, the quantity and composition of the released gases were
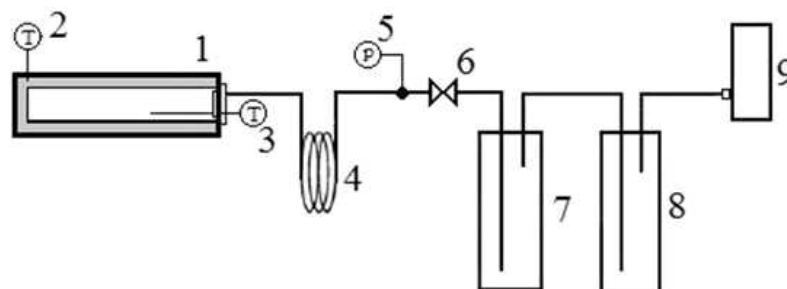
Figure 1. Schematic diagram of conventional and fast pyrolysis system: 1 – batch pyrolyser, 2,3 – thermocouples, 4 – cooler, 5 – pressure meter, 6 – valve, 7,8 – washers, 9 – tedlar bag.

measured. The gas samples were collected at the same temperature ranges to allow their comparison. After that time, the reactor was left to cool down and afterwards the remaining char and oil were weighted.

In the case of fast pyrolysis reactor was preheated up to 500 ºC and 50 g of the RDF or pine chip sample was thrown into the hot reactor. The reactor was kept at 500 ºC, resulting in the heating rate of 100 C/min Like for the conventional pyrolysis, the gas samples were collected to determine the average gas composition.

4   Thermogravimetric analysis

The thermogravimetric analysis (TGA) of RDF and pine chips samples has been used to determine their thermal degradation characteristics and define optimum conditions for pyrolysis. The analyses were carried out under nitrogen atmosphere at three representative heating rates: 5 ºC/min, 10 ºC/min and 15 ºC/min for RDF (Fig.2) and pine chips (Fig.3). In the temperature range of 200–500 ºC is clearly seen that for different weight the loss behavior was clearly seen for different samples. The studies of thermal decomposition show that 75% of RDF feedstock underwent decomposition and conversion to both liquid and gaseous products (Fig. 2) and almost 84% in case of pine chips sample (Fig. 3). The final temperature in both cases was equal to 500 ºC. The presence of two peaks proves that the decomposition of two main fractions contained in RDF took place in different temperature ranges, which could result from the fact that RDF is a mixture of different materials.
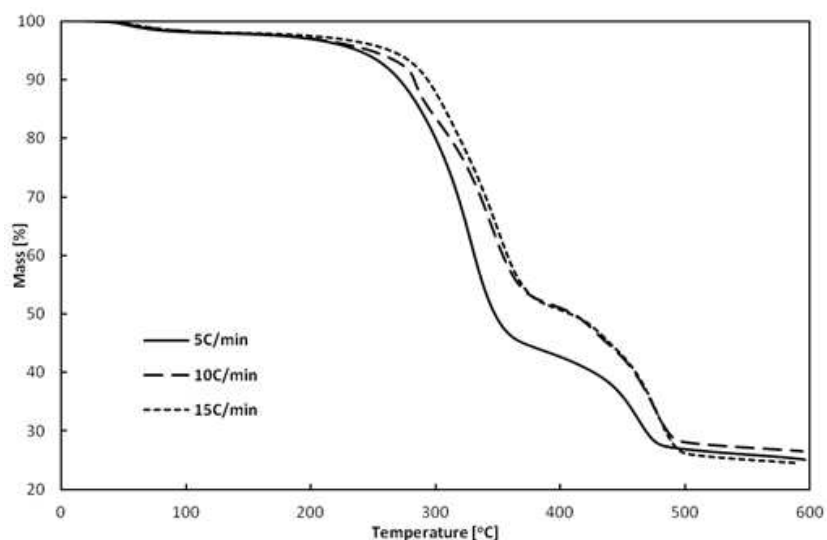
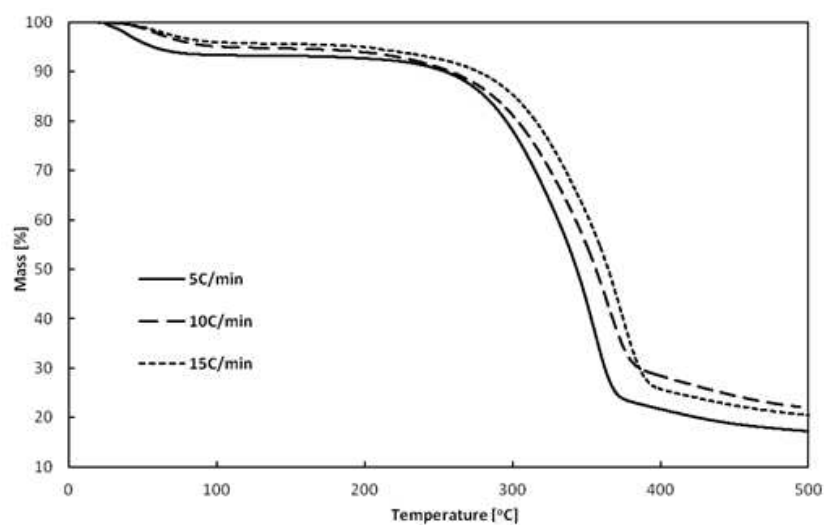Figure 2. Thermogravimetric curves for RDF fraction.

Figure 3. Thermogravimetric curves for pine chips sample.

During heating, the gases produced in the TGA flowed to the down-stream infrared (IR) spectrometer and were monitored on-line via the Fourier transformation infrared (FTIR) analysis (Figs. 4 and 5). A transmission flow-through gas cuvette coupled to the thermobalance with the aid of a thermostatic transfer line was used for this purpose. It was observed
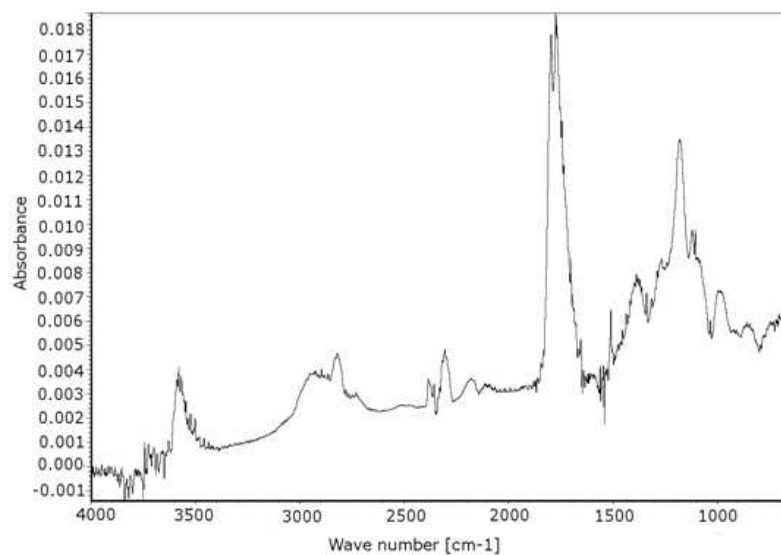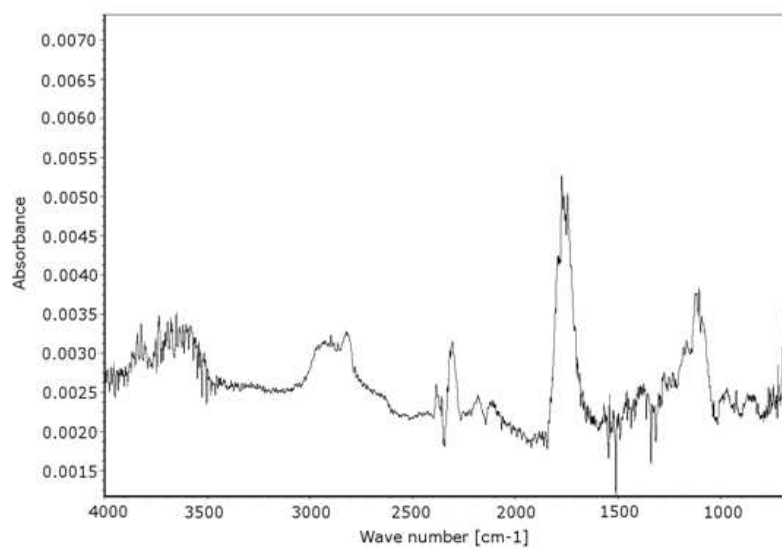
Figure 4. FTIR spectra of pin chips sample.

Figure 5. FTIR spectra of RDF sample.

that for both the RDF and pine chips samples, the main organic functional groups identified by FTIR were similar. The main products turned out to be oxygenated compounds and carbon-hydrogen bonds indentified by means of

IR absorption at 1100 cm^{-1} to 1000 cm^{-1} and at 3000 cm^{-1}, respectively. In case of RDF the decomposition consisted of two stages whereas for pine chips it was only a one-step process. The main products of the second stage (at the temp. of 400–500 ºC) were alkanes indentified by absorption at 3000 cm^{-1}. Since the heating rate does not have significant influence on gas composition the main products remained the same.

5 Results

5.1 The gas fraction

The analyses of the composition of the gas fractions obtained from the conventional and fast pyrolysis at various temperatures are presented for carbon dioxide (CO_2), carbon monoxide (CO), hydrogen (H_2) and methane (CH_4). In case of the conventional pyrolysis (Fig. 6), the volume fraction
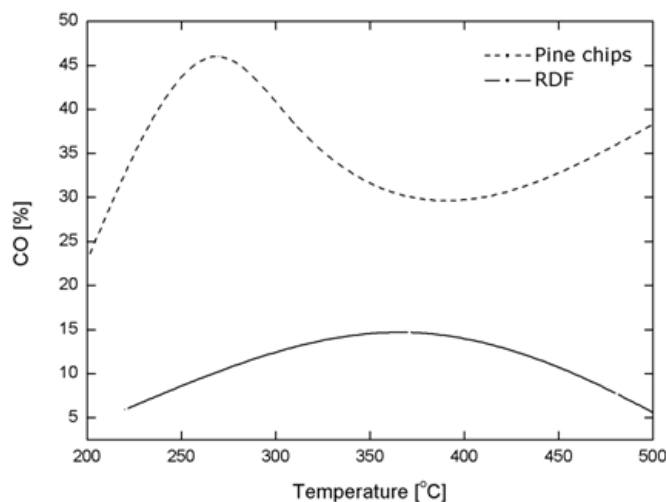

Figure 6. Variation of carbon monoxide in the conventional pyrolysis of RDF and pine chips.

of CO is lower for RDF in the entire temperature range (max. 14.7% at 270 ºC) than for pine chips (max. 46% at 370 ºC). With the same trend of the curve, a similar volume fraction of CO_2 (Fig. 9) was obtained for both samples at 300 ºC, while at 500 ºC the CO_2 content in the pyrolytic gas was significantly higher for pine chips (30%) than for the RDF fraction
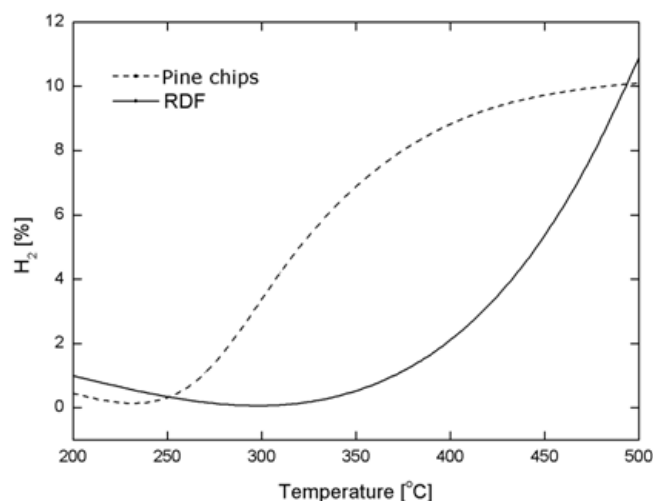
Figure 7. Variation of hydrogen in the conventional pyrolysis of RDF and pine chips.

(15%). The volume fraction of hydrogen (Fig.7) for both samples at around 250 °C looks similar, and does not exceed 2%. Beyond this temperature the increase of the hydrogen content with the increasing temperature can be observed. At 500 °C the volume fraction was equal to 10% for pine chips and to 11% for RDF. Similar characteristics were obtained for CH_4 (Fig. 8), where a significant increase of CH_4 content in the pyrolytic gas, up to 16% for pine chips and to 21% for RDF, was observed above the temperature of 500 °C. The average gas composition from conventional pyrolysis is presented in Tab. 2.

Table 2. The average gas composition from conventional pyrolysis of RDF and pine chips.

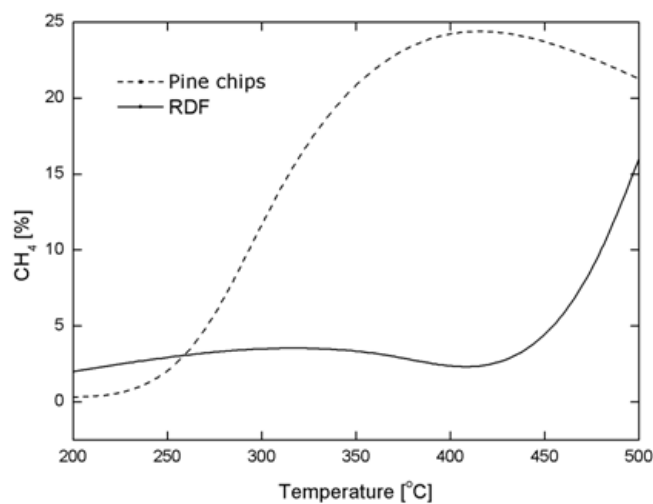| Gas composition [%]	RDF	Pine chips
H_2	4.10	3.86
CO	9.08	36.75
CH_4	6.56	9.18
CO_2	23.90	32.46
N_2	30.44	16.75
other volatile hydrocarbons	25.90	8.31

Figure 8. Variation of methane in the conventional pyrolysis of RDF and pine chips.
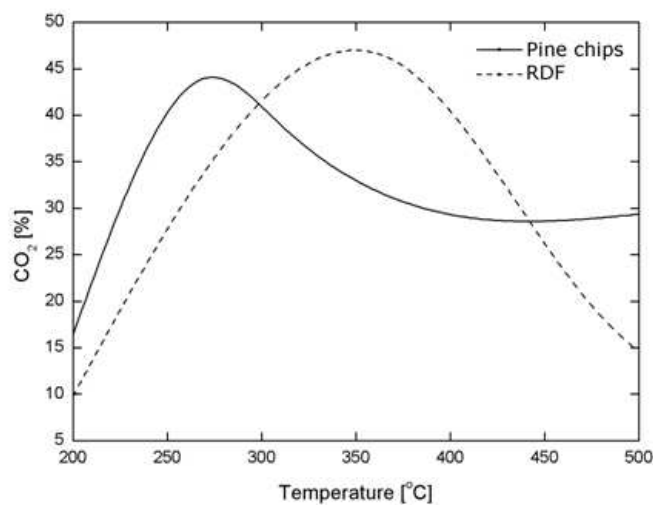

Figure 9. Variation of carbon dioxide in the conventional pyrolysis of RDF and pine
        chips.

The average gas composition for materials used in the fast pyrolysis is
presented in Tab. 3. It is clearly seen that the CO content in the gas from
pine chips pyrolysis is much higher than that from the RDF fraction, while

the content of other volatile hydrocarbons is lower for pine chips than for the RDF sample. This can be explained by the high amount of plastics in the composition of RDF fraction. Carbon dioxide content in gas from pine chips is also significantly higher than that from RDF. The content of H_2 in the produced gas is slightly higher for RDF than for pine chips. The CH_4 content in the resulting gas is similar for pine chips and RDF. In the case of RDF fraction high amount of other volatile hydrocarbons results in high lower heating value of gaseous products for conventional (28 MJ/Nm^3) and fast pyrolysis (50 MJ/Nm^3). For the pine chips pyrolysis lower heating value of gaseous products was similar for both processes (7–8 MJ/Nm^3).

Table 3. Gas composition from pine chips and RDF fast pyrolysis.

Gas composition [%]	RDF	Pine chips
H_2	6.1	2.29
CO	9.8	38.45
CH_4	8.1	6.75
CO_2	15.3	25.1
N_2	8.8	20.19
other volatile hydrocarbons	51.9	7.22

5.2   Pyrolysis yields

The product yields obtained from the fast and conventional pyrolysis (gas, oil and char) using a tubular batch pyrolyser are reported in Tab. 4. It is clearly seen that the fast pyrolysis, as compared to the conventional, is strongly oriented on obtaining liquid products. For the RDF and pine chips samples the same amounts of liquid products were obtained (48%), whereas for the RDF sample only 10% of gaseous products was obtained (against 31% for pine chips). The conventional pyrolysis is characterized by a similar yields of products for both materials.

Table 4. Product yields obtained from conventional and fast pyrolysis for RDF and pine chips samples.

Product	Conventional pyrolysis		Fast pyrolysis	
	RDF	Pine chips	RDF	Pine chips
Liquid [%]	34	39	48	48
Gas [%]	26	23	10	31
Solid [%]	40	38	42	21

6 Summary

Thermogravimetric analysis of the RDF sample indicates the presence of two characteristic peaks, which can be explained by the fact that RDF is a mixture of pine chips and plastics. It also affects the ability of lead the pyrolysis process in two different temperature ranges for the industrial scale. The experimental research of the pyrolysis of pine chips and RDF confirm the strong influence of operating conditions of pyrolysis on the products. Particularly important is the temperature and heating rate. Measurements of the liquid phase in the products show an increase its content with increasing heating rate, which in the case of RDF means an increase of 34% for the conventional pyrolysis to 48% for fast pyrolysis. For the pine chips pyrolysis the highest amount of liquid products — 48%, received also for fast pyrolysis. High amount of gaseous products and high caloric value from RDF pyrolysis shows that pyrolysis can be useful for engineering applications.

Received 8 March 2013

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