

BIO-GASEOUS FUELS FROM AGRICULTURAL WASTE PYROLYSIS (PART I)

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Abstract. The study, presented in two parts, puts in discussion the experimental results of low and high temperature pyrolysis on agricultural residues using a tubular batch reactor. During the experiment, nitrogen was used both as reaction environment and gas products carrier. The work focusses mainly on the pyrolysis gas analytical composition resulted from the process. The first part of the research is dedicated to the effect of process low temperature on rape straw pyrolysis. The experiments were conducted at 300°C, 400°C and 500°C to observe the solid – gas transformation at relative low temperatures. The main results revealed that, by balancing the amount of the nitrogen, the rape straw pyrolysis gas distribution varies by average between: 72%-77% CO₂, 22%-24% CO, 1%-4% H₂. The density of the gas in the devolatilization stage varies by average between 1.6-1.7 kg/m³, while its higher heating value ranges from 4 MJ/Nm³ - 8 MJ/Nm³.

1 Introduction

The effects of climate change are one of today's highest environmental challenges. The greenhouse gas (GHG) emissions are the primary cause of warming effects that negatively impact the ecosystems. At global level, it is estimated that 25-28% of the GHG results from heat and electricity generation [1-2]. To overcome this adversity, over the last decades several efforts have been made by important key stakeholders in research, industry, business, and environmental policy. The preliminary estimates show that EU expects to overreach its 2020 targets of reducing the GHG emissions by 20% [3]. However, more ambition binding targets must be met until 2030: GHG emissions reduction of 40% compared to 1990s levels, a share of 27% of renewable energy sources in EU's final energy consumption and a 27% increase in energy efficiency (compared to projections) [4].

Bioenergy is the main alternative candidate that might ensure a low-carbon footprint future. Nowadays, biomass and combustible wastes represent a sustainable option in substituting fossil fuel dependency [5-7]. The complex structure and properties allow its conversion into various biofuels in gas, liquid (bio-oil) and solid (bio-char) form [8,9].

Pyrolysis represents the thermochemical treatment that can convert the primary fuel into the three mentioned state matters. Different types of biomass and waste have broadly

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subject to the pyrolysis process in view of single stream or in mixtures (co-pyrolysis), low and high temperature process, heating rate (slow and fast pyrolysis), type of reactors, with or without catalysts, influential factors, products characterization and usage, models prediction, environmental and economic assessments [10-14]. However, technical answers must be filled until it's fully constant usage at an industrial scale. The process temperature choice represents one of the key parameters. The final energy applications (electricity, heat or carbonaceous materials/liquid/gaseous products) determine the pyrolysis configuration strongly related to the process temperature, residence time and heating rate. Therefore, three main types of process can be distinguished: slow, intermediate and fast. It is commonly known that slow pyrolysis is used to maximize the char production, while the fast pyrolysis to enhance gas production [15-16]. In comparison with the oil and char, that can be deposited for further usage, the energy stored in the gases can be used in a thermoelectric generator, providing the necessary power input for the pyrolysis process and not only. Therefore, the pyrolysis gas composition resulted from different renewable sources represents a critical point in the design of the pyrolytic plant.

The pyrolysis process can be split into two main steps: primary and secondary. In the primary step, the solid state of the material is converted into volatile gases and char. Primary pyrolysis occurs at relatively low temperatures (<500°C) and produces light gases (e.g. CO, CO₂, H₂O, and H₂), tar, char and mineral ash. In the second phase of the process, the products formed in the primary pyrolysis, particularly tar, pass through additional reactions at higher temperatures (typically > 500°C) and higher residence time [17].

In this context, the study, divided into two parts, presents the experimental results of low and high temperature rape straw residues pyrolysis. The experiments were carried out in a fed-batch reactor under nitrogen atmosphere. The work focuses mainly on the pyrolysis gas analytical composition resulted from the process. The first part of the research is dedicated to the effect of process low-temperature on rape straw pyrolysis. The experiments were conducted at 300°C, 400°C and 500°C to observe the solid – gas transformation at relatively low temperatures.

2 Material and methods

The rape straw residues used in this experimental study were collected from an agricultural area located in the southern part of Romania. First, the samples were dried at 105°C for 24 h, in compliance with the American Society for Testing and Materials (ASTM) standard method E 871-82 (2013). Sequentially, the dried feedstock was minced by a sieved, reaching to an average particle diameter smaller than 7 mm. The simplified scheme of the experimental setup is presented in Figure 1.

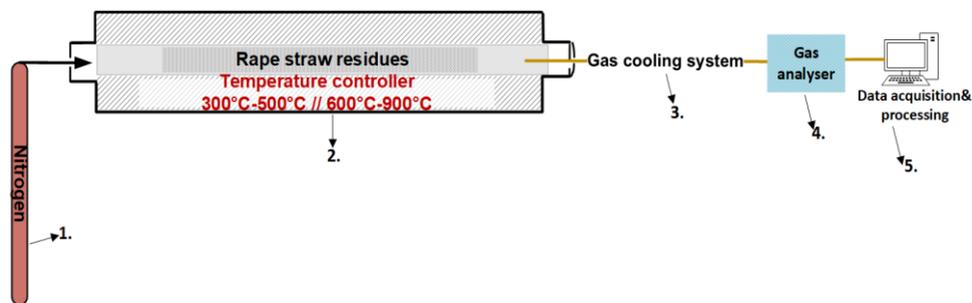


Fig. 1. Fed batch rape straw pyrolysis experimental setup: 1. Nitrogen tank; 2. Electrically heated batch reactor; 3. Gas cooling system; 4. Gas analyser-Testo 350XL, 5. Data acquisition: EASY-emission software, Testo, Inc.

The lab-scale batch reactor is a custom-made tubular reactor heated electrically (model RO 60/750/13 modified, NABERTHERM). Its specific characteristics were already reported by the authors [18-19]. The experimental temperature was chosen based on the biomass pyrolysis state of the art [20, 21]. It is worth noting that commonly reactors use conventional pyrolysis (slow pyrolysis) that involves relatively low process temperature (300–500 °C), slow heating rate (0.1–1 °C/s) and residence time (5-30 min) [22]. In the course of the rape straw pyrolysis process, the reactor was setup at a constant temperature, by turns at 300°C, 400°C, 500°C, respectively. The residence time decreased with the process temperature augmentation as follows: 300 °C- 24 min, 400 °C-19 min and 500°C- 14 min.

In the current experiments, 15 g of rape straw residues were placed in a crucible with a parallelepipedal form and then placed in the horizontal refractory steel crucible at a pre-set working temperature. To create an oxygen-free environment, nitrogen was introduced into the reactor and kept at about 1 l/min during each run. The pyrolysis gaseous fraction resulted from the treatment was passed through a cooling system device connected to the outlet end of the horizontal refractory steel tube. The non-condensable pyrolysis gaseous species composition was determined using the Testo 350-XL gas analyzer. In comparison with other gas sampling and analysis systems, based on chromatography, this portable gas analyzer allows the real-time monitoring of O₂, CO₂, CO, H₂, SO₂, NO_x, NO₂ and NO concentrations. This study pursued the determination of the combustible and non-combustible light pyrolysis gases (CO₂, CO, H₂), along with the gas pyrolysis formation sequences. The pyrolysis experiments were performed in triplicate, and the reported results were the average.

3 Results and discussions

The experimental results revealed that the augmentation of the operating temperature increases the pyrolysis gas yields formation, due to the agricultural residues bond breaking. Studies have shown that a further increase of process temperature raises the yield of gases due to the pyrolysis vapors secondary cracking, hence the decrease of pyrolysis oil [23].

In Figure 2, the effect of temperature on gas compounds evolution ((a) O₂; (b) CO₂; (c) CO; (d) H₂) registered with the gas analyzer are presented. Due to the instrument restrictions, the amount of nitrogen flow was determined by difference. The presence of the O₂ amount in the process (Figure 2.a) could be explained due to the rape straw residual chemical properties, the unoccupied volume of the feedstock in the crucible, and the crucible charged operation in the pre-heated refractory steel tube. The share of O₂ decreases with the process evolution and stabilization, being totally consumed after approximately 2-4 minutes. The O₂ decrease favors the CO₂ and CO formation, reaching to their maximum after the full consumption of the oxygen, converging to zero by the end of the process.

The CO₂ fraction decrease (Figure 2.b, c) with the increase of the process temperature, while the CO and H₂ fractions increases (Figure 2.d). The H₂ increment could be explained by the tars sequentially reactions, that occur in the secondary pyrolysis [24]. The formation of the CO₂ and CO in the second part of the devolatilization stage might occurs due to decarboxylation reactions. Similar change trends on rape stalk low temperature pyrolysis were reported by He et al., 2018 [25].

In the current experiments, the nitrogen is the most dominant compound in the pyrolysis gas, due to its constant presence during the process as inert carrier gas. In industrial application, depending on the type of reactor, the use of nitrogen is desirable only at start-up to remove the oxygen and overcome the possible thermal oxidation of the feedstock [26]. Therefore, the amount of nitrogen was distributed among the primary gas compounds

registered with the gas analyzer: CO₂, CO and H₂. In Figure 3, the pyrolysis gas composition of rape straw is presented.

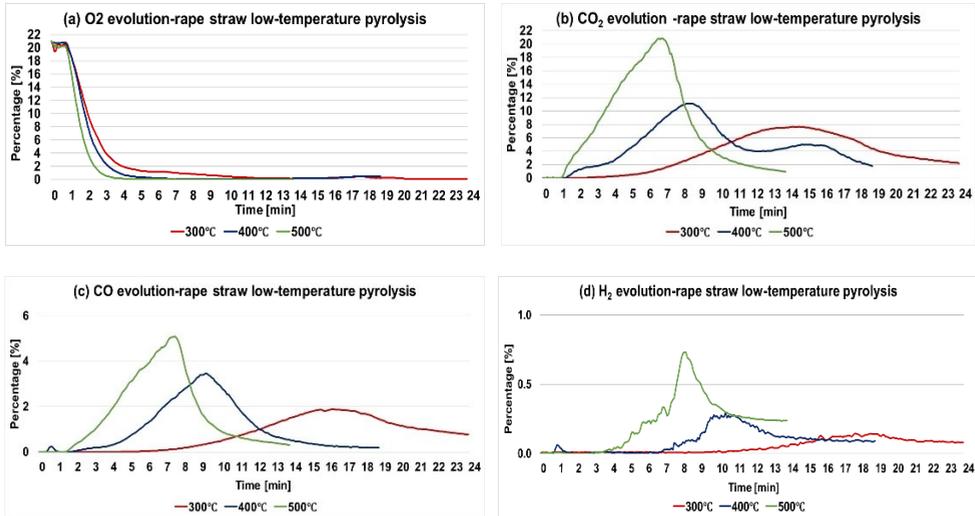


Fig. 2. Temperature effect on evolution of compounds from the rape straw low-temperature pyrolysis gas: (a) O₂; (b) CO₂; (c) CO; (d) H₂

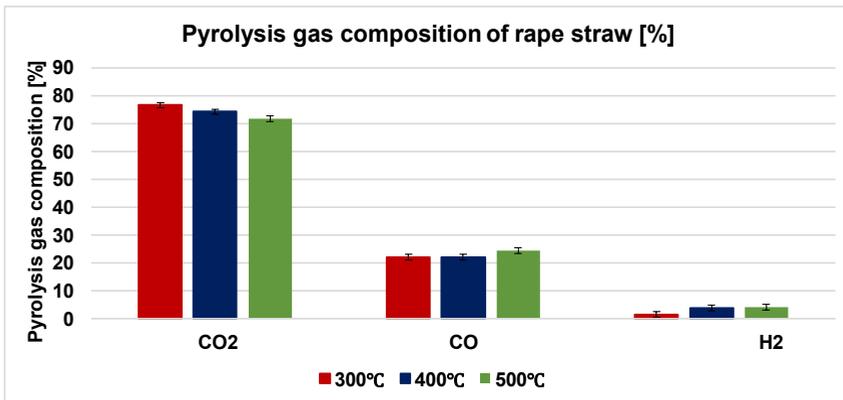


Fig. 3. Composition of rape straw non-condensable pyrolysis gas

The main results revealed that the rape straw pyrolysis gas distribution are at 300°C for CO₂ / CO / H₂ by mean value 77% / 22% / 1.5 % and at 500°C- 72% / 24% / 4 %, respectively.

In a pyrolysis study performed using rape stalk [25] the amount of CO₂ was on average 62% at 300°C, 50% at 500°C, for CO- 37% and 30%, H₂ <1% and 6%, CH₄ 1% and 10% and C_nH_m <0.5% and 4% for the same mentioned temperatures. Even though the authors used similar operation conditions, in this case, the sample was placed in a batch reactor and then externally heated from ambient temperature up to the desired process temperature. In the current research the air infiltration during the batch reactor insertion into the electrically pre-heated tube, along with the gas leaks could support the slight increase of oxygen-based gaseous species.

The average density of the gas in the devolatilization stage varies by average between 1.6-1.7 kg/m³ (Figure 4), while its higher heating value (HHV) ranges from 4 MJ/Nm³-8 MJ/Nm³ (Figure 5). The density of the pyrolysis gases from rape straw

residues decreases with the increase of temperature due to H₂ participation which is less dense than CO₂ and CO. The HHVs of gases obviously increase with temperature doubling its energetic potential from 300°C to 500°C.

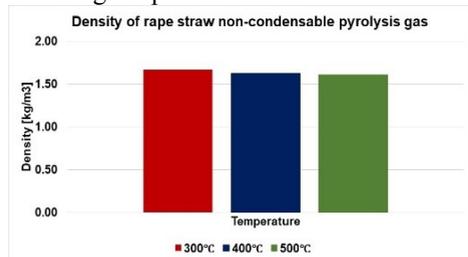


Fig.4. Density of rape straw non-condensable pyrolysis gas

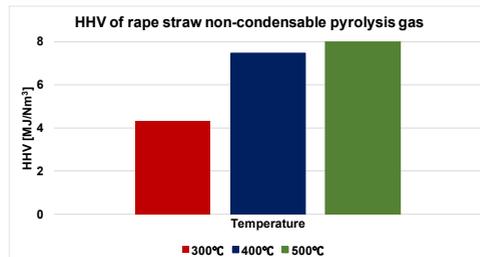


Fig. 5. HHV of rape straw non-condensable pyrolysis gas

Same trends were reported in previous studies, where the increase of pyrolysis temperature can produce high-quality gas which can be used as energy source [25, 27]. In their study [25] the HHV of the rape stalk pyrolysis gas reached out to an equivalent of 5.5 MJ/Nm³ at 300 °C and 11 MJ/Nm³ at 500 °C. In comparison with the current study, in the previous mention research, other pyrolytic low carbon number hydrocarbons such as CH₄ and C_nH_m were considered. As a side note, the constant presence of the inert carrier gas in the pyrolysis process can affect the gas heating value and its ignition properties.

4 Conclusions

The study, presented in two parts, reveals the temperature effect of low and high temperature pyrolysis on agricultural residues. The influence of temperature on the low temperature pyrolysis rape straw residues is presented in the first part of the study. The batch experiments were conducted at 300°C, 400°C and 500°C to observe the solid – gas transformation. The main gases identified during the process were CO₂, CO, H₂. At the studied temperatures, the CO₂ fraction decreases with the increase of the process temperature, while the CO and H₂ fractions increases. Due to the H₂ enhancement with process temperature, the HHVs increase from 4 MJ/Nm³ at 300°C up to 8 MJ/Nm³ at 500°C. The double increase of the energetic potential of bio-gases resulted from the low-temperature pyrolysis of rape agricultural residues has been reported in other studies made in similar conditions. In conclusion, the temperature has an important influence on the gas compounds evolution and composition, hence the energy value. The study is completed by a comprehensive and comparative analysis between low (300°C-500°C) and high temperature pyrolysis (600°C-900°C) on gases from rape straw residues, presented in the second part of the research.

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