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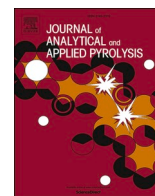
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Pyrolysis of tobacco waste: a comparative study between Py-GC/MS and fixed-bed reactors

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ABSTRACT

Pyrolysis, which converts waste into high-value products, is an appropriate and safe waste disposal solution for use in the tobacco industry. The properties of such high-value products were examined in the temperature range of 300–700 °C in order to establish the optimum pyrolytic operating settings for tobacco waste using a Py-GC/MS and a fixed-bed reactor. At 700 °C, the lower heat value of gas was 14 MJ/m³. When the three waste products (char, oil, and gas) are balanced, the optimum operating temperature for biomass pyrolysis of tobacco waste is found to be 600 °C. With rising temperatures, nitrogen (N) compounds, which are mostly detected below 500 °C, escape from tobacco waste. Nicotine, pyridines, and N-methyl-2-pyrrolidone are the predominant compounds found in the organic portion of the oil (up to a concentration of 1.2% m/m). Furthermore, the study found that the Py-GC-MS did not detect benzene products, unlike fixed bed reactor pyrolysis. Alkynes decreased from 15.4% to 3.9% as the temperature increased from 300° to 700°C. Alkenes (1.3-pentadien) had the most peak area. Due to the prolonged response time, no alkynes were found. Furan is generated from hemicellulose and cellulose breakdown and diminishes over 600 °C. Furan yield decreased from 5.5% to 2.2% as temperature increased from 400° to 700°C. The presence of phenols at 600 °C may be due to char or volatiles decomposing further. This results of this research are useful throughout the tobacco industry for dealing with cigarette waste.

1. Introduction

Tobacco consumption worldwide has been steadily increasing. As a result, a significant amount of toxic waste material has been generated by both the tobacco industry and its customers (for example, cigarette butts) [1]. As a product, tobacco is a major cash crop on the global market. To date, the total global production capacity of flue-cured tobacco has surpassed 4 million tons [2,3]. During cigarette production, approximately 10–20% of the total production output is tobacco waste. This includes agricultural waste, such as tobacco stems, and industrial waste, such as shredded, moldy leaves [2–4]. Conventional disposal methods are problematic in many respects, owing to limited landfill space as well as increased public concern about the potential dangers of releasing carcinogens and other toxins into our atmosphere [3,5].

The use of thermochemical conversion to store carbon reduces the amount of carbon recycled to the atmosphere, and so The United Nations recognizes this approach as a tool for reducing global warming.

However, continued efforts are required to further reduce carbon emissions [6]. Using agricultural biomass residues in thermal processes may help with such energy issues. Thermal routes such as torrefaction [7], gasification [8], pyrolysis (in forms such as fast, slow, ablative, and vacuum ablative) [9], and combustion [5] have been previously shown to be suitable for the agricultural residues.

Pyrolysis is a simple, low-cost technology for processing a wide range of biomass feedstocks, and is also very flexible in terms of process and product [3]. Renewable materials, such as tobacco waste, can be converted into valuable products (such as biochar, bio-oil, and biogas) using pyrolysis [4,10–12]. Bio-oil made from pyrolysis can be used to make biological pesticides, which would reduce the use of traditional pesticides whilst also avoiding the pollution caused by alkaloids leaching from tobacco waste [13]. The majority of the early research on the pyrolysis of tobacco and tobacco residues focused on determining the chemical compounds found in tobacco smoke [14–16]. Therefore, there is little information about the production of condensable liquid products

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from tobacco pyrolysis [17,18].

An in-depth understanding of the pyrolytic properties of tobacco is critical in order to provide a more optimized use for tobacco waste. Previous studies on these properties are typically kinetic or product characterization studies. Putun et al. [19] investigated the differences in yields and chemical composition between slow and fast pyrolysis. They discovered that not only does the type of biomass have an effect on the distribution of the yield and characterization of the liquid oil, but that the operating conditions did too. Gozan et al. [20] investigated the effects of high temperatures, ranging from 500° to 700°C, on the yield of liquid oil and discovered that the best yield was obtained at 600 °C. Cardoso et al. [11] investigated the effects of both temperature, between 400 and 700 °C, and additives of zinc chloride (ZnCl₂) and magnesium chloride (MgCl₂) on the distribution of chemical compounds in pyrolytic liquid oil. Khuenkao et al. [21] used vacuum ablative pyrolysis of tobacco residues to generate bio-oils. The GCxGC/TOF-MS analysis revealed that the oil was primarily composed of alkanes and benzene derivatives, which are useful components for upgrading to diesel fuel. Wu et al. [22] investigated the kinetics and reaction chemistry of both tobacco waste pyrolysis and combustion, and used conversional methods to compute activation energies of the reactions. In order to find the best pyrolysis conditions, Chen et al. [23] investigated the pyrolysis of tobacco waste, as well as the bio-oil product composition and the degree of nitrogen conversion, product characteristics and nitrogen transformation were studied from 250° to 950°C to determine the best way to use tobacco waste pyrolytic polygeneration. Liu et al. [2] investigated the pyrolysis behavior of tobacco using pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS), thermogravimetric Fourier-transform infrared spectroscopy (TG-FTIR), and thermogravimetric mass spectrometry (TG-MS). They discovered that the major pyrolysis products, including furfural, aldehydes, ketones, phenols, naphthalenes, indenes, carbon monoxide (CO), and carbon dioxide (CO₂) were released in the range of 167–500 °C.

Busch et al. [24] used a cigarette smoking simulator and a time-of-flight mass spectrometer (TOF-MS) in tandem to investigate the pyrolysis and combustion characteristics of tobacco in different atmospheres of nitrogen and air. The yields of oxygenated compounds containing carbonyl and carboxyl groups, [polycyclic] aromatic hydrocarbons, heterocyclic compounds, and nitrogen and sulfur containing compounds were all found to be higher under inert conditions than under oxygenated conditions. In addition, it was found that small molecule gaseous products (such as CO, CO₂, H₂O, NO_x, and HCN) were more likely to be produced in oxygenated atmospheres.

Várhegyi et al. [25] used a TG-MS to study the thermal decomposition process of Virginia and white-ribbed tobacco blends, and separately developed a kinetic model for the release of each ionic fragment. Chumsawat et al. [3] investigated the generation of bio-oil and biochar from tobacco waste using ablative pyrolysis, as well as the comparison of the bio-oil and biochar to the original tobacco waste using FT-IR spectrometry. Yildiz et al. [4] investigated the potential use of pyrolysis for the valorization of tobacco waste using TGA analysis. In their study, the distributed activation energy model (DAEM model) was used to investigate pyrolysis kinetics, and TG-FTIR analysis was used to analyze the gaseous products produced. In addition, FT-IR, GC-MS, and ¹H NMR analyses were used to characterize the bio-oil obtained from pyrolysis of tobacco waste in a fixed-bed reactor, where the main decomposition was found to take place between 150 and 390 °C. Lee et al. [6] proposed converting tobacco waste and tobacco stick waste using CO₂-assisted pyrolysis in order to reduce tar. Toxic chemicals like nicotine, acetic acid, 2-methoxy ethanol, limonene, and furanone were broken down into syngas because of the gaseous products that go to the ground. Xia et al. [26] investigated the feasibility of using pyrolysis of tobacco waste to produce aromatic compounds, employing a fluidized bed system to investigate the pyrolysis characteristics of tobacco samples at various temperatures (280–450 °C). The investigation of the pyrolysis and formation mechanism of N-containing compounds during tobacco pyrolysis

revealed that the content of N-containing compounds, particularly nicotine, decreased as temperature increased due to secondary decomposition. Nicotine breaks down into small N-containing compounds, which therefore increases the amount of N-containing heterocyclic compounds in bio-oils. Demirba [27] compared the structural components of flash pyrolysis products from tobacco stalk and yellow pine wood (namely methanol, acetic acid, and 1-hydroxy-2-propanone) obtained in a pyrolysis setup at temperatures ranging from 300° to 650°C. Wijayanti et al. [28] conducted pyrolysis in a laboratory-scale pilot plant using a fixed bed reactor to determine the best product. The setup ran for 2 h at temperatures ranging from 350° to 650°C. In addition to this, the properties of the char (solid yield) and tar (liquid yield) products were also investigated by determining their heating value, flash point, viscosity, density, and char yield morphology properties. Carmines et al. [29] collected and analyzed the gas phase products and particulate matter found in the mainstream gas produced during the thermal conversion of tobacco with varying amounts of glycerol (5%, 10% and 15%). With 10% and 15% glycerol, the amount of acrolein found in the smoke increase. However, concentrations of nicotine, acetaldehyde, propionaldehyde, aromaticamine, nitrosamines, phenols (as well as some other substances) in the smoke decreased. Gomez-Siurana et al. [30,31] used TG-FTIR to investigate the behavior of glycerol-tobacco mixture pyrolysis and catalytic pyrolysis with an MCM-41 catalyst, and proposed that there may be interactions between glycerol and tobacco that affect the composition of the produced gas. Dai et al. [32] investigated the effect of glycerol addition on the pyrolysis mechanism of tobacco using TG-FTIR and Py-GC-FID/MS. The results showed that adding glycerol to the mixture aided in the formation of volatile tobacco products and increased the yield of biochar. According to the Py-GC-FID/MS results, the addition of glycerol increased the release of tobacco pyrolysis gas at low temperatures, when glycerol was mostly present in the form of small gaseous molecules. It helped produce ketones, aldehydes, hydrocarbons, and other products when glycerol was added to pyrolysis at a high temperature. However, it also produced compounds such as furans and N-containing compounds which were less likely to be produced.

Several preliminary studies have been conducted in relation to the conversion process with future potential via the pyrolysis process. However, some specific relevant studies [10,22,26,28], which involved experiments on tobacco pyrolysis, were limited to using tobacco crop residue as biofuel. Pyrolysis is a suitable and safe waste disposal method for tobacco waste. Using a Py-GC-MS and a fixed-bed reactor, we studied the product characteristics in the temperature range of 300–700 °C in order to determine the optimal pyrolytic operating parameters for tobacco waste. To the best of our knowledge, no previous literature has been found that comprehensively compares the analysis of the same raw material under different process conditions using different pyrolysis methods. This study, therefore, helps the tobacco industry in the proper disposal of tobacco waste produced.

2. Materials and methods

2.1. Materials

Tobacco waste (specifically stems and leaves) was gathered in Poland's Krakow district and dried naturally after harvesting. The samples were then kept in a well-ventilated area. The samples were then crushed and sieved to obtain a powder with a particle size of < 1 mm before experimentation. The average particle size was determined to be around 315 μm.

2.2. Proximate and ultimate analysis

After preparation, the following properties were determined for the tobacco waste and biochar obtained in the fixed-bed pyrolysis: ash content (ash), volatile matter (VM), fixed-carbon (FC), and moisture

content (W^a). These properties were determined using a TGA801 thermal gravimetric analyzer (Germany). The carbon (C_f^a), hydrogen (H_f^a), oxygen (O_f^a), nitrogen (N_f^a), sulfur (S_f^a) analysis was performed using a Vario Macro Cube elemental analyzer (Germany). The high heating value (HHV) was measured using an oxygen bomb calorimeter IKA C 5000 (China). Analysis for each of these procedures was carried out using procedures that have been previously reported [33–36].

2.3. Chromatographic analysis

The liquid products from the tobacco waste pyrolysis was analyzed by Karl-Fischer titration (V30 KF, Mettler Toledo, Switzerland) in order to determine the water content of the liquid oil, as well as the content of organic substances. For example, the organic substances of interest include: Volatile Organic Compounds (VOCs), N-containing compounds, carboxylic acids, aldehydes, ketones, furans, phenols, and anhydrocarbon compounds (e.g. levoglucosan). Aromatic hydrocarbons were also of interest, which included, but was not limited to: benzene, toluene, xylenes, styrene, and polycyclic aromatic hydrocarbons (PAHs). An appropriate internal standard was used to quantify the relevant groups of specific compounds. The main components of the liquid product were determined in detail using several GC instruments: (i) Thermo-Scientific gas chromatograph, model Trace GC Ultra (Agilent Technologies, Inc, USA), and (ii) Thermo-Scientific gas chromatograph, model Trace GC (Agilent Technologies, Inc, USA). For instrument (i), a ZB-Wax capillary column, dimensions 60 m x 0.32 mm x 0.25 μ m, was used, and the carrier gas was helium, which was used at a rate of 2 ml/min. Split/splitless dispenser (1:25), 220 °C. The furnace temperature program was set to 50 °C for 5 min, then the temperature was increased to 220 °C at a rate of 10 °C/min (giving a run time of 38 min). A split/splitless dispenser was used (1:25) at 220 °C. For instrument (ii), a ZB-5 capillary column, dimensions 30 m x 0.32 mm x 0.25 μ m, was used, and the carrier gas was again helium, which was used at a rate of 1 ml/min. The furnace temperature program was set to 50 °C for 5 min, then the temperature was increased to 280 °C at a rate of 10 °C/min (giving a run time of 32 min). A split/splitless dispenser was used (1:50) at 280 °C.

After all chromatography analysis was performed, the liquid products were evaporated to obtain the tar mass at a temperature and pressure of 65 °C and 0.1 bar, respectively, until a constant mass was obtained.

The analysis of the gaseous products obtained in the pyrolysis tests, a CP 3800 with an FID/TDC detector (Varian, USA) was used. Analysis on the gas product (which has chemical composition H_2 , CO_2 , CO , CH_4 , C_2H_4 , C_2H_6 , etc.) was carried out both qualitatively and quantitatively. Due to the process being carried out in a nitrogen stream, the results obtained were converted to a nitrogen-free state. The energy parameters were calculated using the PN-EN ISO 6976:2016 standard.

2.4. Analytical pyrolysis (Py-GC-MS)

The analytical pyrolysis of tobacco waste was performed using a CDS 5200 (CDS Analytical LLC, Oxford, USA). The pyrolysis temperatures were set at 300, 400, 500, 600 and 700 °C, while the GC oven temperature was raised by 5 °C each minute from 45° to 275°C. The sample vapors created in the furnace were separated in two, with one half being fed to the column at 1.91 ml/min and 27.3 kPa, whilst the remainder was evacuated. This was carried out on a PerkinElmer Clarus GC/MS (USA) instrument with a temperature-programmed capillary column and MS at 70 eV. A Phenomenex's Zebron ZB-5 capillary column was used, which had a 5% diphenyl and a 95% dimethylpolysiloxane stationary phase, column length of 30 m, column ID of 0.32 mm, and a thickness of 0.10 μ m. The MS was adjusted to the following parameters: 250 °C ion source heater, 300 °C interface heater, 10^{-5} Pa vacuum, 45–300 m/z range, and 1428 scan speed. Post run PerkinElmer (NIST17.0) software was used to analyze the chromatograms and spectra obtained from the analysis.

2.5. Fixed-bed pyrolysis

The pyrolysis of the tobacco waste was carried out using a fixed-bed pyrolysis reactor. The test set-up was made up of an electric furnace, a steel retort (where the tested materials are converted), and a system for collecting the liquid and gaseous phases. Fig. 1 depicts a schematic of the station for solid fuel thermal conversion. The steel retort was filled with tobacco trash and carefully sealed. To produce chemically inert (anaerobic) conditions, nitrogen was dosed from the bottom of the retort for around 30 min at a steady flow rate of 500 cm^3/h . Meanwhile, the furnace at the solid fuel conversion station was heated to 300, 400, 500, 600 and 700 °C. The nitrogen flow rate was reduced to 100 cm^3/h after 30 min, and the retort was placed in the furnace so that product collection can begin. Throughout the process, the temperature inside the retort was constantly monitored, and the pyrolysis process was maintained for another 10 min after achieving the desired temperature inside the retort. After this time, the collection of liquid and gaseous products was stopped, and the retort was removed from the furnace in order to allow it to cool down to ambient temperature. The system used to collect liquid and gaseous products consisted of four scrubbers: one dry, two soaked with isopropanol (IPA), and one filled with glass wool to capture any aerosol before the gas sample was collected in to an air-tight bag. The first scrubbers are designed to retain water, organic waste, and the tar. Next, the two scrubbers with IPA were kept below –15 °C (in cryostat) in order to collect all of the condensable organic components. The leftover tar was captured by the filter system in the glass wool. The filtered gas was collected in an air-tight sample bag, devoid of any condensable materials or contaminants. IPA was then used to extract the filter system after the process. The sample obtained after extraction was mixed with the scrubber solutions before being tested to determine the amounts of water, organic matter, and tar.

3. Results

3.1. Materials

The analytical results for the studied tobacco sample are presented in Table 1.

3.2. Analytical pyrolysis (Py-GC-MS)

In the present study, tobacco waste was analysed by analytical pyrolysis (Py-GC-MS) at temperatures of 300, 400, 500, 600, and 700 °C. These programs offer rich information about the presence of chemical compounds and how they change with temperature. The main compounds identified in the program of tobacco waste (as shown in Fig. 2) are: nicotine (13.38 min), 3-eicosyne (24.70 min), acetic acid (1.28 min), D-limonene (5.49 min), 1,3-Pentadiene (1.15 min), furfural (2.38 min), nitrosometan (1.09 min), phenol (4.85 min) and pyranone (8.50 min).

In Table 2, the distribution of chemical compounds obtained during Py-GC-MS analysis of tobacco waste at various temperature conditions is presented. The yield of components in the liquid product is expected to vary with temperature since the heat fragments chemical linkages in the biomass to release compounds in the liquid product.

3.3. Product distribution from the fixed-bed pyrolysis of the tobacco waste

As aforementioned, the pyrolysis of tobacco waste in the fixed-bed reactor was performed at the same temperature conditions as Py-GC-MS analysis. In Fig. 3, the distribution of solid (biochar), liquid (condensable), and gaseous (unconveyable) products are presented and expressed as a percentage of the yield of each fraction. All fractions from the pyrolysis process in the fixed-bed reactor was collected for chemical analysis. The pyrolysis tests were repeated three times to check the stability of the obtained results.

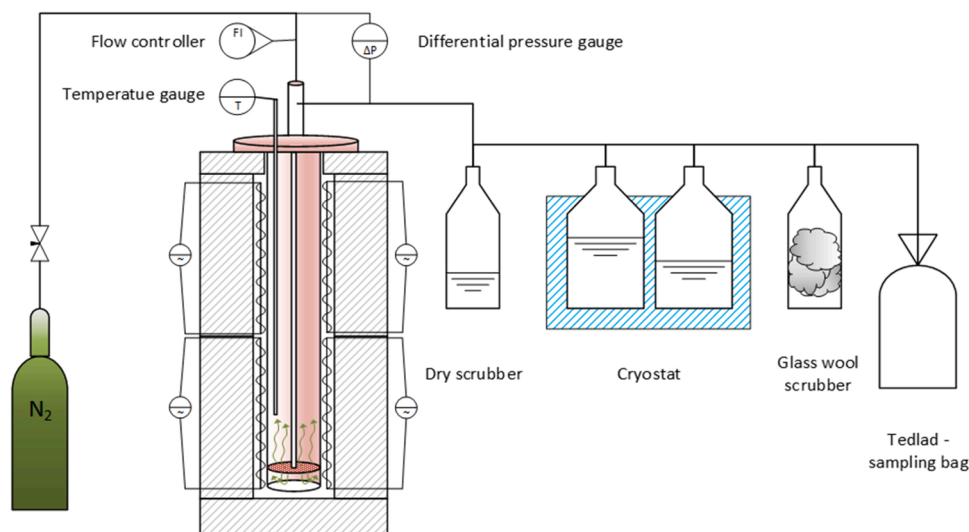


Fig. 1. Test set up for pyrolysis of tobacco waste in fixed-bed reactor.

Table 1

The analytical results of an air-dried sample of tobacco waste.

Characteristics		Tobacco sample
Proximate analysis [%]		
Moisture	W ^a	11.1
Volatile matter	VM	67.2
Fixed carbon	FC*	6.9
Ash	A ^a	14.8
Ultimate analysis [%]		
Carbon	C	41.9
Hydrogen	H	5.7
Oxygen	O	24.1
Nitrogen	N	2.1
Sulphur	S	0.3
Lower Heat Value [MJ/kg]	LHV	13.1

*Determined by difference

At 300 °C, the degradation of tobacco waste is found to be the smallest; hence, the biochar yield is 49 wt%.¹ The biochar yield decreases to 38 wt% when the temperature is increased to 400 °C. Following that, from 500° to 700°C, the biochar yield decreases even further from 32 to 28 wt%. This suggests that major degradation occurs between 300 and 400 °C. The volatile compounds extracted from the solid residue during pyrolysis are present in the oil and gas products, and, with increasing temperature, the distribution of these volatile compounds in oil and gas changes. At temperatures below 600 °C, these compounds are primarily found in the oil, with a maximum yield of 44 wt% at 500 °C. At temperatures over 600 °C, more gas product is formed, and the maximum yield is found to be only 32 wt% at 700 °C.

Fig. 4 shows the results of the proximate and ultimate analysis of the biochar obtained from the pyrolysis tests. Based on the basic analysis of the biochar, we see that with increasing temperature from 300° to 700°C, the ash content increases from 15.5% to 20.2%. FC content also

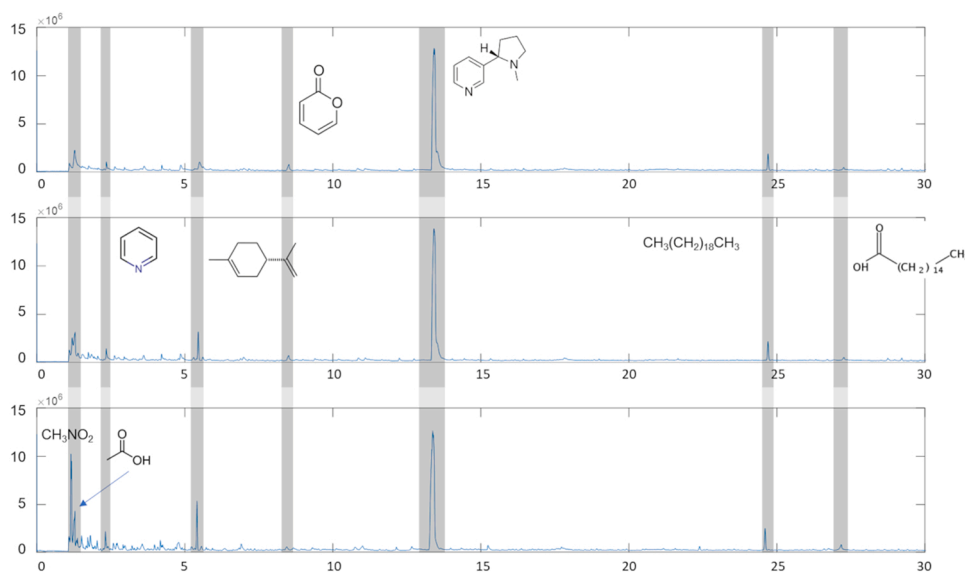


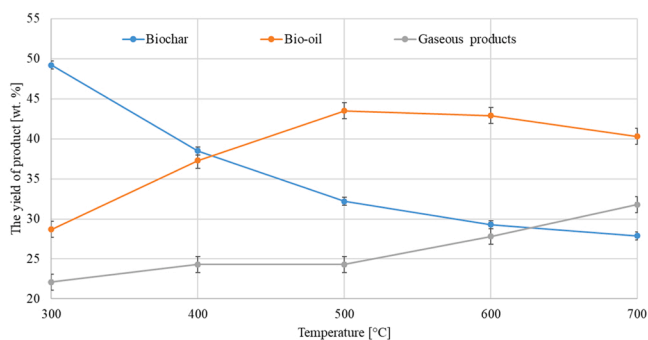
Fig. 2. Pyrograms of tobacco waste obtained at 400, 500 and 600 °C.

¹ The mass percentage derived from the proximate and ultimate analyses

Table 2

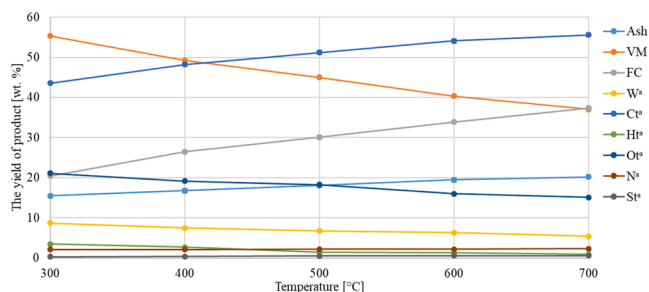
Distribution of chemical compounds by Py-GC-MS analysis at different temperatures (area %).

Retention time / min	Compounds	Area, %				
		300	400	500	600	700
1.09	Nitrosomethane	0.8	4.8	4.9	3.4	2.7
1.15	1,3-Pentadien	2.4	1.2	8.3	12.6	25.0
1.28	Acetic acid	5.5	7.6	10.7	9.6	8.2
1.77	Pirydyna	0.4	2.0	1.9	1.1	1.0
2.38	Furfural	4.7	5.5	3.6	3.3	2.2
2.64	2-Furanmethanol	0.9	2.1	1.7	1.8	0.8
3.64	2-Cyklopenten-1-one, 2-hydroxy	0.1	1.6	1.2	1.0	0.9
4.16	Pyridine, 4-ethyl-				2.4	0.3
4.23	2-Furaldehyde, 5-methyl	2.9	3.8	2.4	1.3	0.7
4.25	Pyridine, 3-ethyl-				1.2	2.5
4.48	4 H-Pyran-4-on, 2,3-dihydro-3,5-dihydroksy-6-methyl	0.4	1.1	0.1		
4.85	Phenol			3.5	2.4	2.2
5.49	D-Limonen		4.9	10.7	13.4	6.0
5.63	1,2-Cyclopentadione, 3-methyl-		1.4	1.7	0.6	
6.69	2,5-Dimethyl-4-hydroxy-3(2 H)-furanone	0.3	0.5	0.3		
6.85	Furyl hydroksymethyl ketone	0.6	0.7	0.4	0.3	
6.99	Phenol, 2-methoxy-		0.5	1.8	2.2	1.1
8.50	Pyranone	6.7	3.0	1.1	0.5	
9.38	Phenol, 4-ethyl-	0.8	0.9	0.8	0.4	
10.82	Benzofuran, 2,3-dihydro-	0.2	1.1	1.3	0.6	0.2
11.09	5-Hydroksymethylfurfural			0.5	0.8	1.2
12.24	Indol		1.4	1.1	1.0	0.7
12.72	2-Methoxy-4-vinylphenol	0.2	1.0	0.6	0.6	0.1
13.38	Nicotine	48.9	33.0	29.0	21.4	11.6
13.57	Pyrrolidine	0.2	1.8			
14.02	Cyclohexanen, 3-methyl-6-(1-methyletyliden	0.7	0.6	0.5	0.4	
14.44	Indolizine, 3-methyl-			0.5	0.5	0.3
15.33	Pyridyne, 3-(3,4-dihydro-2 H-pyrryl-5-yl)	1.1	0.5	0.8	1.6	2.4
17.82	2,3'-Bipyridyl	1.3	0.5	0.6	0.8	0.3
24.70	3-Eicosyne	15.4	13.0	7.9	7.1	3.9
27.25	n-Hexadecanoic acid	1.2	0.7	0.5	0.3	0.1

**Fig. 3.** Yield distribution of tobacco waste pyrolysis at different temperatures.

increases, while the content of VM and W^a decreases from 55.3% to 37.0% and from 8.7% to 5.4%, respectively. Additionally, based on elemental analysis results, we see an increase in the content of C, N, and S from 43.6% to 55.6%, 2.1–2.3%, and 0.4–0.6%, respectively. However, for H and O, we see a decrease in the content from 3.5% to 0.9%, and 21.1–15.1%, respectively.

Compared to the solid fraction (biochar), the liquid fraction was also analyzed. In the liquid products, water content (Karl Fischer method), organic matter content - VOCs (gas chromatography) and tar content (evaporation to constant mass at 65 °C under 0.1 bar pressure) were determined. The water, VOCs, and tar yields at different temperatures

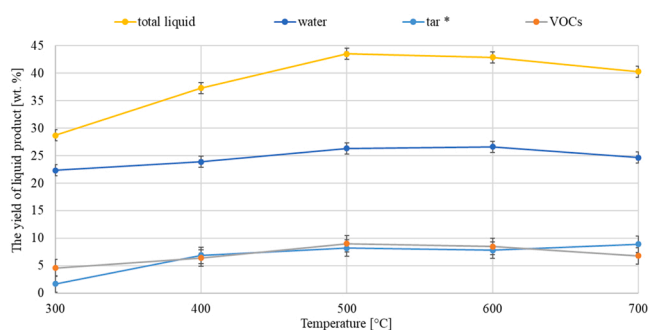
**Fig. 4.** Proximate and ultimate analysis from biochar obtained.

are shown in Fig. 5. At 500 °C, the major degradation reactions occur with a yield of 44 wt%, the water content is 27 wt%, VOCs content is 9 wt%, and tar content is 8 wt%.

To determine the optimum operating temperature based on the properties of the liquids fraction, the amount of water and ultimate analysis were analyzed quantitatively, the results of which are presented in Fig. 6. The ultimate analysis shows that the carbon content ranges from 12 to 23 wt%, which means that the organic component of oil is rather low as a result of the high water content of 20–27 wt%. With an increase in temperature, the C content initially increases, reaches a maximum at 23 wt%, before subsequently decreasing. The H content trend is similar to that of O. However, its peak temperature is 300 °C. It is notable that the N content of the oil is lower than that of all other biomasses.

Fig. 7 shows the concentrations of the organic compounds present in the liquid samples. As can be seen in the Fig. 7, the concentration of furans, phenols, benzene derivatives, and PAHs all increase with increasing temperature. At low temperatures (300 °C), aldehydes, ketones, alcohols, and acids are the main components. However, they diminish rapidly as temperature increases (300–500 °C). Phenol is primarily released between 300 and 600 °C, with its concentration gradually increasing to 0.7% m/m² at 600 °C. The furan content is 0.4% m/m at 300 °C. Benzene derivatives have a low content until 500 °C; however, after 600 °C, a noticeable release occurs, with a maximum value of 0.4% m/m. At low temperatures (300 °C), PAHs are completely absent, but they increase with increasing temperatures (400–600 °C). The concentration trend of the N-compounds show similar trends to acids, furans, aldehydes, ketones, and alcohols. However, only a maximum value of 1.2% m/m is achieved (at 400 °C).

In the third pyrolysis fraction analyzed, the concentration of H₂, CO₂, CO, and alkanes (CH₄, C₂H₄, C₂H₆, C₃H₈, C₃H₆, etc.) were determined,

**Fig. 5.** Yield distribution of liquid product from tobacco waste pyrolysis at different temperatures. Tar concentration (*) was determined as the residue after evaporation to a constant mass of liquid products (at 0.1 bar, 65 °C).

² The mass percentage derived from the chromatographic analysis – results calculated on the internal standard.

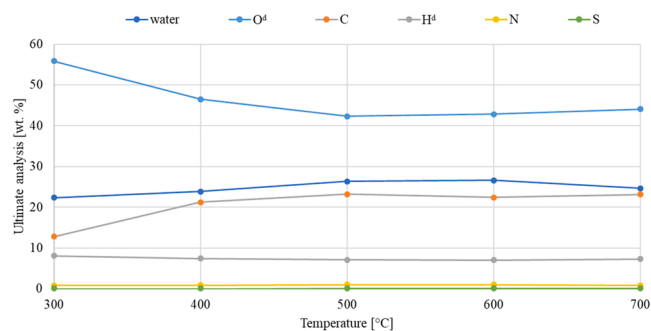


Fig. 6. Ultimate analysis of liquid products obtained at various pyrolysis conditions.

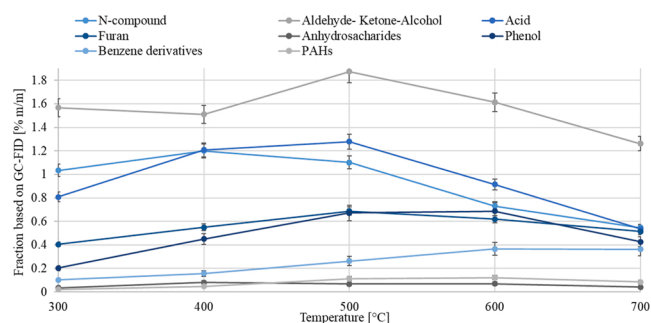


Fig. 7. Amount of grouping composition in liquid oil at different temperatures as determined by GC-FID.

which are presented in Fig. 8.

CO₂ is the first to be detected, and is the dominant compound between 300 and 700 °C. At 700 °C, the CO₂ concentration rises to a maximum of 22.5 wt%. CO₂ is generally formed at low temperatures (300–400 °C) by the decarboxylation of hemicellulose and cellulose. However, above 500 °C, it may be formed by the decarboxylation of volatile compounds during the secondary reaction. In contrast to CO₂, CO is released slowly below 500 °C, at only 2.0 wt%. However, it rapidly increases between 600 and 700 °C, reaching a concentration of 4.3 wt%. Below 400 °C, no H₂ is released; however, a rapid and linear increase is observed as the temperature rises from 400° to 700°C, with a maximum yield of 0.22 wt% obtained. This increase is only observed until 700 °C, which may be due to the demethoxylation of lignin in the solid residue, or the release of volatile compounds during the secondary reaction. From 600° to 700°C, there is a noticeable release of C₂-C₃ compounds. The low calorific value of the gas obtained at 300 °C is < 2 MJ/m³. However, this increases from 8 to 14 MJ/m³ as the temperature increases from 500° to 700°C.

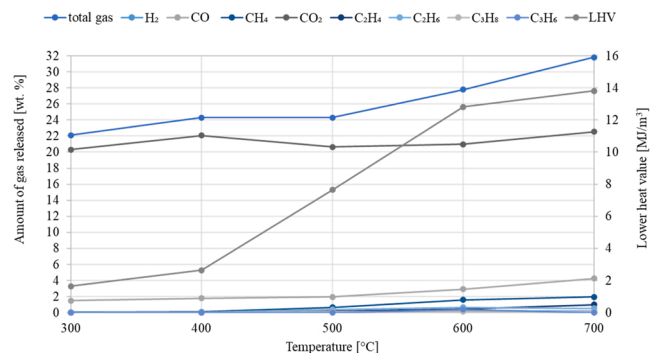


Fig. 8. Amount of gas released at different pyrolysis temperatures (composition converted to oxygen-free and nitrogen-free conditions).

These results are consistent with previous research and with other biomass-derived materials such as wheat straw, sugar bagasse, maize cobs, pine wood, or rice hulls [37–39]. Hemicellulose degrades primarily in the first range of temperature increase. The hemicellulose breakdown temperature ranged between 219 and 290 °C. Then, when the temperature rises, cellulose, which has a stiffer and more rigid structure than hemicellulose, degrades. Cellulose breakdown occurs between 269 and 388 °C. After boosting the pyrolysis temperature, the final step involves the destruction of lignin, the most recalcitrant component of lignocellulosic biomass. Although lignin degrades at a higher temperature than other components, the degradation reactions of these components occur concurrently.

4. Process overview and comparison between Py-GC-MS and the pyrolysis fixed-bed reactor

Pyrolysis consists of four main unit processes. First, drying, which transfers the moisture in the sample and light organic compounds such as waxes, terpenes, and alkaloids (including nicotine) to the gas phase. In the range studied, the efficiency of this process is independent of temperature. Second, the primary decomposition of organic compounds contained in the sample, which leads to the formation of three substances: water, organic matter, and tar (see Fig. 5) [40]. In biomass, there are two main parts that break down differently when heated: (i) polysaccharides (cellulose, hemicellulose), whose decomposition leads to the formation of pyrogenetic water, aldehydes, ketones, carboxylic acids, furans, and anhydrosaccharides (including levoglucosan) [41], and (ii) lignins, whose decomposition is responsible for the formation of phenols (mainly guaiacol and silyngol derivatives) and most tar substances. Third, secondary thermal decomposition of primary decomposition products is strongly influenced by both the temperature and the residence time of the liquid and gaseous components within the reactor's heated zone. It is responsible for the formation of aromatic hydrocarbons such as benzene, toluene, xylenes, styrene and PAHs. It is also responsible for the decrease in yield of liquid products and the increase in yield of gaseous products. Finally, steam gasification, which is a secondary process that occurs between water (mainly pyrogenetic) and highly carbonized carbonaceous material [42]. It also leads to the formation of hydrogen and carbon monoxide.

All of these above processes can be observed during the pyrolysis of the tobacco waste sample under study here. The drying process (the first stage) is responsible for both the high water yield at the lowest temperature (300 °C), and the presence of nicotine [43,44]. The primary decomposition efficiency of the organic compounds (stage 2) in the test sample increases up to 500 °C. At higher temperatures, competitive secondary decomposition reactions begin to predominate and influence the increased yield of gaseous products. A maximum in the yield of liquid organics and a stabilization in the yield of tar are observed at 500 °C. No measurable amounts of anhydrosaccharides, which is one of the primary breakdown products of polysaccharides such as cellulose and starch, were observed (see Fig. 3). The reason for this was most likely due to the short residence time of the tar in the heated zone of the reactor. Increasing the residence time of liquid products at high temperatures should result in increased yields of these compounds. At temperatures above 500 °C, secondary decomposition reactions become visible (stage 3). Increasing the pyrolysis temperature from 500° to 600°C resulted in a visible decrease in the yield of total organics (see Fig. 5), including nicotine, methanol, and acetic acid (see Fig. 7). In the case of nicotine, a slow increase in the yield of one of its degradation products, pyridine, can also be observed. Due to the short residence time of the liquid products in the heated zone of the reactor, the formation of benzene and its derivatives, such as toluene, xylenes, styrene and PAHs were observed small yields [45]. The shortening of the residence time of liquid products was influenced by the pyrolysis in a nitrogen stream, and the turbulence of drying and thermal decomposition reactions connected with the rapid temperature rise inside the reactor (the retort with

the tested sample was inserted into a heated furnace, thus the heating rate was limited only by heat conduction through the retort walls). The steam gasification (stage 4) is seen at the transition from 600° to 700°C. A decrease in water and biochar yields is also seen, as well as an increase in CO yields (see Fig. 6).

The pyrolysis of tobacco waste under such diverse settings ought to have an influence on the volatile components that can be examined following this procedure. So, how do the chemical compositions of liquid samples collected using the two procedures differ? Probably, it has, mostly as a result of the pace of heating, the residence duration of the compounds in conditions conducive to secondary reactions, and the scale of the process. When comparing the peak area and the relative abundance in terms of area percentage, some of the following relationships can be observed: The benzene derivatives were not found via Py-GC-MS in contrast to tobacco waste pyrolysis in the fixed bed reactor, where benzene derivatives have a low content until 500 °C. However, after 600 °C, a noticeable release occurs, with a maximum value of 0.4% m/m. At low temperatures (300 °C), PAHs are completely absent, but they increase with increasing temperatures between 400 and 600 °C. Both benzene derivatives and PAHs may be formed mainly during the condensation and structural reforming of the biochar. The percentage area of alkynes decreased from 15.4% to 3.9% as temperature increased from 300° to 700°C, while alkenes (1,3-pentadien) had the highest percentage of peak area in this temperature region. In the liquids obtained from fixed-bed pyrolysis, no alkynes were observed, which was most likely due to the much longer residence time in the reaction zone. The phenolic compounds in the pyrolytic oils are a typical product of lignocellulosic biomass, mainly produced from the decomposition of lignin. In the present study, it was noted that as the temperature of pyrolysis of tobacco waste in a fixed bed reactor increases, the content of phenolic compounds. In addition to temperature, the long residence time (compared to Py-GC-GM) of the volatile compounds in the heating zone undoubtedly influenced the increase in concentration. In the case of Py-GC-MS, where pyrolysis occurs within a few seconds and the released compounds are directed directly to the chromatographic column, there is little chance of secondary reactions occurring, which may cause an increase in the amount of phenolic compounds. Secondary pyrolysis reactions occur when the pyrolysis temperature is increased from 400 °C to 450 °C, and guaiacols/syringols rapidly change to catechols/pyrogallols and o-cresols/xynolols, along with phenols. The generation of polycyclic aromatic hydrocarbons (PAH) increases at temperatures over 700 °C. Along with PAHs, compounds such as phenols and o-cresols that are stable at high temperatures are detected. It has also been shown that around 400–450 °C, methoxyl group-related processes occur, whereas at 550–600 °C, breakdown includes catechol gasification. For example, in the case of Py-GC-MS from 500° to 700°C, there was a significant decrease in the percentage area of phenolics from 3.5% to 2.2%. In the pyrolysis tobacco waste in the fixed bed reactor, a significant decrease of phenolic compounds was noticeable only above 600 °C. It should further be noted that phenols generally form below 600 °C during the major degradation period of lignin, however, the presence of phenols above 600 °C in the current study may be due to further decomposition of char or volatiles. The results of the Py-GC-MS analysis show that a high concentration of the acid group was found in pyrolysis products at 500 °C. In particular, acetic acid was the main component at 500 °C, reaching a concentration of 10.7%, whereas the highest concentration of this compound for a fixed bed reactor was at 400 °C and amounted to only 0.50% m/m. Consequently, other components are released, replacing aldehydes, ketones, alcohols, and acids as the sample undergoes greater decomposition at higher temperatures. The furan is primarily derived from hemicellulose and cellulose degradation, and it decreases when the temperature exceeds 600 °C. Furan yield, including furfural, decreased as temperature increased from 400° to 700°C, as did furan percentage area, which decreased from 5.5% to 2.2%. On the other hand, the concentration of furan in the fixed bed reactor went up from 0.4% to 0.7% m/m as the temperature increased

from 300° to 500°C. In the bio-oils, nicotine was the main N-containing compound. The group of N-containing compounds decreased significantly from 48.8% to 11.6% going from 400° to 700°C. We also observe a decrease in the content of this substance from 1.05% to 0.30% m/m in the fixed bed reactor.

Nitromethane was the main component at 500 °C, reaching 4.9%. However, in the fixed bed reactor reservoir, the tests did not confirm the presence of nitromethane. Furthermore, a sharp decrease is observed at temperatures higher than 600 °C, which may be due to the secondary decomposition of these compounds at high temperatures.

5. Conclusion

In this study, five pyrolysis experiments were performed on a sample of tobacco waste using Py-GC-MS and fixed-bed reactor. The experiments were conducted at temperatures of 300, 400, 500, 600, and 700 °C. Characterization of the products from both processes was presented. Py-GC-MS was used to find that nicotine, 3-eicosyne, acetic acid, D-limonen, 1,3-pentadien, furfural, nitrosometan, phenol, pyranone, and other similar compounds are the most important compounds made when tobacco waste is rapidly pyrolyzed.

On the other hand, the obtained results from the biomass fixed-bed reactor for each experiment were solid (biochar), liquid, and gaseous products, which were collected and analyzed in detail according to the scope of the study.

It was observed that the calorific value of the gas obtained increased with increasing temperature. It should also be noted that the energy parameters summarized in Fig. 8 are for dry gas and are devoid of organic and tarry substances. The actual calorific value will strongly depend on the system for cleaning the ash gas from the aforementioned components. The increase in calorific value at temperatures above 600 °C is due in large to the steam gasification reaction, i.e., the conversion of the thermal energy supplied to the reactor into chemical energy.

The observed high yields of tar and the absence of noticeable amounts of anhydrosuccarides and derivatized benzene are related to the short residence time of the liquid products in the hot zone of the reactor. This is typical of how fast pyrolysis biomass in both types of experiments was carried out.

CRedit authorship contribution statement

Roksana Muzyka: Methodology, Software, Validation, Formal analysis, Investigation, Data Curation, Writing – original draft, Writing – review & editing. **Maciej Chrubasik:** Methodology, Software, Validation, Formal analysis, Investigation. **Mariusz Dudziak:** Writing – review & editing. **Miloud Ouadi:** Writing – review & editing. **Marcin Sajdak:** Conceptualization, Methodology, Software, Formal analysis, Investigation, Visualization, Supervision, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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