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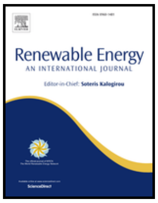

Benefits from co-pyrolysis of biomass and refuse derived fuel for biofuels production: Experimental investigations

Aneta Magdziarz*, Wojciech Jerzak, Mariusz Wądrzyk, Małgorzata Sieradzka

AGH University of Krakow, Mickiewicza Av. 30, 30-059, Krakow, Poland

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ABSTRACT

The application of renewable fuels and waste for energy production is crucial environmentally and economically. Co-pyrolysis of biomass and refuse derived fuel (RDF) offers a promising pathway for valuable products that combine various benefits including enhanced energy recovery, waste valorisation, improved product quality, and environmental sustainability. Consideration of specific feedstocks and optimization of process parameters are necessary to maximise the efficiency and effectiveness of the co-pyrolysis process. This work presents investigations of the co-pyrolysis process of lignocellulosic biomass wastes (rye straw and agriculture grass) and RDF. These biomasses ensure efficient decomposition. The RDF, high in carbon (78.5 %) and hydrogen (11.8 %), was predominantly plastic based. Based on Py-GC-MS studies at 600 °C, it was observed that the addition of RDF to biomass caused a significant decrease in the share of organic oxygen compounds among the released decomposition products. Laboratory tests were performed in a fixed-bed reactor for raw biomass and RDF and 1:1 and 3:1 biomass to RDF mass ratio. The results demonstrated that the yield of char production decreased with the addition of RDF, which promoted the bio-oil yield. Despite, RDF pyrolysis meets problems, it was proved that co-pyrolysis of biomass and RDF is a good solution for their utilization.

1. Introduction

The growing production of a wide range of wastes, environmental pollution, and simultaneously higher energy consumption has led to search for new solutions to use wastes in parallel to the production of fuels and added value materials. Moreover, the actual political and energy crisis caused by the unstable world situation requires the search for additional energy sources. Applying renewable fuels and wastes for energy production is necessary from an environmental and economic point of view and is also a response to the energy crisis. The demand for more action from the EU to find alternative energy supplies is growing.

Biomass wastes such as agricultural residues (including crops, crop residues, and animal waste) and food scraps can be used as a renewable energy source, as they can be thermochemically converted into fuel, chemicals, and other biobased materials for a wide range of applications, simultaneously reducing the amount of waste going into landfills [1,2]. Despite many advantages of biomass (e.g. ecological energy source, availability), biomass wastes are characterised by high moisture and high volatile matter contents, the presence of alkali metals in ash, and a wide variety of physical and chemical properties [3]. These parameters determine the choice of its thermochemical or biochemical conversion process (pyrolysis, gasification, hydrothermal gasification, direct combustion, hydrothermal liquefaction, anaerobic digestion, fermentation, and enzymatic hydrolysis) [4,5].

The high energy potential for energy purposes has refuse derived fuels (RDF). RDF is mainly composed of plastic waste (polymers such as polyethylene, terephthalate, polypropylene, polystyrene and polyvinyl chloride), paper, textiles, and wood; therefore, it contains a high content of organic matter giving a high calorific value [6]. RDF is a fuel produced from municipal solid waste that has been processed to remove non-combustible materials such as metals, glass, and other inorganic materials, this leads to obtaining relatively stable chemical properties and low moisture content, thus it has high energy potential. RDF has a higher energy content than raw municipal solid waste, making it a more efficient fuel source. RDF can also be easily transported and stored, making it a convenient fuel source for energy generation in the cement industry (combusted in a rotary cement kiln) or in energy plants, but direct combustion of RDF can cause the emission of hazardous substances [7,8]. Co-combustion of RDF and coal is also a process that is often applied [9,10]. Nowadays, pyrolysis of RDF as a thermal conversion process seems to be a good solution to produce solid (after the upgrading named “bio-char) and liquid products (after the

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* Corresponding author.
E-mail address: amagdzia@agh.edu.pl (A. Magdziarz).

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Table 1
Overview of biomass and plastics co-pyrolysis technology.

	Material		Process parameters	Ref.
	Biomass/waste	Plastic		
1	Softwood and hardwood biomass	polyethylene (PE) and polystyrene (PS)	Reactor: Py-GC-MS Process temperature: 550 °C Residence time: 20 min	[15]
2	Sawdust	low density polyethylene (LDPE)	Reactor: fixed-bed system Process temperature: 500 °C Residence time: 10 min AC catalyst	[17]
3	Pine sawdust	LDPE	Reactor: TGA-FTIR, Py-GC-MS Process temperature: 600 °C Catalysts:ZSM-5, CaO, CaAl, CaFe	[18]
4	Pinewood	polypropylene (PP), polyethylene terephthalate (PETE), polycarbonate (BPC)	Reactor: TGA Atmosphere: Ar Process temperature: 1000 °C Heating rate: 10 °C/min	[19]
5	Paper biomass	plastic mixture (HDPE + PP + PET)	Reactor: laboratory scale fixed-bed Process temperature: 800 °C Residence time: 15 min	[20]
6	Acid pretreated corn stover	polyethylene (PE)	Reactor: micro-pyrolyzer system (fast pyrolysis) Process temperature: 900 °C Zeolite catalyst	[21]
7	Microcrystalline cellulose	polyethylene (PE)	Reactor: two-stage fixed bed Process temperature: 600 °C and 800 °C	[22]
8	Wood pellets	polystyrene (PS)	Reactor: two-stage fixed bed Process temperature: 500 °C Residence time: 20 min Metal-modified zeolite catalysts	[23]
9	Palm kernel shell	polypropylene (PP)	Reactor: fixed-bed Process temperature: 700 °C Residence time: 45 min	[24]
10	Corncob	polystyrene (PS)	Reactor: TGA Atmosphere: N_2 Process temperature: 600 °C, Reactor: microwave-assisted Atmosphere: N_2 Process temperature: 450 °C, Residence time: 15 min	[25]
11	Coffee grounds	polyethylene (CP73)	Reactor: TGA Atmosphere: N_2 Process temperature: 900 °C Heating rate: 10, 20, 40 °C/min HZSM-5 and HY catalysts	[26]
12	Bamboo waste	polypropylene (PP)	Reactor: TGA Atmosphere: N_2 Process temperature: 800 °C Heating rate: 10 °C/min Reactor: one-stage fixed-bed Process temperature: 400, 500, 600, 700 °C Residence time: 30 min	[27]
13	Poplar wood	polystyrene (PS) and polyvinyl chloride (PVC)	Reactor: fixed-bed Atmosphere: N_2 Process temperature: 750 °C Heating rate: 20 °C/min	[28]
14	Waste wood in form of wood pellets	high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET)	Reactor: two stage fixed-bed reactor system, 1st reactor – co-pyrolysis (500 °C, heating rate 10 °C/min), 2nd reactor – catalytic reactor (500 °C) Atmosphere: N_2 Zeolite ZSM-5 catalyst	[29]
15	Pine wood	polystyrene (PS)	Reactor: semi-batch fixed-bed Atmosphere: N_2 Process temperature: 900 °C	[30]
16	Coffee grounds	polyethylene (PE)	Reactor: TGA Atmosphere: N_2 Process temperature: 1000 °C	[16]

upgrading named "bio-oil") as alternative energy carriers [11,12]. Pyrolysis is a thermochemical conversion process that is carried out in an oxygen-free atmosphere (mainly in nitrogen or argon) at a temperature above 300–400 °C and leads to production of three main products: gas, pyro-oil, and pyro-char. The distribution of product yields depends directly on the conditions of the process (operational parameters) such as temperature, heating rate, residence time of the volatiles, and the particle size of the feedstock. Among them, the heating rate constitutes a classification parameter which classifies pyrolysis into the following types: i) slow pyrolysis, ii) intermediate pyrolysis, iii) fast pyrolysis, and (iv) flash pyrolysis.

When biomass and RDF were analysed, it was found that co-pyrolysis can be a good solution [13], because: i) it helps reduce deposited waste, ii) improves the quality of bio-oil produced during pyrolysis by combining the properties of both materials, iii) provides a higher heating value and a lower ash content to the bio-oil, iv) helps overcome some of the challenges associated with the pyrolysis of biomass alone, such as poor quality of the bio-oil due to the presence of impurities, and v) the process supports the development of circular economy principles and reduces the consumption of fossil fuel resources [14,15]. Studies concerning co-pyrolysis processes of biomass are mainly focused on co-pyrolysis of biomass and plastics (Table 1), it is recognized lack of knowledge related to co-pyrolysis of biomass with RDF. During co-pyrolysis of municipal solid waste and biomass pine sawdust under sludge fly ash minimizing of concentration of complex liquid compounds and heavy hydrocarbons was observed improving the quality of syngas and liquid products [13]. The application of catalysts further improved bio-oil quality by increasing the content of hydrocarbons and reducing the content of oxygenated compounds in bio-oil. In studies [16] the authors proved that with the increase in the ratio

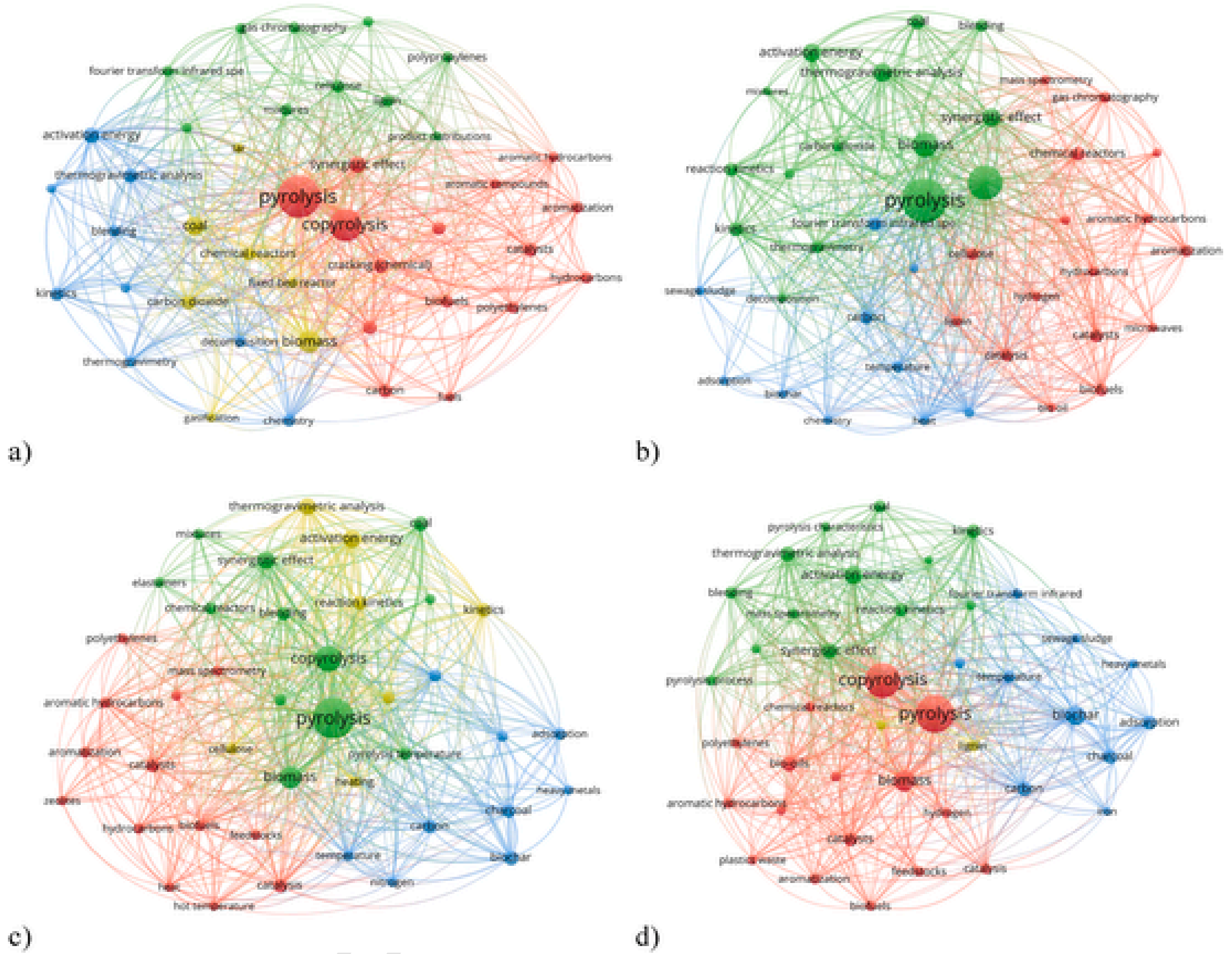

Fig. 1. Visualization of the main clusters based on the keyword “co-pyrolysis” in the Scopus database in the years: a) 2016–2017, b) 2018–2019, c) 2020–2021, and d) 2022–2023.

Table 2
Proximate, ultimate and fibre analysis of studied feedstocks.

Parameter	Rye straw (RS)	Agriculture grass (AG)	RDF
M, wt%	7.77	8.06	0.11
A, wt%	4.39	7.65	6.64
VM, wt%	72.73	68.39	93.15
C, wt%	39.45	42.28	78.54
H, wt%	5.90	6.39	11.79
N, wt%	1.79	2.04	0.18
Hemicellulose, wt%	25.96	27.12	–
Cellulose, wt%	41.19	38.49	–
Lignin, wt%	6.79	8.29	–

of polyethylene to the spent coffee grain, the co-pyrolysis showed better performance. During co-pyrolysis the yields of coke and ethers, ketones, and esters production were reduced while the yields of hydrocarbons and alcohols decreased.

Despite the benefits mentioned of co-pyrolysis of biomass and RDF, the final results strongly depend on the composition of feedstocks. Pyrolysis of pure RDF in the form of powder meets with some operational problems because of formation of tar, wax and other volatile organic compounds, which can cause equipment fouling (wax is deposited on reactor surface in consequence leads to plug reactor pipes), reduce product quality, and increase emissions. Managing wax and tar formations through process optimization and the use of appropriate catalysts or additives is essential for mitigating these issues. Thus, addition of biomass to RDF is good solution and investigations to better understanding of interactions between RDF and biomass during pyrolysis are required.

A comprehensive bibliometric analysis encompassing all facets of co-pyrolysis is imperative to solidify understanding and assess the present state of the field. The primary objective is to streamline the task of reviewing contemporary trends in co-pyrolysis technology. The involves tracking the progression of keywords, detecting nascent clusters, and gauging the prevalence of various research themes across temporal scales. Co-pyrolysis of biomass with various raw materials has attracted increasing interest from scientists in recent years. Based on the keywords “co-pyrolysis” in the article titles, abstracts, and keywords indexed in the Scopus database, a systematic increase in the number of articles was noted. Over the last eight years, the upward trend has been clear, 116 articles were published in 2016, while in 2023 as many as 508 articles were published. Analysing articles in subsequent years, the evolution of research area targets was observed. To increase the num-

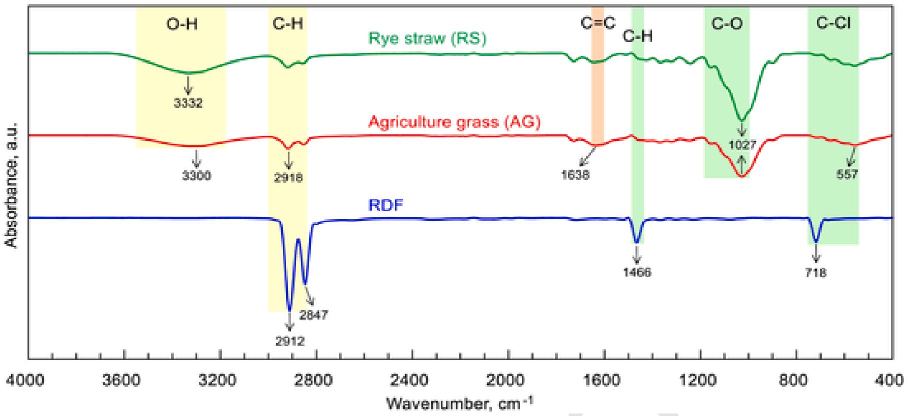

Fig. 2. FTIR spectra of biomass and RDF feedstocks.

Table 3
Share of groups of volatile compounds released during the microscale decomposition of studied feedstocks using the Py-GC-MS technique.

Compounds	Rye straw (RS)	Agriculture grass (AG)	RDF
Oxygen compounds, %	59.3	48.7	14.3
Hydrocarbons, %	4.1	7.2	84.8
Nitrogen compounds, %	0.3	6.5	0.0
Carbon dioxide, %	36.3	37.3	0.0
Organic chlorine compounds, %	0.0	0.3	1.0

ber of keywords, the two-year periods 2016–2017, 2018–2019, 2020–2021, and 2022–2023 were analysed. The changes in the cluster of the 40 most frequently used keywords are shown in Fig. 1.

The mapping was performed using VOSviewer version 1.6.20 [31]. This presentation of results allows you to identify connections between topics within the cluster. The red cluster is focused on research using catalysts for the production of biofuels. In 2022–2023, a new keyword “plastics waste” appeared in the red cluster. This can be interpreted as the focus of research on the use of plastics as feedstocks for co-pyrolysis. The number of keywords in the green cluster was usually lower than in the red cluster, with the exception of 2020–2021, where there were the same number of keywords. The keywords “co-pyrolysis” and “biomass” were always in the red or green cluster. When the keywords were analysed in the illustrated time periods, their migration between clusters was observed. In 2016–2017, the blue cluster focused on thermogravimetric research, based on which reaction kinetics and activation energy can be determined. However, from 2018 to 2023, biochar and adsorption were a hot research topic. To conclude, research directions regarding co-pyrolysis have evolved significantly in recent years. Research priorities include the use of plastics as a raw material for co-pyrolysis to increase the content of aromatic compounds in bio-oils and the hydrogen content in pyrolysis gas.

The multifaceted results of investigations of the pyrolysis of agricultural biomass and co-pyrolysis of biomass and RDF using advanced instrumental methods with special emphasis on the obtained product properties are exactly what this work has to offer. The novelty of co-pyrolysis of biomass and RDF lies in its ability to integrate waste valorisation, diverse feedstock utilization, and environmental sustainability into a single conversion technology. Especially the conversion of RDF (powder form) and specific lignocellulosic biomass waste via the co-pyrolysis process brings benefits in terms of its utilization. This study contributes to the field by exploring the co-pyrolysis of specific biomass wastes with RDF, aiming to optimize process parameters, enhance product quality, and provide a sustainable solution for waste utilization and energy production. The presented results are promising for advancing efficiency and innovation in the production of value-added products from waste.

2. Materials and methods

2.1. Materials

Two agricultural biomass feedstocks and RDF were investigated. Agricultural biomasses were rye straw (RS) and agriculture grass (AG). They came from the Polish agricultural region. The biomass feedstocks were milled (Fritsch Pulverisette 15 grinder) to obtain a uniform particle distribution (250–750 μm). The studied RDF in the form of power was obtained from the industrial company and it was a mixture of plastics.

2.2. Methods

Proximate analysis was done according to the following European standards: moisture (M) - ISO 18134–3:2023, ash content (A) - ISO 18122:2022, volatile matter (VM) - ISO 18123:2023.

Elemental analysis (carbon (C), hydrogen (H), and nitrogen (N) contents) was determined using Leco Analyser TruSpec 628 based on ISO 16948:2015–07. The fibre analysis was carried out according to PN-EN ISO 13906:2009 (to determine acid detergent fibre (ADF) and acid detergent lignin (ADL)) and the PN-EN ISO 16472:2007 standards (to determine neutral detergent fibre (NDF)).

FTIR ALPHA II apparatus (Fourier Transform Infrared Spectroscopy) was used to study the structure of studied materials. IR is adsorbed by defined frequencies directly connected with vibration energy of bonds between atoms in molecule. The FTIR spectrum is presented as a result of this analysis.

Pyrolytic gas from the pyrolysis was collected in the Tedlar bag and analysed using a gas chromatography (GC) system (Agilent Technology 7890A). GC apparatus was equipped with two detectors: a thermal conductivity detector (TCD) and a flame-ionization detector (FID). The following gases were detected: CH_4, C_xH_y, H_2, O_2, N_2, CO. C_xH_y means the sum of hydrocarbons such as C_2H_6, C_2H_4, C_2H_2, C_3H_6, C_4H_8, C_4H_{10}, C_5H_{12} that were present in trace concentration.

The Py-GC-MS technique was used to study the pyrolysis process toward detection of volatile matter released during this process. This unit consists of pyrolyser reactor coupled with GC-MS consisting of a gas chromatograph unit (Agilent Technologies, model 7890B) and a mass spectrometer (Agilent Technologies, model 5977A). The Py-GC-MS tests of studied feedstocks were done at 600 °C under inert atmosphere (helium) with 100 °C/s heating rate and next residence time 20 s. Mass sample was c.a. 1 mg. Compounds and their peak areas were found us-

Table 4
Share of the groups of volatile compounds released during the microscale decomposition of biomass and RDF mixtures using the Py-GC-MS technique (exp.) compared to the values estimated based on the linear model (cal.).

Mixture of biomass and RDF	75RS-25RDF		50RS-50RDF		75AG-25RDF		50AG-50RDF	
Identified compounds	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal
Oxygen compounds, %	38.5	48.1	10.5	36.8	25/6	40.1	20.8	31.5
Hydrocarbons, %	40.1	24.2	80.8	44.4	58.6	26.6	62.4	46.1
Nitrogen compounds, %	1.28	0.2	0.0	0.1	2.3	4.9	2.0	3.1
Carbon dioxide, %	16.7	27.3	7.6	18.2	13.6	28.02	14.7	18.7
Organic chlorine compounds, %	3.6	0.2	1.1	0.5	0.2	0.4	0.1	0.6

ing the deconvolution algorithm. Only compounds with a peak height greater than 0.5 % of the highest peak were considered. The MS spectra were interpreted based on the reference MS library (chemical base G1034C). The details of this procedure were described previous work [32]. In the case of co-pyrolysis of biomass and RDF the samples were not mixed but were putted in quartz pipe separated by quartz wool.

Thermal analysis (TGA) was carried out to investigate the thermal behaviour of studied feedstocks and their mixtures under nitrogen atmosphere to simulate pyrolysis conditions. The experiments were carried out under the following parameters: 40 mL/min of flow rate of nitrogen, 10 K/min heating rate, mass sample – c.a. 5 mg, crucible of Al_2O_3. The TG and DTG and DSC curves were obtained as an output.

The pyrolysis process was carried out in the fixed bed reactor at 600 °C under a nitrogen atmosphere (N_2 flow was 200 mL/min). A detailed description of this laboratory setup can be found in the previous work of authors [33]. Pyrolysis process parameters were as follows: mass sample – 1 g and residence time 3 min. Firstly, the pyrolysis of raw feedstocks was conducted to collect and analyse the properties of solid (char), liquid and gas products. Next, the co-pyrolysis experiments were conducted to investigate the impact of RDF addition on the properties of products. Mixtures of 75:25 and 50:50 wt % ratios (biomass to RDF mass ratio) were investigated. Respectively, the samples were named: 75RS-25RDF, 75AG-25RDF, 50RS-50RDF, and 50AG-50RDF.

3. Results and discussion

3.1. Biomass and RDF characteristics

The proximate and ultimate analyses of the feedstocks are presented in Table 2. Rye straw and agricultural grass are characterised by similar physical and chemical properties, but AG contains a higher ash content and, consequently, lower volatile matter. Ash content and volatile matter are factors that can influence the yield of products. Ash can catalyse undesirable secondary reactions (char oxidation or tar formation) which can reduce the yield of bio-oil. The higher volatile matter content generally correlates with the higher yield of gaseous products, as these compounds are thermally decomposed into gases such as methane, carbon monoxide, and hydrogen. The carbon and hydrogen contents in AG are slightly higher than in RS. Results of proximate and ultimate analysis for RS are in line with those presented by Chakravarty et al. [34]. Analysing the structural composition of biomass samples (based on fibre analysis) it can be observed that both biomasses were mainly built of cellulose (c.a. 40 %), followed by hemicellulose (c.a. 26 %) and the lower content of lignin. Thus faster pyrolysis rate can be expected because of cellulose-rich biomass. On the other hand, lignin can inhibit the thermal polymerisation of cellulose, and lignin (complex and aromatic structure compound) can contribute to the formation of char during pyrolysis. RDF characterises quite different properties than biomass feedstock. It contains very high carbon and hydrogen contents, and volatile matter (93 %), and negligible water content. The differences in structural composition between biomass and RDF were additionally confirmed by the FTIR analysis (Fig. 2).

For biomass samples, the spectra coming from vibrations of O–H (3330 cm^{-1}), C–H (2918 cm^{-1}), C═C (1638 cm^{-1}), and C–O (1027 cm^{-1}) are visible. The cellulose strong peak was identified in the range 1200-1000 cm^{-1} (C–O stretching) for RS and AG. The relative intensity of this peak confirms that RS contained a higher amount of cellulose [35]. For RDF, the peaks at 2912 and 2847 cm^{-1} are attributed to the presence of an alkene is suggested by the symmetric and antisymmetric stretching modes of the CH_2 group [36]. 1466 cm^{-1} is attributed to the bending vibration of aliphatic C–H indicating the presence of a methyl group in alkanes [36]. The peak at 718 cm^{-1} is related to functional groups such as C–H and C═C bending (alkene) confirming the presence of high and low-density polyethylene (HDPE and LDPE) [36].

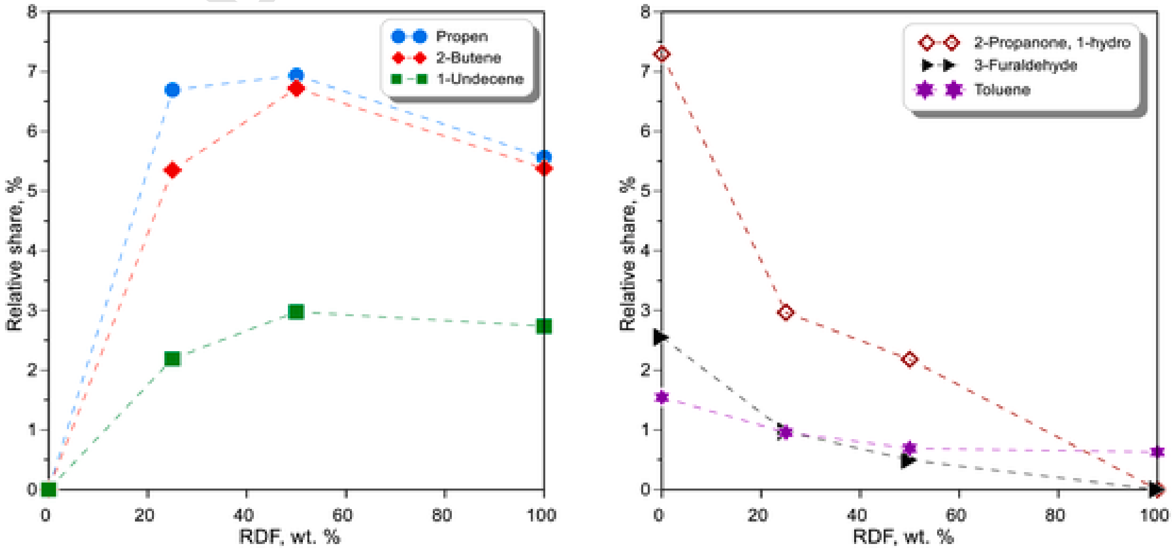

Fig. 3. The relative share of selected compounds released during the microscale decomposition of a mixture of rye straw with the addition of RDF (Py-GC-MS).

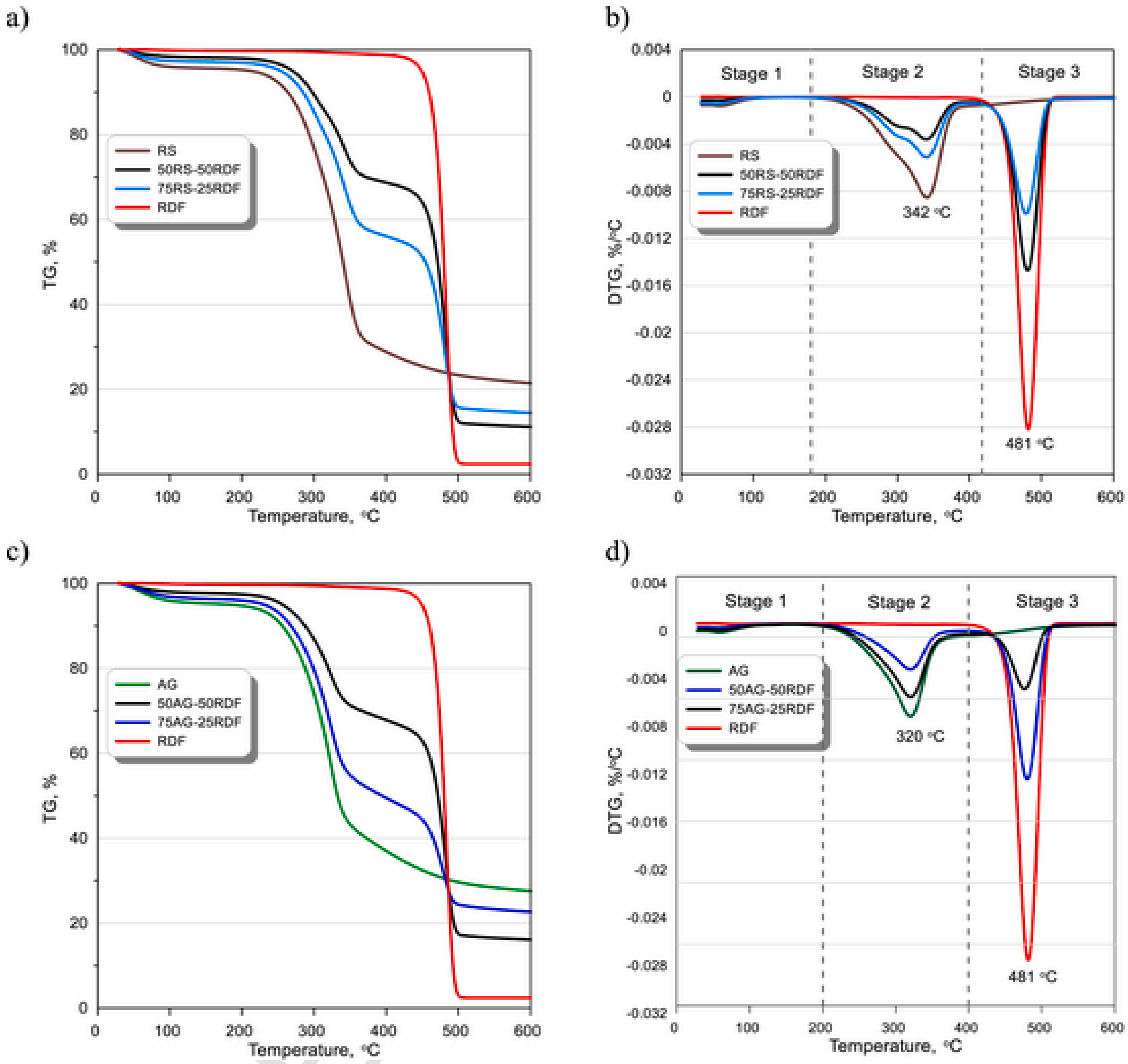

Fig. 4. Thermogravimetry results of pyrolysis (under N_2 atmosphere): a) TG curves for rye straw (RS), RDF and mixture RS-RDF, b) DTG curves for rye straw (RS), RDF and mixture RS-RDF, c) TG curves for agriculture grass (AG), RDF and mixture AG-RDF, d) DTG curves for agriculture grass (AG), RDF and mixture AG-RDF.

Table 5
Elemental analysis of products of pyrolysis and co-pyrolysis.

Sample	N, wt%	C, wt%	H, wt%
Char (solid phase)			
RS	1.07	77.35	2.82
AG	2.19	67.25	2.50
RDF	0.47	9.76	0.78
75RS-25RDF	1.13	76.94	2.62
50RS-50RDF	1.20	70.68	2.50
75AG-25RDF	2.11	66.32	2.41
50AG-50RDF	2.07	62.96	2.25
Liquid phase			
75RS-25RDF	0.28	55.74	10.95
50RS-50RDF	0.25	63.75	11.50
50AG-50RDF	1.17	57.62	11.00

3.2. Py-GC-MS analysis

The Py-GC-MS technique allowed us to analyse the composition of volatile matter released during the pyrolysis process for the feedstocks studied and the next for the mixture of biomass and RDF. The investigation aimed to evaluate the potential of utilization of biomass and RDF mixtures through pyrolysis, as well as the identification of raw material building blocks, i.e. polymer type (for RDF) based on the composition of formed thermal degradation products. The obtained results indicated that the amount of released compounds during thermal decomposition varied between studied feedstock. In the case of the RDF sample, it reached even c.a. 300 chemical compounds, while pyrolysis of biomass samples caused the release of around half of the mentioned number. Thus, the released analytes (particularly for RDF) can be recognized as highly complex mixtures composed of compounds with different volatility (low- and high-boiling fractions). To facilitate discussion of the results, the organic species identified by Py-GC-MS analysis were divided into the following five groups of compounds: i) carbon dioxide (CO_2), ii) hydrocarbons (C_xH_y), iii) oxygen compounds having at least one O atom, iv) nitrogen compounds having at least one N atom, and v) chlorine compounds. The yield of each group is calculated relatively as a ratio of the peak area of all compounds within the group to the total peak area of all compounds in all groups. Table 3 shows the share of groups of compounds identified during the microscale pyrolysis process.

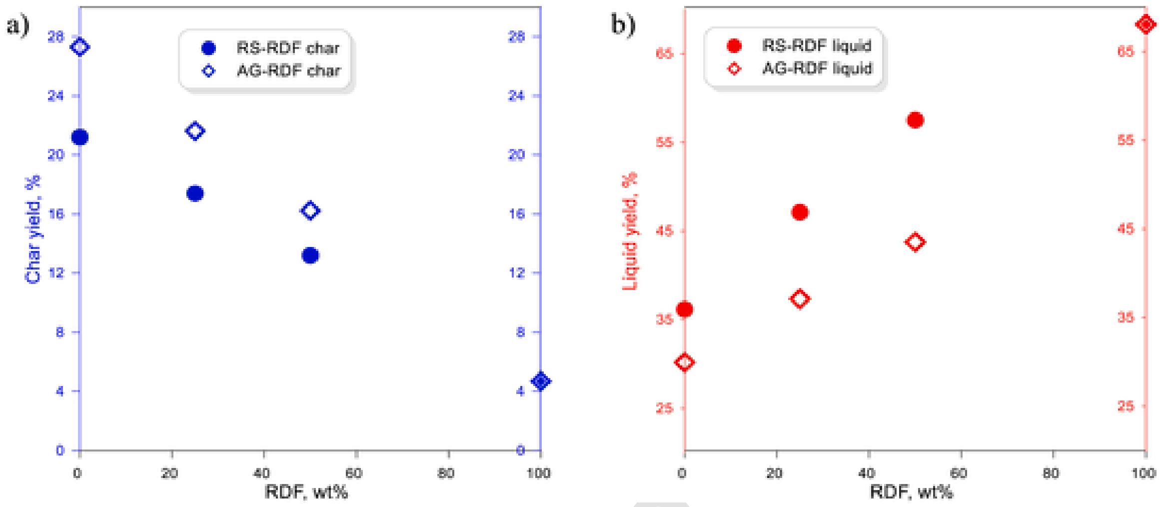

Fig. 5. Chars (a) and liquid (b) yields of biomass and RDF co-pyrolysis process.

As can be seen in Table 3, the hydrocarbons were dominant among volatile products of the pyrolysis of RDF. In the hydrocarbons group, the aliphatic hydrocarbons with saturated and unsaturated as well as single and double bonds were mainly presented. Monounsaturated alkenes were formed in the greatest amount. Among the identified hydrocarbons, the following exemplary compounds were identified:

(i) alkanes (hexane, heptane, decane, tridecane, pentadecane, octadecane, pentacosane),
(ii) alkenes (2-butene, 1-pentene, 1-decene, 1-dodecene, 1-pentadecene, 1-nonadecene),
(iii) dienes (1,4-pentadiene, 1,5-hexadiene, 1,9-decadiene, 1,19-eicosadiene),
(iv) cyclic hydrocarbons (cyclopropane, cyclopentene, 1,3-cyclohexadiene, and cyclohexene).

This, together with the characteristic shape of the chromatogram, suggests the noticeable contribution of polyolefins (PP, PE) in the studied RDF. Thermal cracking of polyolefins occurring during pyrolysis generates mainly a mixture of kinds of paraffin and olefins of varying lengths. It is caused by the radical mechanism that relies on the random homolytic cleavage of C–C bonds which form two different radicals. Primary decomposition products are not stable and consequently could undergo a series of secondary reactions involving hydrogen transfer, tending to form more stable radicals. Random scission of the macromolecular structure and intensive secondary reactions lead to radicals of varying molecular sizes [37]. Ultimately, this leads to a dominating share of linear paraffins, olefins, and dienes with a wide range of molecule sizes. This is in line with the present investigation, where molecules with shorter chain lengths (C4–C10) have been identified together with those with longer chain lengths (C20 +). These findings are in line with previous reports in the literature [37,38]. Various types of naphthene and aromatic compounds were also detected, indicating the presence of, e.g., polystyrene. However, it is worth mentioning that the formation of aromatic compounds could also occur in a limited range during the pyrolysis of the mentioned polyolefins. Some halogens had also been identified in the evolved products, but the amount was not significant (1 %), for example, 1,3-dichloropropanol and 5-chloro-pentyne suggested the presence of PVC (polyvinyl chloride) in the RDF.

The share of products generated during the pyrolysis of rye straw and agricultural grass was noticeably different from that of the thermal decomposition of RDF. For RS and AG, the main group of compounds was oxygen compounds such as cyclic oxygen compounds (e.g. furans: methyl furan, cyclic ketones), and aliphatic oxygen compounds (acids, aldehydes, and ketones). The high content of oxygen compounds directly corresponds to the biochemical composition of studied biomass samples. Both biomass feedstocks were characterized by a noticeable content of polysaccharides which can be recognized as high-oxygen building blocks. The total content of hemicellulose and cellulose was equal to 67.15 wt% and 65.61 wt% for RS and AG samples, respectively. The release of hydrocarbons during biomass pyrolysis was rather low. It should be noted that, in the case of AG, the presence of nitrogen compounds was higher than that of RS. This could be linked to a higher protein content. In the case of biomass feedstocks, approximately 37 % of the share constituted CO_2. It proves that, during processing, deep deoxygenation of pristine building blocks occurs *via* the decarboxylation reactions. On the contrary, a very low oxygen content for RDF (< 2.85 wt%) resulted in a negligible CO_2 content. As mentioned above, RDF pyrolysis is mainly dominated by cracking of high-molecular polymer structures.

The second part of the Py-GC-MS analysis focused on the co-pyrolysis process of biomass and RDF feedstock. It should be noted that the released volatile mixture was a highly complex group containing both saturated and unsaturated hydrocarbons, as well as oxygen compounds with a wide spectrum of functional groups. To facilitate comparative analysis of the co-processing effect, all compounds identified in this series were divided in the same way as for individual raw materials. Furthermore, for comparative analysis, the results of calculation using a linear model (weighted average of feedstock mass fractions and shares of identified groups of compound) were added to Table 4.

In an analysis of the results obtained, it can be stated that regardless of the ratio of biomass to RDF in the mixture, hydrocarbons and their oxygen derivatives were the dominant group of compounds released during co-pyrolysis. Even 25 % of the mass of RDF added to rye straw significantly increased the share of hydrocarbons (40 %). The share of oxygen compounds decreased by more than 1/3 compared to the results obtained in the case of decomposition of raw biomass. The release of hydrocarbons seems to be very beneficial from the perspective of increasing the application potential of volatile pyrolysis products that can be a type of alternative fuel. They can enhance the energy value of the fuel and after additional treatment can be used as by-products to value-added materials. It should be noted that the share of hydrocarbons released during the pyrolysis was significantly higher than the one calculated from the linear model. The experimental share of hydrocarbons increased in the range of 10–25 %. The increase in hydrocarbon content in mixtures even with a small addition of RDF may be related to (i) the

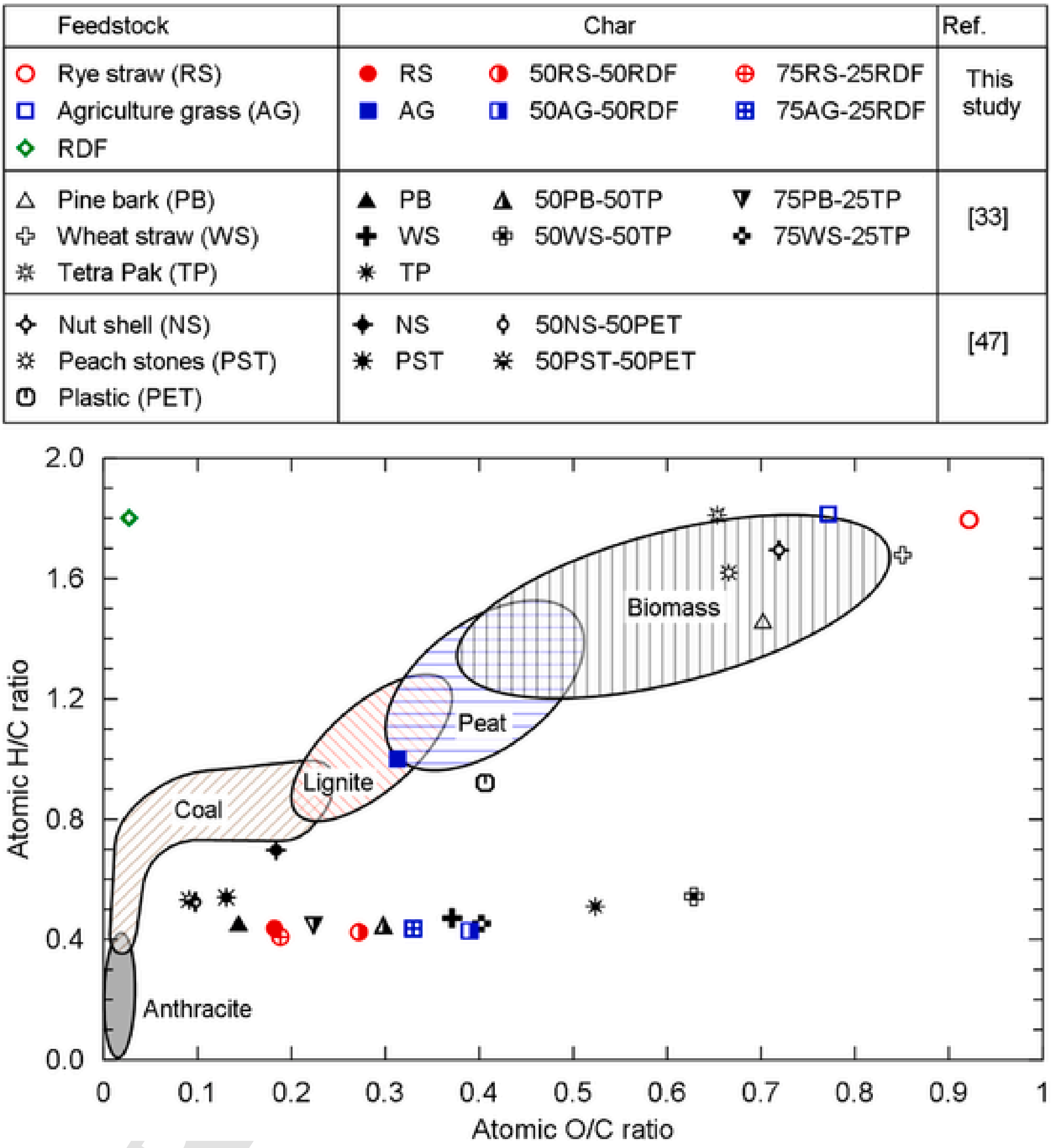

Fig. 6. Van Krevelen diagram.

positive impact of the presence of unsaturated alkenes in the formed products, i.e. stabilisation of the released reactive oxygen compounds, and (ii) incomplete pyrolysis of rye straw. These conclusions are consistent with the observation of changes in the share of other groups of compounds (oxygen compounds, CO_2, nitrogen, and chlorine compounds), where their shares are below the estimated values. For example, the share of oxygen compounds in the case of conversion of RDF and rye straw (Table 4) was 10 % and 26 % lower, respectively, by 25 % and 50 % of RDF addition. It should also notice significantly lower CO_2 content from the experiment than from the model. Upon analysis of individual feedstock, it was observed that during the pyrolysis of agricultural straw, the nitrogen content was the highest, which was reflected during co-pyrolysis with RDF. Similar trends in volatile released during of co-pyrolysis of agriculture grass and RDF were recorded. The increase of hydrocarbons was observed with a simultaneous reduction in the relative share of other groups of compounds, especially oxygen compounds. Hydrocarbons increased by 15–30 %. The amount of CO_2 was lower than expected.

Overall, differences between the theoretical and experimental results can be assigned to the various levels of conversion ratio and consequently noticeable differences in the yields of solid residue and released volatiles. The RDF sample is converted almost completely, forming mainly a mixture of volatiles (only ca. 2.4 wt% of residue), while the pyrolytic residual matter after pyrolysis of biomass was between 21.4 wt% and 27.5 wt%. Taking into account that the presented results of Py-GC-MS analysis are calculated as a relative ratio it can affect observed differences between theoretical and experimental values. Moreover, in the present contribution, we used a resistive pyrolyzer unit in which some inaccuracies can arise from inconsistent pyrolysis temperatures and non-uniform sample heating. Thus, resistive Py-GC-MS is use-

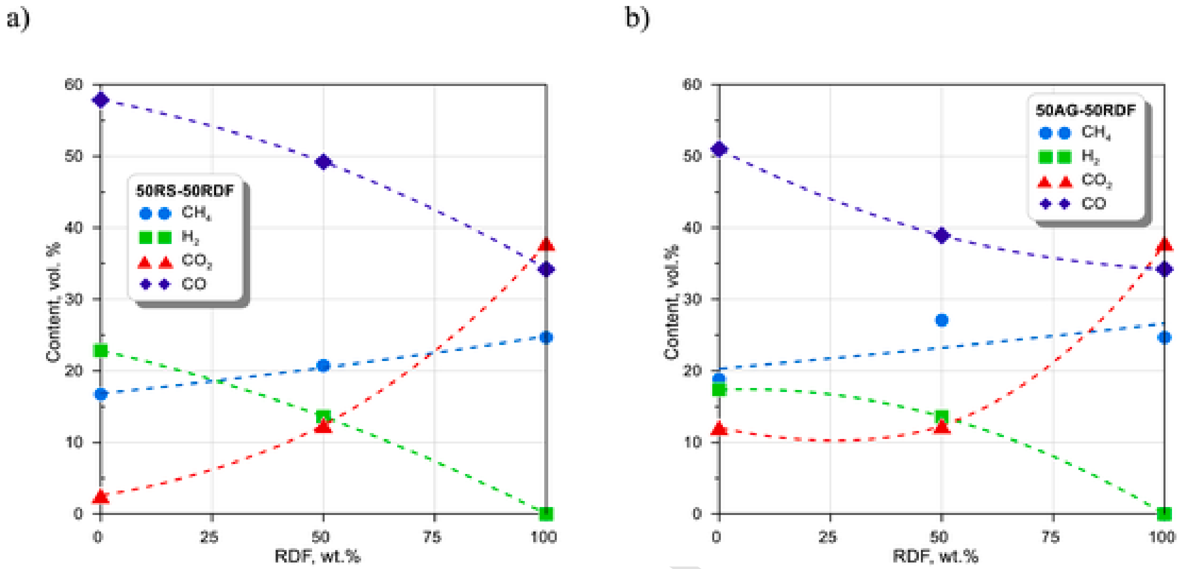

Fig. 7. Chemical composition of pyrolysis gas from pyrolysis of raw feedstocks and mixtures: a) 50RS-50RDF; b) 50AG-50RDF based on gas chromatography analysis.

ful for qualitative or identification analysis of raw material, but quantitative determinations may be burdened with greater uncertainty [39].

Chemical compounds, typical for the decomposition of saccharide, lignin, and polymer origin were selected and presented as a function of the addition of RDF in Fig. 3. The differences between biomass (rye straw) and RDF are very strong. The addition of 25 % of RDF caused a high share of hydrocarbons (e.g. propene, 2-butene, and 1-undecene). These compounds are released during the cracking of primary polymer structures. The high share of monounsaturated aliphatic hydrocarbons allows them to be attributed especially to the decomposition of polyolefins. The share of hydrocarbons as a function of the share of added RDF deviates significantly from the linear model. In the case of the demonstrated oxygen compounds, the decrease in their amount went with the increase of RDF amount. The high share of oxygen-containing compounds resulted directly from the structure of biomass, which is built with rich-oxygen biopolymers.

3.3. *Thermal analysis*

To investigate the thermal behaviour under pyrolysis conditions, a thermal analysis was carried out. The relative contributions of volatile matter and residue can be defined to the overall decomposition process by analysing the mass loss rate at different temperature intervals. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves for biomass pyrolysis, RDF and the biomass and RDF mixture are presented in Fig. 4. The results of pyrolysis of rye straw and agricultural grass showed similar behaviour. The pyrolysis of RDF took place in a different temperature range due to the different chemical composition, which was expected and proofed by other studies [36]. For biomass samples, small weight loss reflected moisture release (stage 1) was observed at 200 °C, whereas for RDF no weight loss was detected (as was expected according to the final analysis). The main weight loss (stage 2) during rye straw pyrolysis was in the wide temperature range from 220 °C to c.a. 500 °C with a DTG peak at 342 °C. For agriculture grass thermal behaviour under pyrolysis conditions looks similar with the maximum rate at 320 °C. In this stage, the amount of mass loss was c.a. 70 % mainly due to decomposition of hemicellulose, cellulose, and lignin. Based on the DTG curve, the characterised peak for hemicellulose was not observed, but cellulose was strongly visible at 342 °C (RS) and 320 °C (AG). Temperature range of 230–400 °C is typical for decomposition of fiber compounds like hemicellulose, cellulose, and partial lignin during the pyrolysis process [25]. Solid residues were 21.4 % for RS and 27.5 % for AG. The thermal decomposition of RDF occurred in a narrow temperate range of 410–500 °C with a peak DTG at 481 °C reflecting the decomposition of hydrocarbons. The single-step decomposition pattern observed within a specific temperature range aligns with previously reported data on the decomposition of PE (both LDPE and HDPE), PP, and PET [40]. The residual mass of RDF can be seen to be 2.4 %. For the mixture of biomass and RDF, the TG and DTG curves are the result of raw feedstock. The maximum heating rate ($DTG_{max.}$) was detected at the same temperature as for raw feedstock, but the values were lower.

Results of thermogravimetric analysis were used for the calculation of the characteristic parameter describing pyrolysis reactivity (Eq. (1)) [26,41]:

$$RM_{tot.} = 100\sum_{i=1}^{n}\left(\frac{-DTG_{P,\max}}{T_{P,\max}}\right)_i \qquad (1)$$

where peak temperature $T_{P,max}$ (°C) an average and maximum pyrolysis rate, $-DTG_{P,max}$ (%/min) [42].

The RM_{tot} for biomass samples was similar 0.043 and 0.458 %/min°C for AG and RS, respectively whereas for RDF significantly higher at 0.0748 %/min°C. The co-pyrolysis (addition of RDF to biomass) had increased the reactivity of pyrolysis (75AG-25RDF - 0.0486; 50AG-50RDF - 0.0576, 75RS-25RDF - 0.0539; 50RS-50RDF - 0.0576 %/min°C). These data shows that the co-pyrolysis of agricultural biomass with RDF (plastic waste) gives better results than the pyrolysis of individual agricultural biomass [43].

3.4. *Co-pyrolysis in a fixed-bed reactor: yield and product characteristics*

During the pyrolysis of raw feedstocks and co-pyrolysis of biomass and RDF the char (solid phase and carbon-rich material), pyro-oil (liquid phase obtained from the condensation of volatile gases and vapours released during pyrolysis), and gas (mixture of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), hydrocarbons and other trace gases) were collected to further analysis.

The elemental analysis of chars and liquid phases obtained by pyrolysis of biomass and RDF samples and its mixture is presented in Table 5. There was a significant increase in carbon content up to 77.35 % rye straw char and 67.25 % for char from agricultural grass suggesting the char yield was high. For RDF the carbon content dramatically decreased up to 9.76 % confirming high liquid yield. The addition of 50 % of RDF to biomass did not affect carbon content as it could have resulted from the calculation. For 50RS-50RDF and 50AG-50RDF the waxes were collected, too, and there were detected c.a. 55 % of C and 11 % of H. As presented in Ref. [44] additives of PE plastics result in a decrease of carbon and hydrogen content. These results additionally indicate a decrease in volatile matter content in solid residue. The yields of char and liquid phases are presented in Fig. 5. The char yield for AG was higher (27.3 %) than for RS (21.2 %). The addition of RDF to biomass (75:25 and 50:50) decreased the char yields to 16.2 % and 13.2 %, respectively for AG and RS. Studies described in the publication [45] indicate that the highest char yields were achieved at 500 °C and a 50:50 proportion of plastic waste additives. The liquid yield was higher for RS (35.9 %) than for AG (29.9 %). Other studies reveal an increase of liquid yield with an increase of RDF additive at the same time decreasing char-yield [11], which is in line with presented results. Co-pyrolysis of RDF with biomass gave a better synergetic effect for RS than for AG. Based on the experiment the liquid yield was 57.3 %, whereas based on calculations, the liquid yield should be 5 % lower. Interesting results were obtained for gas yield. The gas yield was calculated by difference (100 % – char yield – liquid yield). The yields for pure feedstocks were comparable (c.a. 40 %). The presence of RDF did not influence on gas yield for agricultural grass, but for rye straw (50RS-50RDF) caused a decrease of the yield by 13 %.

To analyse the carbonization process the Van Krevelen diagram (Fig. 6) was created [46], with the molar ratios of H to C and O/C calculated based on the compositions from Tables 2 and 5. Moreover, the results obtained in this study are compared to other literature reports [33,47]. Rye grass is close to the typical biomass area, but not included in it. Increasing the degree of carbonization due to co-pyrolysis of biomass and RDF manifests an increase in H/C and O/C molar ratios compared to biomass raw materials.

Fig. 7 shows the compositions of the main components of gas from pyrolysis and co-pyrolysis of feedstocks. The thermal breakdown of biomass components (cellulose, hemicellulose, and lignin) and RDF results in the creation of a mixture of gases. Obtained gaseous products consist mainly CO, CO_2, H_2 and CH_4, as it was expected based on the other studies [48]. The calorific value of gas from RS pyrolysis was higher than for AG. The addition of RDF for both biomass (50RS-50RDF and 50AG-50RDF) decreased the content of CO and H_2, and simultaneously increased CO_2 and CH_4. CO emission during the pyrolysis is correlated to the decomposition of hemicellulose and cellulose [48], due to this fact increase in RDF content results in decrease of CO content. The content of C_xH_y, which included hydrocarbons like C_2H_6, C_2H_4, C_2H_2, C_3H_6, C_4H_8, C_4H_{10}, C_5H_{12}, was negligible (below 1 %). The quality of gas from co-pyrolysis is not a problem, because in this study the main aim was to obtain bio-oil.

4. Conclusions

In this work, co-pyrolysis of rye straw (RS) and agricultural grass (AG) with RDF (75RS-25RDF, 50RS-50RDF, 75AG-25RDF, and 50AG-50RDF) was investigated. The main conclusions are as follows:

- for mixture of biomass and RDF the content of oxygen in volatiles was significantly reduced simultaneously the content of hydrocarbons increased,
- thermal behaviour of biomass and RDF mixtures was resultant of individual feedstocks,
- the addition of RDF to biomass did not cause the expected reduction of the carbon content in the chars, which resulted from biomass to RDF ratio,
- analysing the liquid yield, it was observed a positive effect of the addition of RDF to rye straw.

Co-pyrolysis of biomass and RDF confirmed the benefits of RDF application. The addition of RDF positively influenced product yields and quality. The co-pyrolysis of these two types of waste materials offers a novel approach to their valorisation according to the circular economy and sustainable waste management, especially because the studied RDF is a difficult material for the pyrolysis process. In conclusion, co-pyrolysis of biomass and RDF has the potential to be an effective way to convert waste into energy and produce useful char, bio-oil and even gas. However, careful consideration of the feedstock used and the pyrolysis conditions is needed to ensure that the process is efficient, sustainable, and environmentally friendly.

CRediT authorship contribution statement

Aneta Magdziarz: Writing – review & editing, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Wojciech Jerzak:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis. **Mariusz Wądrzyk:** Writing – original draft, Methodology, Investigation, Formal analysis. **Małgorzata Sieradzka:** Writing – review & editing, Writing – original draft, Visualization, Investigation.

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.

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