



Conversion of microwave pyrolysed ASR's char using high temperature agents

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ABSTRACT

Pyrolysis enables to recover metals and organic feedstock from waste conglomerates such as: automotive shredder residue (ASR). ASR as well as its pyrolysis solid products, is a morphologically and chemically varied mixture, containing mineral materials, including hazardous heavy metals. The aim of the work is to generate fundamental knowledge on the conversion of the organic residues of the solid products after ASR's microwave pyrolysis, treated at various temperatures and with two different types of gasifying agent: pure steam or 3% (v/v) of oxygen. The research is conducted using a lab-scale, plug-flow gasifier, with an integrated scale for analysing mass loss changes over time of experiment, serving as macro TG at 950, 850 and 760 °C. The reaction rate of char decomposition was investigated, based on carbon conversion during gasification and pyrolysis stage. It was found in both fractions that char conversion rate decreases with the rise of external gas temperature, regardless of the gasifying agent. No significant differences between the reaction rates undergoing with steam and oxygen for char decomposition has been observed. This abnormal char behaviour might have been caused by the inhibiting effects of ash, especially alkali metals on char activity or due to deformation of char structure during microwave heating.

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1. Introduction

The automotive industry generates worldwide about 50 million tones of waste every year [1]. Presently, roughly 75% of a vehicle's weight is recovered, mostly its metal contents. The remaining part of 25% seeks for an appropriate waste management system apart from land-filling. This remaining part is mechanically processed to a fraction called automotive shredder residue (ASR) or "car fluff".

ASR is a complex mixture containing a variety of materials, some of which may be toxic or potentially harmful. In the recovery process, useful and possessing higher value materials have to be separated and the hazardous species neutralized or destroyed. Magnetic and mechanic separation is used to separate ferrous materials, non-ferrous materials and fluff [2]. Separation is, however, not ideal thus foreign fractions can always be found in the main fraction. Fluff consists of plastics, rubber, paints, textiles, ceramics, glasses, metals and other materials [1–6]. Its exact composition can vary a lot, since ASR derives from different year, type and brand of vehicles. Nevertheless, the organic part of ASR (polymers, rubber, textiles, fibers, etc.) contributes to about 50–80% of

ASR weight, which suggests treating ASR with thermal methods for feedstock and energy generation. It also contains heavy metals including copper, aluminium, lead, cadmium, chromium and others which should be recycled due to their harmful effects on the natural environment. Poly-vinyl chloride (PVC) and halogen-containing materials should be removed before thermal treatment [4–6].

The most common and cost-efficient method of handling ASR is energy recovery via combustion [7,8]. However, the drawbacks of combustion such as: low energy efficiencies (13–24%), fouling and slugging problems, along with emissions of following pollutants HCl, SO_x, NO_x, HF and VOCs call for other methods of ASR treatment. Among the most promising methods are pyrolysis [9–13] and/or gasification [14–18]. In case of ASR, one of the most important advantages of the pyrolysis and gasification over combustion is that, that the process is conducted under an oxygen-free/oxygen-lean, respectively, and relatively low operating temperature conditions (500–1000 °C). The first process, pyrolysis, turns organic matter into volatile hydrocarbons (both is liquid and gas phase) and solid charcoal, meanwhile gasification generates synthesis gas (producer gas). Both gasification and pyrolysis' products can be used for an energetic purpose, directly, or can be utilized as an intermediate raw resource for feedstock (i.e. feedstock recycling). Therefore, both highlighted processes, enable thermo-chemical recycling of an organic content of ASR in which value-added feedstock is generated, whilst most of metals remain densified in solid residues. Furthermore, metals contained in ASR

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should be recycled not only from an environmental point of view, but also because they have high marketable values. Even though the metals content in fluff can be relatively low (in the range of 5–10%), they should be recovered with the highest possible yield. However, along with metals in solid fractions after pyrolysis, a significant amount of char/coke is formed – up to 50% of product distribution [10,11].

In current paper ASR was pyrolysed using a novel microwave technique [10,11]. In this process, (similarly to microwave cookers) a magnetron generates microwaves that induce the oscillations of certain molecules, mainly dielectrics. The frequency of waves is set to attract hydrocarbon – a main constituent of polymers. The heat is generated volumetrically within the material so the material is heated up more uniformly from inside [10,11,19–23]. Thus improved heating efficiencies are achieved as compared with conventional techniques that use external heating sources [20]. However, the heating induced by microwave is selective to the type of material which differs in its response to microwave radiation. The materials can be grouped into three types according to their interactions with microwave: (a) conductors which reflect radiation, creating on the surface eddy currents; (b) insulators which are transparent for radiation; (c) dielectrics which absorb microwave radiation [22]. Thanks to these properties of microwave radiation, this technique found many applications involving heating i.e. drying, synthesis, pyrolysis, etc. Due to the good thermo-isolative properties of plastics, the heat absorbed for pyrolysis, can be used more effectively (Forsgren) [11]. Therefore similar product distribution can be obtained for relatively lower temperatures compared with conventional pyrolysis. From the other hand the difference in absorption of microwave radiation by different substances creates some difficulties for handling mixtures like waste in order to maintain a stable operation (mainly temperature) conditions. This was observed by Forsgren [11] who noticed that charcoal (carbon black) present in tires, as a good dielectric, absorbs microwave radiation with a higher efficiency. He also found that it is capable of generating at the same input power, local hot-spots of over 1000 °C inside the waste mixture, but for the same conditions the polyurethane foams can be barely heated up to 200 °C.

This has an effect on solid residues after microwave treatment of ASR, in which the char structure should be less uniform compared with the pyrolysis using external heating systems. Also porosity of char can be reduced which will effect on heterogeneous carbon – steam and carbon oxygen reaction rates [10,16,19,20]. The treatment of ASR using microwave pyrolysis reduces the volume of waste up to 90% (75% by weight) and generates the product consisting 11–16% of gaseous, 22–30% of liquid and 59–62% of solid products, dependently on a type of fraction used for investigations [10].

In order to decrease the stream of waste generation from pyrolysis and increase the process efficiency, the resulting solid fraction needs to be also utilized. This research suggests using the pyrolysed char as a fuel for high temperature agent gasification (HTAG) process. The use of HTAG is advantageous comparing to conventional gasification in terms of obtaining higher conversion of fuel to gas, higher hydrogen yields and relatively lower tar content, which has been found by number of researchers, involved in HTAG development [16–18,24–28]. Hence, the application of HTAG to reduce the post-pyrolysis products would result in maximizing the material and energy recovery rates from a unit of waste/fuel. Such system has been introduced and discussed in our previous work presented in [10].

The aim of this paper is to provide the knowledge of the char reactivity for steam and oxygen gasification in respect to two different types of solid residues obtained from microwave pyrolysis of a low and a high density fraction of ASR, respectively. This work should build a better understanding of an influence of microwave

pyrolysis process on char formation and its reactivity with gasifying agents which is desirable for designing the whole system.

2. Materials and methods

2.1. Sample pretreatment

In order to be able to apply sink-float separation method, materials that absorb water need to be removed. Therefore, raw ASR was separated into “light” and “residual” fractions in an air separator. The light fraction comprises materials absorbing water i.e. expanded polyurethanes, lighter plastics and textiles. It also contains fine metal particles sustaining in foamy materials which were difficult to remove. After removing the light fraction, the residual fraction was further treated by a magnetic separator and a wet-process in which metals, PVC, ceramics were captured leaving the mixture rich in thermoplastics, resins and rubber. This mixture creates a heavy plastic fraction. Both light and heavy fractions were treated separately by means of microwave pyrolysis. The product distribution comprises gaseous/liquid/solid products in the ratio 16/22/62 for the light fraction, and 11/30/59 for the heavy fraction, respectively [10,11]. The generated solid residues after microwave pyrolysis, which are the subject of this investigation, received the corresponding nomenclature “Light Fraction” – LF and “Heavy Fraction” – HF.

Both samples were shredded in a mortar and later grinded in a knife miller to reduce a maximum particle diameter, then they were sieved on mesh 0.5 mm. This procedure was repeated until the sizes of the particles were below 0.5 mm. In order to improve the grinding process, the sample was kept in liquid nitrogen to reduce the sample temperature far below the glassy temperature.

2.2. Sample characterization

The pyrolysis experiments have been conducted by the Stena Metall AB. The samples have been sent for further treatment using HTAG. An ultimate and proximate analysis of solid products generated, separately, from the microwave pyrolysis is presented in Table 1.

The light fraction after treating with a microwave pyrolysis denoted 40% of organic carbons and 50% of ashes. This fraction is referred in the current paper as a light fraction (LF). The ash content in the LF is rich in zinc (Zn), iron (Fe) and aluminium (Al).

Contrary to LF, the ash content in HF is relatively low ca. 10% and the organic carbon contributes to ca. 80% of the sample weight. Ash composition in HF is also differing from LF, showing that its main component is zinc as it is presented in Table 1.

2.3. Experimental set up and procedure

A unique high-temperature air/steam, batch-type reactor powered by a 10 kW burner build at Royal Institute of Technology Stockholm, Sweden was used for char investigation. The general view of this facility is showed in Fig. 1.

The system works in three different modes: heating up, main process and cooling down. In the beginning the facility is heated up by combustion of natural gas. Air and natural gas (CH₄) is fed to the burner (20) via the inlets (1). The ceramic honeycomb (3) accumulates the heat from combustion that afterwards is used for gasification or pyrolysis, dependently of gas going to be used.

For current investigations two types of gasifying agents were used: steam or a 3% oxygen–nitrogen mixture. Dry steam of a temperature around 180 °C and nominal pressure of 2 bars generated in a steam boiler or a mixture of 3% oxygen enters the system via one of the inlet (1). The gasifying agent while passing through a ceramic honeycomb is rapidly heated up to desired temperatures,

Table 1
The proximate and ultimate analysis of tested material.

Analysis	Symbol	Units	Heavy fraction	Light fraction	Method
Proximate analysis					
Moisture	W	%	0.8	2.34	IB/TL/26/01:2008 met. gravimetric
Ash	A	%	9.11	49.74	IB/TL/31/01:2008 met. Thermogravimetric
LHV	Q	kJ/kg	32,124	14,982	IB/TL/07/05:2007 met. calorimetric
Volatiles	V	%	20.3	27.67	IB/TL/28/01:2008 met. gravimetric
Ultimate analysis					
Dry basis					
Carbon	C	%	84.58	38.76	IB/TL/30/01:2008 IR absorption
Hydrogen	H	%	2.82	2.67	IB/TL/30/01:2008 IR absorption
Sulfur	S	%	1.01	1.18	IB/TL/29/01:2008 IR absorption
Nitrogen	N	%	0.12	3.58	IB/TL/30/01:2008 met. calorimetric
Oxygen	O	%	2.3334	3	By difference
Chlorine	Cl	%	0.0266	0.6044	PN-ISO 587:2000 p7.2.1. met. Titration
Ash composition					
Zinc	Zn	ppm	10,534	9508	IB/TL/04/04: The analysis have been performed with plasma spectrometer: ICP OES using ASCRM-010 as the reference substance.
Copper	Cu	ppm	76	1199	
Lead	Pb	ppm	50	1253	
Nickel	Ni	ppm	20.1	292	
Chromium	Cr	ppm	17	605	
Cadmium	Cd	ppm	nd	19	
Manganese	Mn	ppm	66	1491	IB/TL/08/04:
Aluminium	Al	ppm	2516	14,057	
Iron	Fe	ppm	2524	91,677	

which is measured by the S-type thermocouple (19). The maximum operating temperature can be around 1050 °C. The initial temperature of the gas should be higher for about 100 °C than the expected temperature for the experiment. The honeycomb, in addition, can keep a homogeneous temperature distribution inside the reaction chamber and constant delivery gas temperature for about 12 min. The reaction chamber is a tube of a diameter 80 mm. In this study a fine powdered sample, in amount of approximately 2 g, is placed in a cylindrical basket (18) specially designed for the purpose of the current investigations. The basket is attached through a thin platinum wire (6) from the top of the reactor to the digital scale (7) which is fixed above the tight-air hatch of facility (8). The wire passes through a small hole drilled through the hatch of the gasifier but can freely move inside. A small and controlled amount of nitrogen is added via inlet (5) in order to create overpressure,

which will prevent uncontrolled air penetration into the reaction system. The basket within a portion of approximately 2 g of sample can be hanged in two positions: inside the cooling chamber above the reaction zone, fed with nitrogen (for conditioning, adjusting present parameters, initial sample scaling etc.) and in the middle of the reaction chamber for the mass loss measurements. The basket has an 8 mm diameter, 80 mm height and mesh size diameter of 40 μm. It is made of cobalt and nickel based-alloy resistant for temperatures up to 1200 °C. The balance measures the weight of sample with accuracy up to 0.01 g and the response time of scale is 0.5 s. It continuously records the mass loss of sample during the process. The mass decrement, ambient/steam temperature are recorded on PC within the 1 s intervals. The system works as a batch, plug-flow reactor since the hot streams of gases are continuously supplied to the reaction chamber, passing through the mesh basket within the

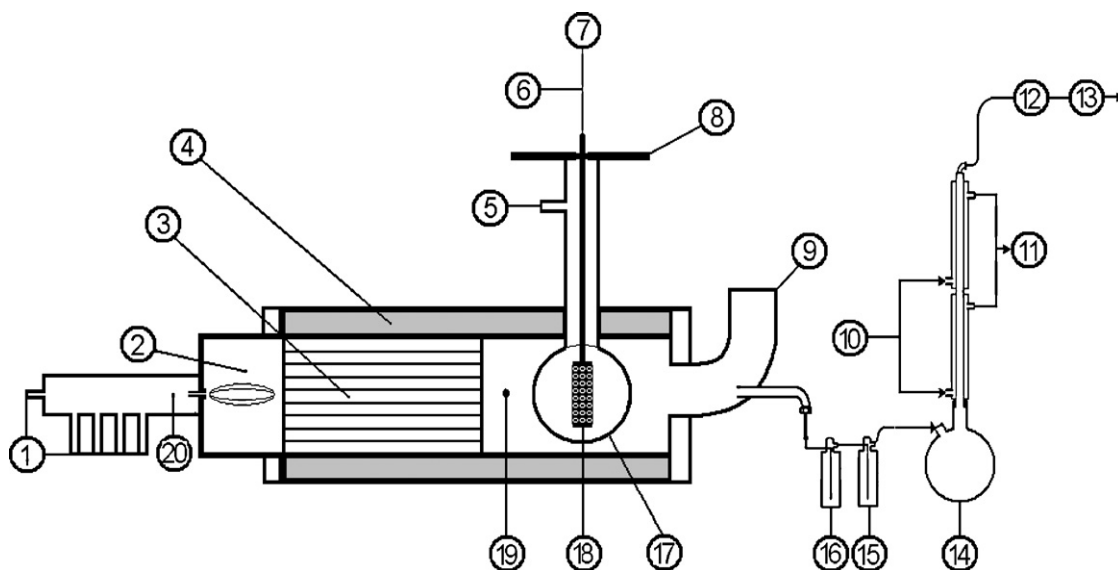


Fig. 1. Small lab scale batch type gasifier: 1-air, methane, oxygen, nitrogen, steam inputs; 2- combustion chamber; 3-honeycomb; 4-heat insulation; 5- cooling chamber with nitrogen input; 6-tiny wire; 7-digital balance; 8-hatch; 9-exhaust; 10-cold water supply; 11-water sink; 12, 13 input to gas analyzer; 14-water coil cooler with iso-propanol trap; 15-first iso-propanol trap; 16-water trap; 17-glass window; 18-basket with samples and thermocouple; 19-thermocouple; 20- nozzle with mixing chamber.

Table 2
List and conditions of experiments.

Char type	Agent type	Agent temperature [°C]	Sample weight [g]	Name of experiment
Light fraction	Steam, 6 g/min	750	2.01	LF S 1
		830	1.98	LF S 2
		950	2.03	LF S 3
	3% O ₂ 97% N ₂ , 5 l/min	750	2.03	LF O 1
		850	1.97	LF O 2
		950	2.00	LF O 3
Heavy fraction	Steam, 6 g/min	750	2.02	HF S 1
		830	1.99	HF S 2
		950	2.03	HF S 3
	3% O ₂ 97% N ₂ , 5 l/min	750	1.98	HF O 1
		850	2.02	HF O 2
		950	1.99	HF O 3

sample inside, and ending up into the exhaust system (9). Some portions of the exhaust gases (flue gas or syngas) are sucked into the on-line gas analyzer (12,13), which indicates the process performance and actual CO₂, CO and O₂ concentration. Concentration of O₂ is carried out using M&C Analysentechnik instrument, type PMA 25, equipped in a paramagnetic detector, while CO and CO₂ concentrations were measured using Maihak analyzer type MULTOR 610 equipped with a non-dispersive infra red detector (NDIR). Before the gas enters to the gas analyzers it passes through the condensation-cleaning unit, which consists of one water trap (16), two iso-propanol traps and a water coil cooler (14,15).

After an experiment is completed, the basket with remaining residues is lifted up to the cooling chamber, where subsequently is scaled and quenched by the cooling nitrogen to approximately 200 °C.

Table 2 shows the list of experiments and parameters which have been investigated in the work.

2.4. TG experiments

The thermogravimetry tests have been conducted on Perkin Elmer TGA7 instrument. Throughout the whole experiments the purge gas (air) was added with rate of 25 ml and the balanced gas (nitrogen) was added with rate of 50 ml. The temperature has been measured via thermocouple placed inside the furnace. The thermocouple was calibrated for the range of temperature 50–1030 °C.

The start up temperature was set on 105 °C. Then, the temperature was holding for 10 min and subsequently, non-isothermal temperature scan with heating rates of 10, 20, 40, 60, 100 °C/min, respectively, vs. mass loss and derivative of mass loss have been plotted.

The mass of sample was 5 ± 0.5 mg. The sample was grinded and sieved to the particle average diameter of 0.5 mm. Then, the sample was inserted to a sample holder. The sample holder was hanged up on the hookup platinum wire. After balanced, the furnace was raised automatically to cover the sample holder.

3. Results and discussion

The conversion of material was estimated based on normalized ash free basis and calculated accordingly to the Eq. (1):

$$x_i = \frac{w_i - Aw_0}{w_0 - Aw_0} \quad (1)$$

Thus, the reaction rate can be written as in Eq. (2):

$$r_i = \frac{dx}{dt} \times 100\% \quad (2)$$

where: w_i and w_0 are actual and initial net weights of the sample [g], A is the weight fraction of ash taken from Table 1 [g/g] and r is reaction rate [%/s].

Figs. 2 and 3 show the normalized mass loss (left vertical axis) and reaction rate (right vertical axis) vs. elapsed time, for the gasification of the two types of solid products derived from the microwave pyrolysis of light fraction (LF) or heavy fraction (HF), using either steam or 3% of oxygen as the gasifying agent, respectively.

In general, the mass loss and also derivative of mass loss exhibit a similar behaviour in respect to both agents that have been used for current investigations: three stages can be distinguished which correspond to different phenomena. Initially, a massive decrement of sample's weight is observed which lasts for about 150 s and occupied 20–40% of mass loss. This is the fastest part of the process; it denotes maximum decomposition rate and contributes to pyrolysis. Subsequently, the gasification of char appears while the pyrolysis still keeps on going which corresponds to stage 2 in Figs. 2 and 3. In this stage pyrolysis and gasification reactions are overlapping and the reaction rate decreases about six times which appears as a second maximum on derivative plot. This takes another two hundreds seconds and consumes further 10–20% of mass loss for the light fraction and barely difficult to be observed for the heavy fraction. After this intermediate step a third stage appears, when the pyrolysis process is completed and only slow process of char gasification undergoes consuming remaining carbon. This stage denotes almost constant reaction rates varying between different cases from 0.03 to 0.06%/s for oxygen gasification and 0.02–0.03%/s for steam gasification. In the case of LF the main sample decomposition contributes to the pyrolysis process and occurred in the first 100 s of the process. This process is promoted for lower temperature experiments (see Fig. 2). The characteristic intervals, mass losses, maximum and average reaction rates corresponding to each of discussed stages are presented in Tables 3A and 3B, for LF and HF, respectively.

The results indicate also that the steam gasification positively influences on the pyrolysis rate, which is higher roughly 25% compared with process carried out under oxygen for the corresponding temperatures. Similarly to experiments performed on light fraction, the char from heavy fraction also exhibits the decreasing of overall reactivity of char with the raise of temperature, which contributes to different values of final conversion degree at the same time interval. However, decomposition through pyrolysis and gasification proceed differently with respect to the temperature of the gasifying agent. Regardless of the kind of agent used for investigations, the decomposition rate of HF through the pyrolysis process (stage 1) increases with the raise of temperature, but further decomposition of sample through gasification of char shows an opposite relation. The effect of an agent has not a significant influence on pyrolysis, favouring, however, the process undergoing with steam at higher temperatures. This can be contributed to the fact that higher heating rates promote the pyrolysis rate. It can be seen from Fig. 3 that the higher heating rate (which is more intensive for a process at higher temperature) stimulates a pyrolysis rate

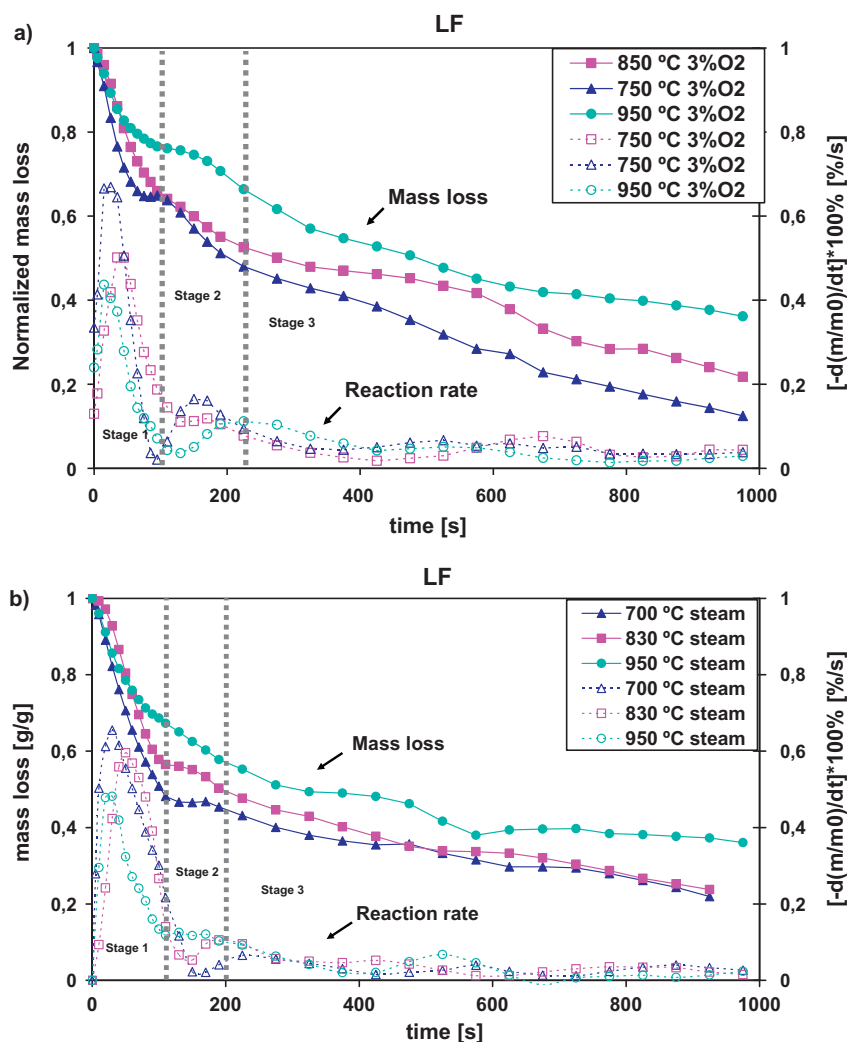


Fig. 2. Normalized mass loss and reaction rate for gasification of LF: (a) using 3% of oxygen at 750, 850 and 950 °C and (b) using high temperature steam, respectively.

and reduces the time needed for reaching maximum reaction rate. The pyrolysis rates for experiments with steam in respect to HF in a raising temperature order from 750 °C to 950 °C showed a raising trend, whereas in respect to LF the trend is opposite (see Table 3B). Similarly, the process undergoing with the mixture of 3% of oxygen, at the raising temperature order, indicates that pyrolysis rates with respect to HF increases and in respect to LF shows a decreasing trend (see Tables 3A and 3B), at the corresponding temperatures.

Another important observation in current investigations is that the intermediate step, in which both pyrolysis and gasification process are located (stage 2), is not well distinguishable for HF as it was for LF. Both these phenomena suggest that LF is less decomposed and has a higher content of un-reacted materials compared to HF. Hence, due to the fact that foaming materials (comprising raw LF), absorb microwave radiation less, and the heat conduction within the material is reduced due to the low density and high porosity of the sample it is believed that the pyrolysis mechanism governs

Table 3A

Collected results of mass and reaction rates for gasification of the solid residues after microwave treatment of the light fractions of ASR.

LF	Obtained result	Unit	LF S 1	LF S 2	LF S 3	LF O 1	LF O 2	LF O 3
Period	External gas temp	°C	950	850	750	950	850	750
Stage 1	Duration of period (t)	s	130	150	150	130	95	130
Stage 2	Duration of period (t)	s	295	425	275	295	280	275
Stage 3	Duration of period (t)	s	500	400	500	500	500	500
Stage 1	Mass loss (x)	%	34.95	44.82	53.44	24.38	36.21	37.78
Stage 2	Mass loss (x)	%	16.92	21.49	11.09	22.85	23.86	16.02
Stage 3	Mass loss (x)	%	12.08	10.24	14.28	16.6	11.7	24.45
overall mass loss (xf)		%	63.95	76.55	78.82	63.82	71.77	78.24
Stage 1	Maximum rate (r_{max})	%/s	0.482	0.596	0.655	0.437	0.502	0.669
Stage 2	Maximum rate (r_{max})	%/s	0.121	0.106	0.065	0.112	0.165	0.119
Stage 3	Maximum rate (r_{max})	%/s	0.046	0.035	0.04	0.051	0.067	0.077
Stage 1	Average rate (r_{av})	%/s	0.251	0.315	0.371	0.154	0.278	0.292
Stage 2	Average rate (r_{av})	%/s	0.072	0.063	0.037	0.068	0.094	0.073
Stage 3	Average rate (r_{av})	%/s	0.022	0.024	0.027	0.026	0.046	0.059

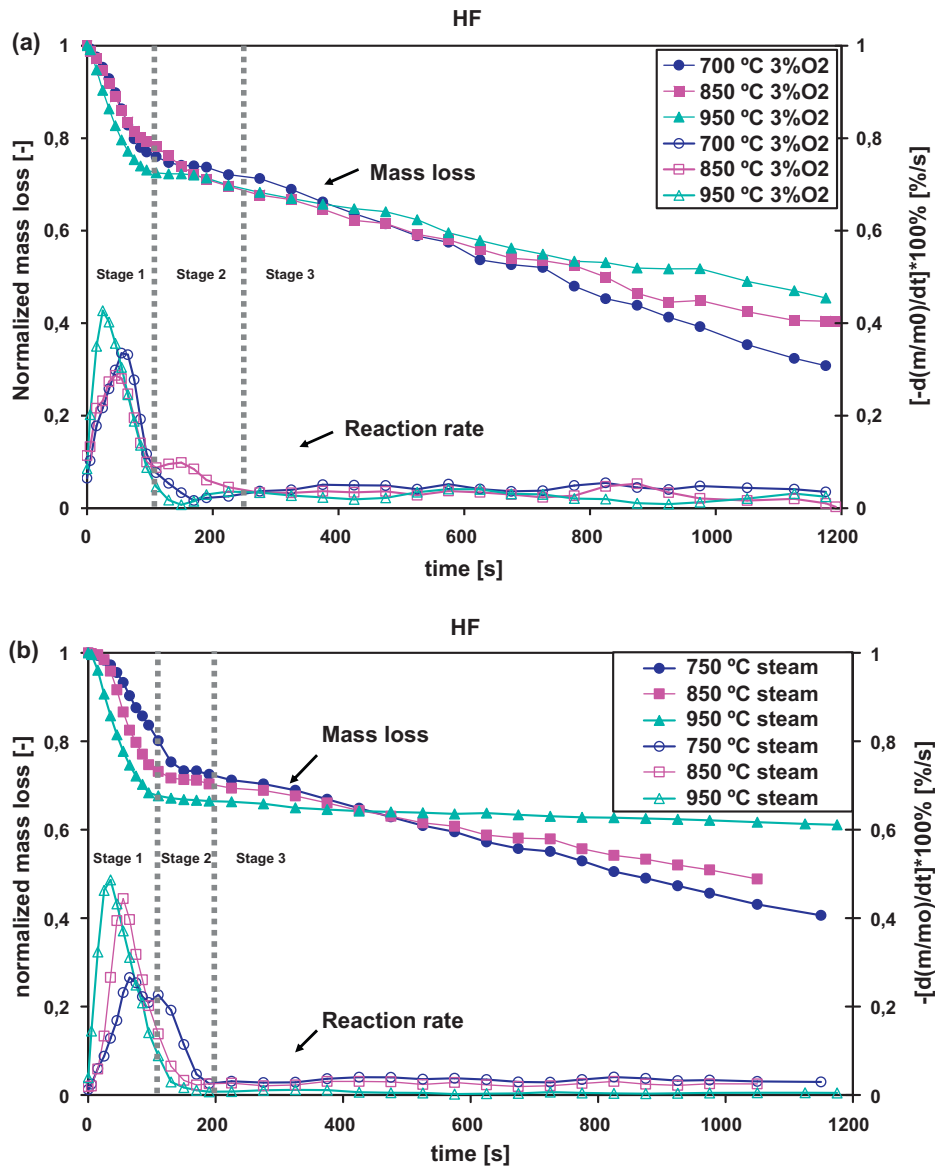


Fig. 3. Normalized mass loss and reaction rate for gasification of HF: (a) using 3% of oxygen at 750, 850 and 950 °C and (b) using high temperature steam, respectively.

a decomposition process differently with respect to LF and HF and this has an influence of char properties. The influence of microwave pyrolysis was greater for HF than it was for LF and this has a direct consequence on the differences in samples' behaviour exposed to an external heating source in the current investigation.

During char gasification (stage 3) both tested fractions exhibit nearly linear decomposition of sample and thus gasification reaction rate becomes a constant value, depending on temperature of the gasifying agent. Normally, the increase of temperature accelerates the reaction rate, at least kinetics and diffusion. However,

Table 3B

Collected results of mass and reaction rates for gasification of the solid residues after microwave treatment of the heavy fractions of ASR.

HF	Experiment	Unit	HFS 1	HFS 2	HFS 3	HFO 1	HFO 2	HFO 3
Period	External gas temp	°C	950	850	750	950	850	750
Stage 1	Duration of period (t)	s	130	130	90	110	110	110
Stage 2	Duration of period (t)	s	20	90	90	40	60	115
Stage 3	Duration of period (t)	s	1000	1000	1000	1000	1000	1000
Stage 1	Mass loss (x)	%	32.34	28.44	17.36	27.5	21.85	23.99
Stage 2	Mass loss (x)	%	1.01	2.48	2.8	0.47	4.15	3.9
Stage 3	Mass loss (x)	%	5.13	20.05	31.9	27.58	33.4	39.7
Overall mass loss (xf)		%	38.48	50.97	52.06	55.55	59.4	67.59
Stage 1	Maximum rate (r _{max})	%/s	0.486	0.444	0.265	0.427	0.287	0.335
Stage 2	Maximum rate (r _{max})	%/s	0.017	0.033	0.226	0.047	0.099	0.054
Stage 3	Maximum rate (r _{max})	%/s	0.012	0.031	0.040	0.041	0.053	0.055
Stage 1	Average rate (r _{av})	%/s	0.253	0.21	0.145	0.236	0.192	0.204
Stage 2	Average rate (r _{av})	%/s	0.014	0.027	0.158	0.013	0.093	0.030
Stage 3	Average rate (r _{av})	%/s	0.006	0.025	0.033	0.026	0.030	0.043

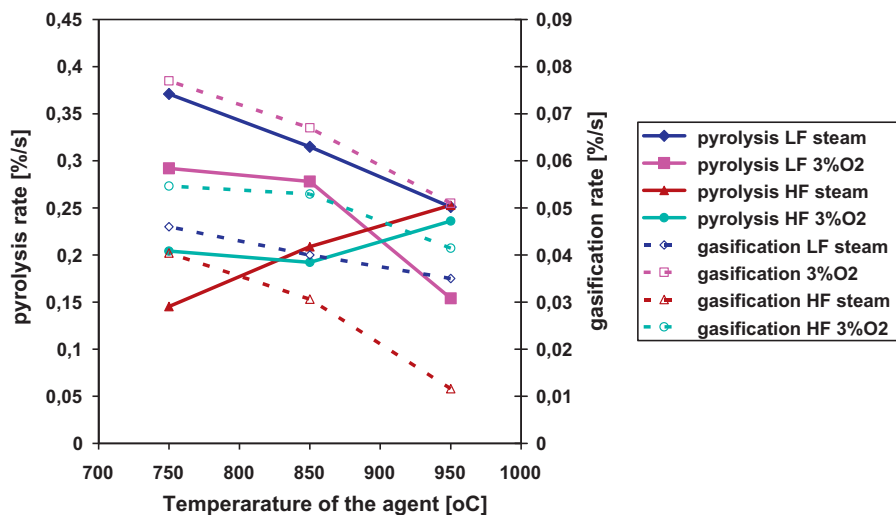


Fig. 4. Maximum pyrolysis rate (solid lines) and maximum gasification rate (dashed lines) vs. the temperature of gasifying agent, for LF and HF.

the results, presented in Figs. 2 and 3 show differently: when the temperature rises, the overall decomposition rate slows down and the conversion reaches lower values. This phenomenon is clearly seen in Fig. 4, which shows the maximum pyrolysis and gasification rates, with respect to the agent temperature.

In all analyzed cases the reaction slows down with the increasing temperature of the agent. In particular, for HF at steam temperature of 950 °C the char gasification becomes almost 6 times slower than for the same sample at 750 °C. Moreover, the reaction rates between oxygen and steam gasification are comparable, which suggests that the process is neither controlled kinetically nor by diffusion, because otherwise the oxygen which is more reactive and has a higher diffusivity than steam would significantly increase the reaction rate. It also demonstrates that both intrinsic reaction rates for oxygen and steam reaction are, in fact, much faster at these temperatures since they are not influencing significantly on the overall apparent reaction rate. The overall apparent reaction rate, is the one which is observed in Figs. 2 and 3, corresponds, in fact, to the sum of all effects of undergoing processes.

Although the average gasification rates (stage 3) are approximately two times higher for reactions with oxygen when compared to steam, the difference should be much higher, unless the ash enhanced a dissociation of steam into OH radicals and afterwards increased reactivity of steam. This, however, does not provide an explanation for the reason why the reaction rates decrease when the temperature goes up. Similar observation can be found for the experiments on HF (see Fig. 3). The reaction rates for gasification show a little difference in reactivity between the steam and oxygen gasification. The only significant difference between LF and HF can be found in the pyrolysis regime. One explanation for this could be a different mechanism of microwave heating compared to the conventional external heating systems i.e. inside the furnace. The microwave radiation induces molecules of dielectric materials, causing oscillations [20,21]. The sample is heated up in the direction from inside to outside and its more intensive for material with higher density. However, the microwave induction poorly excites vapours and gases resulting in pyrolysis products, which means that secondary pyrolysis reactions are not favoured. So the transfer of pyrolysis products from the overheated solid particles is restricted. This may strongly influence on char structure.

The light fraction denotes higher contribution of pyrolysis process and intermediate stage in its overall conversion degree compared to the heavy fraction. It suggests that the light fraction has higher content of volatile matter. This could be a consequence of low absorption of microwave radiation by the material of lower

density, which means that the material was partially not pyrolysed. The heavy fraction shows opposite: in this case more than 50% of the mass loss accounts on gasification of char (excluding the experiment "HF S 3"). This has an influence on the overall conversion which shows the highest degree for the process conducted at lower temperatures, regardless from the agent which was used.

The obtained results suggest an existence of three main factors being responsible for decreasing char reactivity with a growth of agent temperature:

- char nature (including properties of plastic char, ash content its variety and composition),
- high temperature treatment (rapid heating rate and extensive heating),
- microwave pyrolysis that creates uncommon char structure.

Although there have been reported many research works conducted on microwave pyrolysis of biomass and biomass wastes [19,21,22], unfortunately, there is lack of information in literature resources dedicated to properties and structure of solid residues generated from plastics waste after microwave treatment. Hence, this part of discussion on our results will be referred to the available literature resources focusing on biomass treatment hoping to find at least similar tendencies to plastic char. However, plastic chars have usually very low activity, compared to one obtained from cellulose. This is due to the amorphous structure of char which is formed during melting, swelling and cracking of macromolecular chain [29]. Another type of plastic char is created during secondary and tertiary pyrolysis process at temperature above 800 °C in which along with cracking reactions, the cyclization are promoted leading to form an aromatic structure. Subsequently, the generated aromatic structure condenses to form polycyclic aromatic hydrocarbons (PAHs) which are responsible for coke formation [29].

It is a well known fact that the history of char generation plays a very important role for its further reactivity. A highly developed char possesses a porous, large surface area and promotes solid–gas phase reactions. Huang et al. who pyrolysed rice straw using microwave induced pyrolysis at different range of power from 200 to 500W, which corresponds to different heating rates and different sample temperatures, found that generated char has different properties and structures, dependently on the applied power [22]. They depicted that with an increase of microwave power, the specific surface area increased as well as the tendencies of total pore volume and mesopore volume, whereas the average pore diameter denoted almost no difference between diameters.

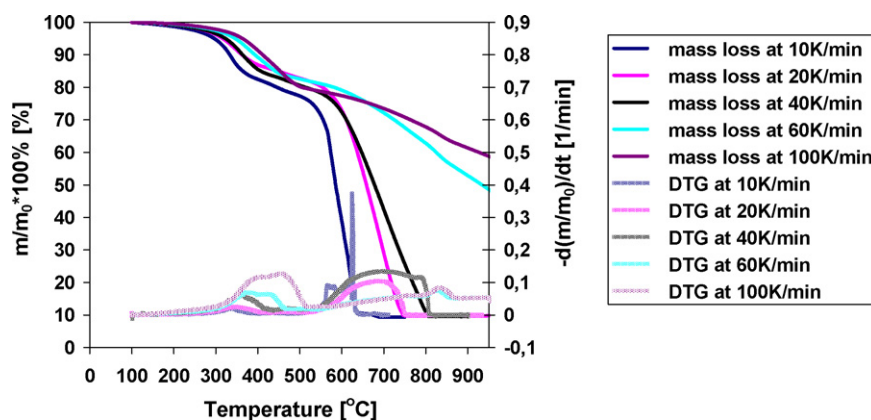


Fig. 5. TG and DTG in air atmosphere for HF at different heating rates.

They suggested that the specific surface area of solid residues produced by microwave pyrolysis might be considered “as a kind of adsorbent”. They observed also that with an increase in microwave power which translates to pyrolysis temperature, the calorific value of char increased to a certain degree, but after applying more power than 350 W it reduces. The authors suggested that some of the fixed carbon might be pyrolysed when the power is high enough. Additionally, high ash content found in ASR’s char would definitely contribute on the overall reaction rate; however both the catalytic and inhibitive effect is expected. Many researchers show its catalytic effect on the overall gasification or pyrolysis rates. However, an interesting study was conducted by Bazardorj et al., who showed that alkali and alkaline earth metallic species can change the catalytic effect with the progress of the gasification [30] and after certain temperature inhibit reaction rate.

Nevertheless in case of current research, the ash content in both analyzed samples are very high (10% and 50% respectively) of the sample weight. Such high concentration of ash suggests that it cannot be considered just as a catalyst but rather as an important factor taking part in the whole process and contributing to its performance. Thus, one of the reasons for decreasing the overall reaction rate with increasing temperature could be the melting of inert materials (salts and metals) and thus creating physical “obstacles” for the oxidizer’s penetration into the carbon active sites. Therefore, metals could be adsorbed in active carbon sites, blocking the access to the oxidizer, and this would be enhanced for the process undergoing at higher temperatures. This concept can be supported by the results obtained by Bradshaw et al. [21] who conducted research on regeneration of activated carbon using microwave heating with steam in range of temperature 650–750 °C. They concluded that the higher carbon activation was favoured at higher temperatures. In this case higher agent temperatures can locally promote adsorption of ash onto active carbon centres. This suggestion leads to a conclusion that even though, the high temperature agent promotes activation of carbon at higher temperatures, the inert materials occupy the active sites slowing down the char–gas phase reactions and protecting against further carbon decomposition. This inhibiting effect, fairly explains both the discussed phenomena: reducing gasification rate with the growth of temperature and the low sensitivity of the gasifying agent type on reaction overall reaction rate.

Another factor influencing on the mass loss performance vs. temperature of the gasifying agent is the heating rate. In order to test an influence of heating rate on the interaction with the oxidizer, TG experiments using air as the purging gas have been conducted. The influence of heating rate on the sample decomposition of HF in an air environment using microbalance (thermogravimetry) is showed in Fig. 5.

This research showed a similar dependence between the heating rate and char reactivity, like it is seen in the batch, lab-scale gasifier. More information about the TG tests can be found in our previous studies presented in [16]. The results showed that during the heating rate of 10 K/min, sample decomposition through combustion proceeds rapidly after reaching approximately 630 °C at 90% of mass conversion. However, with the increasing heating rate the maximum decomposition of sample shifts towards higher temperatures and conversion of sample decreases. For the fastest heating rate (100 K/min) the process even at 930 °C is not completed and mass loss reaches only the value of 40% which is similar to pyrolysis process. This indicates that the heating rate is a major factor responsible for “abnormal” behaviour of tested material, in which with the growth of reactor (agent) temperature the reaction rate of char-oxidizer decreases. The heating rate of sample in the lab-scale, batch reactor is varied, dependently on agent temperature and fuel-to-oxidizer ratio in batch gasifier, in the range of 1–8 K/s, which was reported in [10]. This puts some light on the explanation of the reason of decreasing reactivity with increasing agent temperature. In this sense it is believed that for higher heating rates the diffusion of hot agent to the particle is limited due to swelling and melting of polymers residues present in samples and existing of the high pressure barrier caused by released volatiles. In such conditions the oxidizer has a restricted access inside the particles and flows around them. In this case the oxidizer at higher temperatures is consumed as a pyrolysis agent but not as reactant.

This is also in agreement with observations carried out by Kanarelis [18], who conducted investigation on pyrolysis’ kinetics of electric and electronic wastes in highly preheated agents. They pointed out that, the higher heating rates decrease diffusion of volatiles from the particles to the gas phase. This, along with the internal gradients within a sample may generate local tensions and cracks, which affect the carbon matrix and increase its porosity. This factor increases in the reactivity of char and speeds up the pyrolysis process. However, there is another phenomenon which takes place during extensive heating; the rearrangement and deformation of char structures (e.g. shrinkage of char), which inhibits decomposition. This could be an effect of decreasing pyrolysis rate with increasing agent temperature observed for LF (see Figs. 2 and 3 for stage 1).

Another reason for which it may have a high contribution to the phenomenon of the reduction oxidizer–carbon reaction rate with the growth of temperature, could be in the mechanism of the char formation and the history of its development. The char itself is varied because of the variety in raw ASR’s composition. Nonetheless, it is presumed that, the microwave pyrolysis produces a char of the highly diverse morphological structure and composition, because of the difference in microwave absorption by different

materials comprising ASR; e.g. existing of local hot spots. In this case it is believed that, the porosity structure of char has not been well developed during microwave pyrolysis, especially when the char derived from plastic mixture which occupied the lion part of the organic compound found in raw ASR. The char obtained from plastics is poorly formatted because most of plastics are thermally decomposed to gaseous and liquid hydrocarbons. Therefore, the solid structure has much lower activity than a one generated from biomass on coal [29].

This suggestion is supported by the results obtained by Wang et al. [19], who conducted research on microwave pyrolysis of pine sawdust. The researchers pointed out that with increasing the pyrolysis temperature from 400 °C to 600 °C the pore size of chars decreased gradually. They also suggested based on SEM photography that char could melt and deform resulting in shrinking and even closing of pores at higher temperatures. On the other hand, rapid heating up of the material would effect on structure of deformed char, which in turn reduces its reactivity.

However, it is not well recognized which of the identified source has a dominating effect on whether the declining char reactivity with the growth of temperature is a material property or an effect of the microwave treatment that changed drastically the structure of char.

4. Conclusions

The current work shows the results of treatment of the solid residues after microwave pyrolysis using two different type of oxidizing agents: steam and 3% oxygen at temperature ranges between 700 °C and 950 °C. Similarly to the virgin ASR the solid products after pyrolysis are much diversified, both in their morphological structure and material composition. The results reveal, however, two undesirable phenomena:

- (1) With increasing temperature of the process the reaction rate decreases.
- (2) No significant differences between steam and oxygen gasification rates.

This suggests that the process is not controlled kinetically or by diffusion but rather by the other sort of transport phenomena occurring on the carbon matrix at elevated temperatures. This also explains the existence of a very little difference in char reactivity during gasification with steam and oxygen, which should be much higher if the process is controlled kinetically. Moreover, the slowest reaction limits an overall reaction rate and this suggests intrinsic reaction rates both for steam–carbon and oxygen–carbon are much faster, at the range 750–950 °C than the one obtained from mass loss curves.

The results suggest that, the access of the oxidizer to the carbon is restricted and that could possibly reduce the reaction rate. The gasification/partial oxidation is inhibited at higher temperatures due to probable deformation of char structure, caused both by currently conducted experiments in which the sample was rapidly preheated by hot gases and during microwave pyrolysis in which a non-uniform, low porous char matrix had been formed. Another reason for these phenomena could be blocking active sites of carbon by adsorption of inert materials. In this way the carbon, activated by the oxidizer at higher temperature, was consumed to adsorb ash, resulting in the reducing the overall reaction rates. This inhibiting effect, fairly explained both the reducing gasification rate with the growth of temperature and the low sensitivity of the gasifying agent type on the overall reaction rate.

The information provided in this work indicates that increasing the temperature of reaction is not always the best option to

improve the gasification process and increase its rate, since this is not the only effect influencing the process performance. In fact, the raise of temperature positively influences on the kinetics and diffusion of the process, but in the same time has a negative impact on the overall decomposition reaction rate due to existence of other circumstances discussed in this paper. The char structure and its composition (including ash content) play a key role for its reactivity. Hence, it is believed that, the reaction rate could be significantly increased if the ash content was reduced from char prior applying the gasification process. This could be also beneficial for the metal recovery rate; however, it would increase the operation costs for pre-treatment of char. Therefore, optimization of the process taking to account economical feasibility and availability of a proper separation technique should be also investigated.

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