

Recycling of automobile shredder residue with a microwave pyrolysis combined with high temperature steam gasification

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ABSTRACT

Presently, there is a growing need for handling automobile shredder residues – ASR or “car fluff”. One of the most promising methods of treatment ASR is pyrolysis. Apart of obvious benefits of pyrolysis: energy and metals recovery, there is serious concern about the residues generated from that process needing to be recycled. Unfortunately, not much work has been reported providing a solution for treatment the wastes after pyrolysis. This work proposes a new system based on a two-staged process. The ASR was primarily treated by microwave pyrolysis and later the liquid and solid products become the feedstock for the high temperature gasification process. The system development is supported within experimental results conducted in a lab-scale, batch-type reactor at the Royal Institute of Technology (KTH). The heating rate, mass loss, gas composition, LHV and gas yield of producer gas vs. residence time are reported for the steam temperature of 1173 K. The sample input was 10 g and the steam flow rate was 0.65 kg/h. The conversion reached 99% for liquids and 45–55% for solids, dependently from the fraction. The H₂:CO mol/mol ratio varied from 1.72 solids and 1.4 for liquid, respectively. The average LHV of generated gas was 15.8 MJ/N m³ for liquids and 15 MJ/N m³ for solids fuels.

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1. Introduction

In Europe every year end-of-life vehicles (ELV) generate 8–9 million tonnes of waste [1]. In 2000 the European Commission (EC) enforced the Directive 2000/53/EC which gives the guidelines about the ELV's recycling projections. The Directive's objective was to ensure that 95% of ELV's weight will be recycled by the year 2015 with additional de-pollution tasks being progressively introduced.

Presently, about 75% of a vehicle's weight is recovered, mostly its metal contents, the rest being approximately 2.5 million tonnes (25 wt.%) a year is shredded. This remaining part creates a fraction called Automotive Shredded Residue (ASR) or commonly called “car fluff” [2,3]. ASR is a heterogeneous and a difficult-to-recycle mixture of different types of material. The exact material or chem-

ical composition of ASR is not easy to estimate as several authors reported different values [2–16], e.g. Day et al. reported that ASR comprises (19%) of plastics, (20%) of rubber, (10%) of textiles and fibre materials and (2%) of wood, and the rest are metals (8%), and oils (5%) [13]. However, Galvagno et al. indicated that ASR has a higher amount of plastics (31%), textiles and fibre materials up to (42%) and wood (5%) [14]. ASR also contains hazardous materials roughly about 10%, e.g. PCB, cadmium and lead [11,13,14]. Therefore, due to the complexity and diversification in chemical composition and material structure of ASR most of authors would consider handling ASR via the thermal treatment methods [7–22] and minimizing mechanical recycling. Nevertheless, it is possible to apply some low-cost methods of ASR's pre-treatment to separate materials into those groups that further on would be easy to recycle or to eliminate hazardous substances, e.g. using pre-treatment techniques to reduce polyvinyl chloride (PVC) contents in ASR [4–7]. Other pre-treatment methods could involve separating ASR into light and heavy fractions using various density separation techniques (air lift, wet separation, etc.) [11]. Pyrolysis, can also be used as a one step of pre-treatment/reprocessing leading to homogenization and densification of ASR. It was observed that the amount of ASR after pyrolysis can be reduced up to 50% by weight and even 90% by volume [11], which significantly reduces volumes of waste and preserve metals.

According to the Directive 2000/53/EC, land-filling cannot be considered as an option for ASR waste management. Many authors

Abbreviations: ASR, automotive shredder residue; C, conversion degree of organic matter content in fuel (kg/kg); ELV, end-of-life vehicles; HTAG, high temperature agent gasification; HTSG, high temperature steam gasification; GC, gas chromatography, gas chromatograph; KTH, Royal Institute of Technology, Stockholm, Sweden; LHV, lower heating value (MJ/kmol); Liquid, liquid residue after microwave pyrolysis containing 43% of water; PAH, polycyclic aromatic hydrocarbons; PVC, polyvinyl chloride; PUR, solid residues after microwave pyrolysis rich in polyurethane and textiles fraction; RUBBER, solid residues after microwave pyrolysis rich in plastic and rubber fraction with low ash content.

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propose solutions using one of the following thermal methods: combustion [8,17], pyrolysis [6,7,9–16,18] and/or gasification [15,16,19–22].

Combustion creates environmental impacts as it is contributing to the green-house gas emissions; however it seems to be the simplest method of dealing with ASR, since it does not involve costly separation techniques. One of the drawbacks of combustion is that heavy metals can be lost in form of fly ash therefore being unrecoverable [4,5,8].

Gasification is an alternative option for recycling ASR [15,16,19,20]. The operating conditions for gasification are carried out under limited oxygen presence, and are milder than those taking place in combustion; however metals and salts can be melted or evaporated. On the other hand, gasification is less sensitive for the variation in material composition of ASR compared to pyrolysis. Also the products are more homogenous, since mainly producer gas is generated, and therefore easier to handle. The ASR's gasification was studied in various conditions and experimental setups by Kondoh et al. [16].

Pyrolysis, which is one of the most promising methods of ASR treatment, has been widely studied [9–15]. Recently, several pyrolysis techniques have been reported in the area of ASR: screw kiln pyrolysis [10–14], microwave pyrolysis [2,11] and plasma pyrolysis [2]. Apart from obvious benefits of pyrolysis: energy and metal recovery, there is serious concern about the residues generated from that process needing to be recycled. Unfortunately, not much work has been reported providing a solution for treating those residues. The solid residues, mainly charcoal and ash, contribute to 20–50 wt.% of the product distribution after pyrolysis [9–15]. They contain roughly 40–80 wt.% of carbon and 20–50% ash which is rich in iron, copper, aluminium. The solid residue limits the commercial application of the pyrolysis operation in a large scale, unless there will be sustainable methods of handling this by-product.

The current work suggests a new concept which can fill in the gap in ASR's waste management systems. This concept is created to treat ASR and proposes ways of handling residues generated after microwave pyrolysis using high temperature steam gasification, further explained in Sections 1.1 and 1.2. The study is supported with experimental results obtained from a batch-type, fixed-bed gasifier at the Royal Institute of Technology (KTH), Stockholm, Sweden.

The main goal of this current work is to propose a system that will deal with the residues after microwave pyrolysis. The conversion rate of organic contents of pyrolysed ASR will be investigated and the producer gas composition will be reported.

A thermodynamic simulation of the process, in which the solid and liquid products of microwave pyrolysis of ASR had been gasified using high temperature steam, was developed by Kubik [21], and further developed by Donaj et al. [22]. The results from their work indicated that pyrolysed residues treated by steam of temperature above 900 °C at the steam-to-fuel ratio of 1.4 (mol/mol) can be utilized to generate electrical power by gas engine at an overall efficiency of around 25%. This is likely to happen under condition that the conversion of organic content of ASR has achieved 100% and the system reached a steady state. In practice, 100% of carbon conversion is difficult to achieve, therefore it is necessary to validate this condition by experimental results.

1.1. Microwave pyrolysis

Microwave heating is a process occurring in the molecular level [2]. The heat is generated volumetrically within the material. Microwave radiation effects differently on different materials: induces dielectrics, penetrates glassy and ceramic materials and generates Eddy currents of the surface of metals [23]. Due to the good thermo-isolative properties of plastics, the heat absorbed

by pyrolysis can be consumed more effectively [23,11]. Therefore similar product distribution can be obtained for relatively lower temperatures compared with conventional pyrolysis. The drawbacks associated with microwave pyrolysis is the difference in absorption of microwave radiation by different substances, i.e. charcoal absorbs it with high efficiency, therefore, there are possibilities of generating high temperatures (>1000 °C) in materials locally but some substances like foams absorb microwave radiation in a lesser way. This has an effect on char structure which might become less uniform compared to the conventional pyrolysis using external heating systems [23,24]. Also porosity of char can be reduced which will effect on heterogeneous carbon – steam and carbon oxygen reaction rates [24]. Nevertheless, the product after microwave pyrolysis will result in both relatively high molecular weight olefins, and a high proportion of gaseous products such as ethylene, propylene, butane and aromatics. The potential application of using microwave pyrolysis to handle ASR at the average temperature of 500 °C in a 60 kW microwave reactor of capacity 1712 tons/year was performed by Forsgren, who reported the following product distribution of: 11% gases, 30% liquids and 59% solids [11].

1.2. High temperature agent gasification

The high temperature agent gasification (HTAG), where the agent is steam, air or air/steam mixture and the feedstock is biomass, wastes, or coal have been widely studied [20,25–30]. In this process the gasifying agent is heated up to temperature above 900 °C and provides all necessary heat in order to conduct gasification.

In this work, steam at 950 °C was used for gasification of solid and liquid products after microwave pyrolysis of ASR and referred as high temperature steam gasification (HTSG). Steam gasification is an endothermic process, thus highly elevated temperatures for running are required. A need for seeking the solution to generate high temperatures steam pushes toward development of ultra-high-efficient heat exchanger which is capable of rapid preheating of the gasifying agent. The use of highly preheated agent results in high conversion of fuel to gas, higher calorific value in the range of 10–15 MJ/N m³ and lower tar content compared to conventional gasification [25–29]. However, there are no traces in literature resources regarding treating microwave pyrolysed products from ASR, using high temperature steam.

1.3. The development of a two-stage system for handling ASR

This work provides a novel and holistic approach to ASR waste management and other similar multi-component wastes. It considers the application of HTSG for handling ASR pyrolysed via microwave technique.

A general concept is displayed in Fig. 1.

This method leads to maximization of energy and material recovery from a single waste unit. In this case gasification is predicted to be used as a *complementary* method to microwave pyrolysis taking benefits of both of these techniques. The results of microwave treatment of ASR obtained by Stena Metall AB [11] were used to build a model of the system based on thermodynamic simulation. Subsequently, the model was supported with a set of experiments performed on a lab-scale, batch-type gasifier using high temperature steam. The current work reveals and discusses these results, and shows the process performance and quality of the produced gas. The scope is to determine optimal conditions to generate high quality producer gas that can be used for heat or electricity generation.

It was found that the use of high temperature steam increases the hydrogen yield [20–22,25–30] and reduces tar content

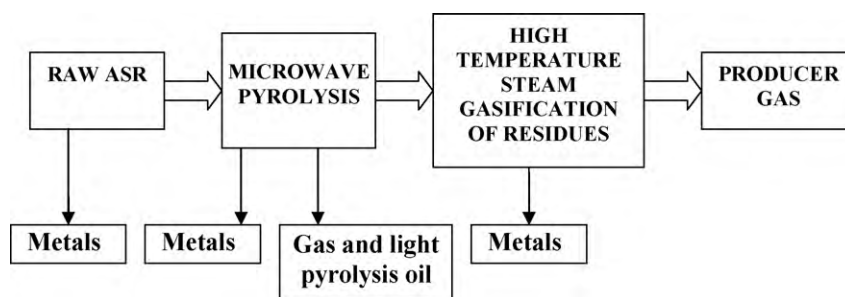


Fig. 1. A general concept of combining microwave pyrolysis with high temperature steam gasification for treating ASR.

[20,22–26] in producer gas. Additionally, the producer gas is not diluted by nitrogen, which normally takes place during air gasification, and thus it results in lower heating value in range of 10–15 MJ/Nm³ [20,25,26]. The high content of hydrogen is also potentially attractive for 2nd-generation fuels and chemical synthesis markets. However, conversion of char needs to be carried out in the most efficient and flexible way, in order to find a general commitment for this solution. Thus, a key factor to be examined is the conversion rate of the gasification using high temperature steam and the specific gas production rate expressed as the ratio of volume of produced gas per mass of organic matter containing tested sample.

During material preparations it was found that the metals could be easier recovered from pyrolysed fractions than from raw ASR. The recovery of metals can be achieved even before adding the char into the gasifier via various separation techniques. Therefore, it is believed that it can increase the efficiency of the gasification process and reduce the risk of melting or even evaporating mineral matter inside the gasifier.

A potential application of using our considered two-stage process can be extended as well for treating other hazardous and/or multi-component waste mixtures like: electronic and electric wastes, cable residues, household appliances wastes, vehicle tires, construction and demolition waste, residues from oil refineries and petro-chemicals.

2. Materials and methods

2.1. Methodology of the system development

The system proposal was built based on product streams generated during microwave pyrolysis ASR. This was performed by Stena Metall AB [11]. The chemical composition of the residues after pyrolysis served as an input data for a thermodynamical simulation, which was performed to optimize the steam temperature and steam/fuel ratio, and subsequently, predict the gas composition for the identified mass flow rates of the fuel within the gasification process. For simplicity it was assumed, that char conversion in solid residues at thermodynamically equilibrium state has reached 100% of conversion.

2.2. Methodology of the experimental procedures

The information presented below is related to the experimental part of this work which was conducted on liquid and solid products after microwave pyrolysis in a lab-scale, fixed-bed gasifier.

2.2.1. Microwave pyrolysis facility

The experiments on microwave pyrolysis of ASR have been conducted by Stena Metall AB [11]. A batch of ca 500 g of raw, finely grounded ASR was inserted to a modified microwave oven of 800 W with the collection system for gas and liquid products.

The setup consisted of a microwave oven with on/off temperature control system, a water-coil cooler, and two series-connected scrubbers/washing bottles, a gas flow meter, and a flare for gas combustion. Gases were sampled every 20 min into gas bottles and analyzed via GCs with FID and TCD detectors. Liquids were collected during the separation process and then weighted and analyzed. The remaining solid fraction was sent for further analysis. The tests were run with on/off regulation of full heating effect, controlled by a thermocouple connected to electronic thermostat. The target temperature was set on 425 °C. During heating up it was found that raw material contained a lot of water because the temperature remained relatively low for about 15 min at 120 °C until most of the water had been evaporated. The tests were terminated when the degassing ended. The whole process lasts for about 80 min.

2.2.2. High temperature agent gasification facility

A unique high-temperature air/steam reforming batch-type reactor at Royal Institute of Technology (KTH) was used for the studies. The general side view of this facility is shown in Fig. 2. It is a horizontal tubular plug flow reactor of an inner diameter 85 mm.

The system works in three different modes: heating up, main process, 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 of a capacity 10 kW via the inlet no. 1 and no. 2. The ceramic honeycomb no. 4 accumulates the heat from combustion that afterwards is used for gasification. In this facility, dry steam of a temperature around 180 °C and pressure 2 bar produced in a steam boiler is entered via the inlet no. 3. During heating up the steam is bypassed to exhaust system and the valve on inlet no. 3 is shut. For the gasification tests the burner is shut down and steam valve becomes open. While passing throughout a ceramic honeycomb it can be heated up over 1000 °C. The honeycomb, in addition, can keep a homogeneous temperature distribution inside the reaction chamber no. 5. In current work the steam flow rate was set for 10 g/min for all cases. The cooling chamber no. 6 enables to store the sample in mild conditions (<50 °C) before it is inserted inside the reaction chamber and after each test to protect the char against combustion. The cooling nitrogen can be fed to the cooling chamber via inlet no. 11. After reaching the process controlling parameters (steam flow, oxygen level below 0.1% and temperature) according to the experimental plan, the sample can be inserted to the reaction chamber no. 5. The sample of approximately 10 g is hold inside the rectangular basket of dimension 25 mm × 60 mm × 85 mm, made of perforated, stainless steel no. 12. The basket is attached to the hook of the balance located over the facility no. 8, through an airtight tube in which an s-type thermocouple is inserted. The end of thermocouple no. 10 is located in the middle of the sample's basket and covered by sample material. The mass decrement, ambient temperature (steam temperature) no. 9 and the sample's temperature no. 10 are recorded on PC within 1 s intervals. The generated gases (producer gas) are evacuated to the stack no. 7 and part of it is

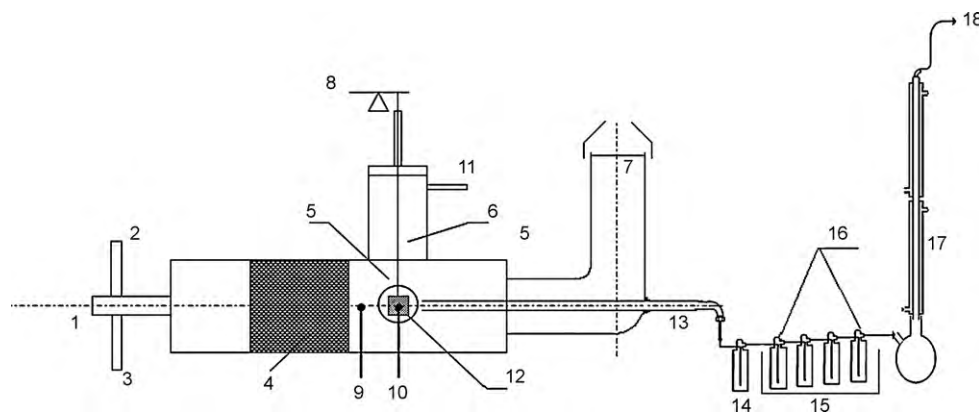


Fig. 2. Side view of the lab-scale batch-type gasifier. (1, 2, and 3) CH₄, steam, O₂ and N₂ mixture inlet; (4) ceramic honeycomb; (5) reaction chamber; (6) cooling chamber; (7) gas exhaust system; (8) scale/balance; (9 and 10) gas and sample thermocouples; (11) cooling N₂ inlet; (12) sample in mash basket; (13) outlet to gas cleaning/condensation system and analyzers; (14) washing bottle with water; water and ice cooling bath; (15) washing bottle with water; (16) washing bottles with iso-propanol; (17) water cooler; (18) inlet to the gas analyzers.

continuously sucked into the gas analyzers no. 18 from the tube no. 13. The sampled gas passes through the gas piping condensation-cleaning units, which consist of: one water washing bottle no. 14 for particles and steam removing, four series-connected washing bottles no. 16 containing iso-propanol trapped in an ice-water mixture batch for capturing tar no. 15, and a water coil cooler no. 17. Cleaned and dried gas is sampled into the on-line gas analyzer and micro GC.

2.2.3. Material characterization of products after microwave pyrolysis of ASR

In order to be able to recycle thermoplastics and metals from ASR using sink-float methods, materials that absorb water need to be removed. Therefore, raw ASR was separated into “light” and “heavy” fractions in an air separator. The light fraction comprises materials absorbing water, i.e. expanded polyurethanes, lighter plastics and textiles, whereas the heavy fraction contains rubber, plastics and heavier particles (metals, glass, soil, etc.). The heavier particles (metals, ceramics) and PVC were removed from the heavy fraction by the wet-process, and the remaining mixture was rich in thermoplastics, resins and rubber. 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, which have been generated after microwave pyrolysis [11]. The solid fractions after pyrolysis together with mixed liquid fraction were collected from Stena Metall AB microwave pyrolysis facility, and sent to KTH laboratory for further investigations, where the material was characterized and used as the a feedstock for a batch tests with a high temperature steam. They received the corresponding notification as followed: “RUBBER”, “PUR” and “Liquid”. Both solid fractions were pulverized in order to maintain a more homogeneous representation of the product distribution. The sample characterization after ASR microwave pyrolysis is presented in Table 1.

RUBBER is a solid heterogeneous mixture, which is high in carbon content, relatively low ash content and a high calorific value. PUR has a very high ash content reaching almost 50 wt.%. It denotes the largest reduction in volume by 90% and in weight by 75% compared to the raw feedstock. Both solids have relatively low volatiles and very low moisture contents as it was expected due the fact that both materials were derived from pyrolysis. In Liquid there was a high water content around 40%, which significantly decreased the LHV of the substance. The LHV of fuel was calculated via Boi’s formula [20].

2.2.4. Experimental procedure and sample preparations

ASR was primarily separated into two fractions rich in plastics and rubber, and rich in foams and textiles. They were indicated as “RUBBER” and “PUR”, respectively. Each of the fractions, treated by microwave pyrolysis, generated gaseous, liquid and solid products. Gaseous fractions were not taken into consideration in this paper. Liquid fractions, containing hydrocarbons, esters and organic acids, exhibit relatively low calorific values of around 15 MJ/kg and high water content 43 wt.%. In the case of solid fractions both samples were treated separately. Pyrolysis reduces the weight of raw ASR by 50% and the volume by 90% [11]. Not only reduction and densification are observed, but also changes in the mechanical properties, which make it easier to handle and process the material after pyrolysis. Afterwards, the processed material becomes more brittle and therefore the costs and complexity of grinding and separation systems could be reduced. After applying the wet separation technique on pyrolysed RUBBER it denotes a reduction in the ash content up to 10% of the residue weight. However, the ash content in PUR was still around 50% since the metals content could not be removed efficiently by the float and sink wet separation techniques.

Table 1

The proximate and ultimate analysis of tested material.

Analysis	Symbol	Units	RUBBER	PUR	Liquid
Proximate analysis					
Moisture	W	%	0.80	2.34	43.00
Ash	A	%	9.11	49.74	0.04
LHV	Q	kJ/kg	32.12	14.98	14.68
Volatiles	V	%	20.30	27.70	99
Ultimate analysis					
Carbon	C	%	84.58	38.76	47.19
Hydrogen	H	%	2.82	2.67	3.13
Sulfur	S	%	1.01	1.18	0.03
Nitrogen	N	%	0.12	3.58	4.10
Oxygen	O	%	2.33	3.00	45.42
Chlorine	Cl	%	0.03	0.60	0.09
Ash composition					
Zinc	Zn	ppm	11	9508	50
Copper	Cu	ppm	76	1199	37
Lead	Pb	ppm	50	1253	16
Nickel	Ni	ppm	20	292	7
Chromium	Cr	ppm	17	605	9
Cadmium	Cd	ppm	nd	19	3
Manganese	Mn	ppm	66	1491	2
Aluminium	Al	ppm	2516	14	10
Iron	Fe	ppm	2524	92	85

Table 2
The number and parameters of experiments.

No. of exp.	Type of sample	Mass of sample	Steam temperature
1	RUBBER	10 g	1000–950 °C
2	PUR	10 g	1000–950 °C
3	Liquid	10 g	900–850 °C

The gasification experiments have been conducted using facility shown in Fig. 2. The samples were added in amounts of 10 ± 0.01 g for each experiment. The mass flow rate of steam was fixed at 0.62 kg/h (10 g/min). Fluctuations were observed in the flow of steam in the range of ± 0.1 kg/h during the process. The steam temperature for gasification was adjusted to 1000–950 °C with the ± 25 °C of uncertainty. The accuracy of weight measurement was disturbed by oscillations of around ± 0.5 g which was estimated on runs with empty and filled basket for the similar flows and temperatures of steam.

The process was continuously monitored by measurement of steam and sample temperature (R and S type thermocouples, respectively) and concentrations of oxygen, carbon monoxide and carbon dioxide in the generated gases. The O₂ was analyzed using M&C Analysentechnik instrument, type PMA 25, equipped in a paramagnetic detector, while CO and CO₂ concentration were measured using Maihak analyzer type MULTOR 610 equipped with a Non-Dispersive Infra Red detector (NDIR). The cleaned and dried gas was analyzed by a dedicated micro GC-Varian CP-4900 coupled with a thermal conductivity detector (TCD). The gas was automatically sampled every 90 s. Nitrogen was used as a tracer gas. The nitrogen coming from the sample was neglected. The heat capacity of the honeycomb enables to keep the temperature of steam at a stable level for about 15 min, after the gasification process has started. All experiments had been conducted until the sample mass loss was not noticeable and the concentration of CO dropped below 0.1%. The conditions and number of experiments are presented in Table 2.

3. Results and discussion

3.1. Concept of combined system for ASR treatment

The idea of using this two-staged process was created to present a holistic method of handling complex and hazardous wastes such as ASR. The system is meant to work in a continuous operation. Fig. 3 presents the conceptual idea for dealing with ASR by means of microwave pyrolysis and then upgrading their by-products by taking an advantage of HTSG.

The feedstock streams are indicated with bold arrows (see Fig. 3). The thin arrows correspond to the directions of media streams (water, steam, air, etc.). Three fractions were used as feedstock for steam gasification: RUBBER (containing 85% of carbon), PUR (containing 50% of carbon) and Liquids (with 43% of water), as it is indicated in Table 1. High temperature steam (or mixture of steam and air) is produced in an ultra-efficient, fast regenerative steam generator. The system works under normal pressure. Detailed descriptions of the HTAG system and steam generator are available elsewhere [25–27]. The feedstock is fed from the top of the fix-bed gasifier while the high temperature agent (steam or mixture steam and air) is introduced from the bottom.

In the simulation, 15% of the generated producer gas is consumed for steam generation used internally for gasification process. This was estimated, based on thermodynamical simulation for the optimal steam-to-fuel ratio 1.4 (mol/mol) at steam temperature of 1000 °C and heat losses of 10%. At these conditions it is expected for producer gas to have the highest LHV and mass flow rate [20,21]. However, in order to sustain the flexible operation the steam-to-fuel ratio is assumed to be 20% higher than that of a theoretical requirement and this would raise the internal producer gas consumption up to ca. 20%. The rest of the producer gas can be used directly as a fuel for gas engine or gas turbine, but for maintaining a constant delivery and pressure of fuel, the producer gas is compressed and stored in a tank. For the simplification of the model development, it was assumed that the total solid carbon was con-

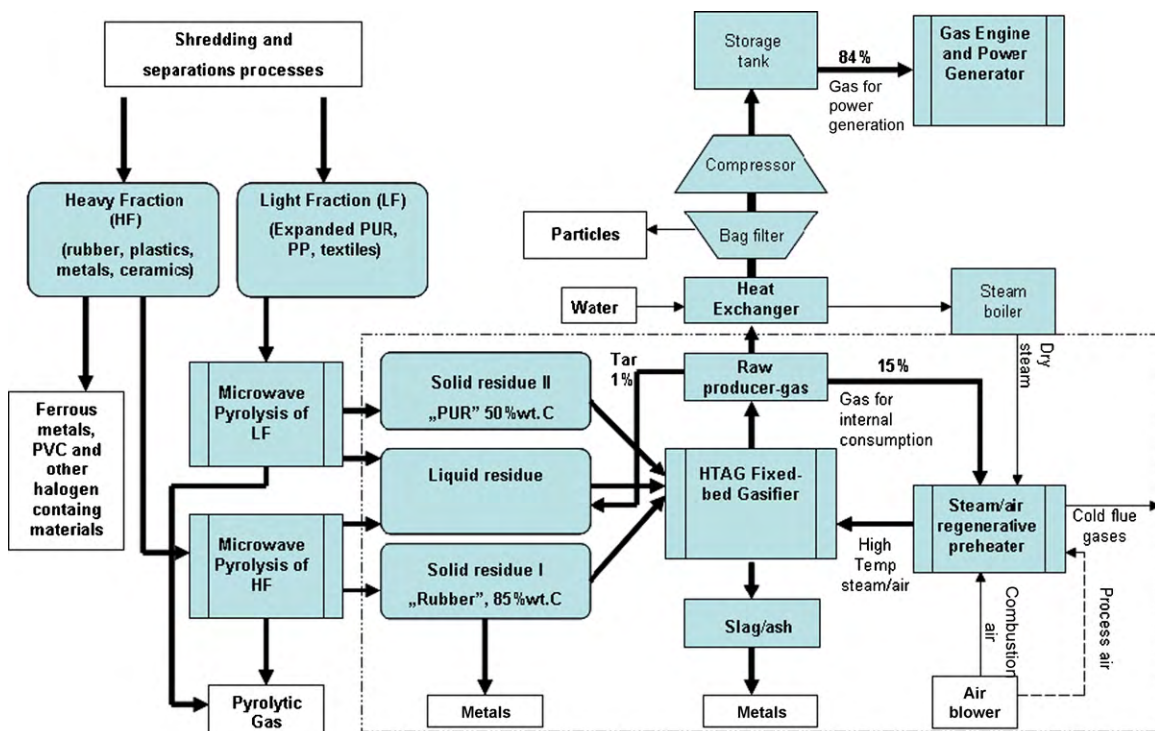


Fig. 3. A novel conceptual solution of the ASR treatment process.

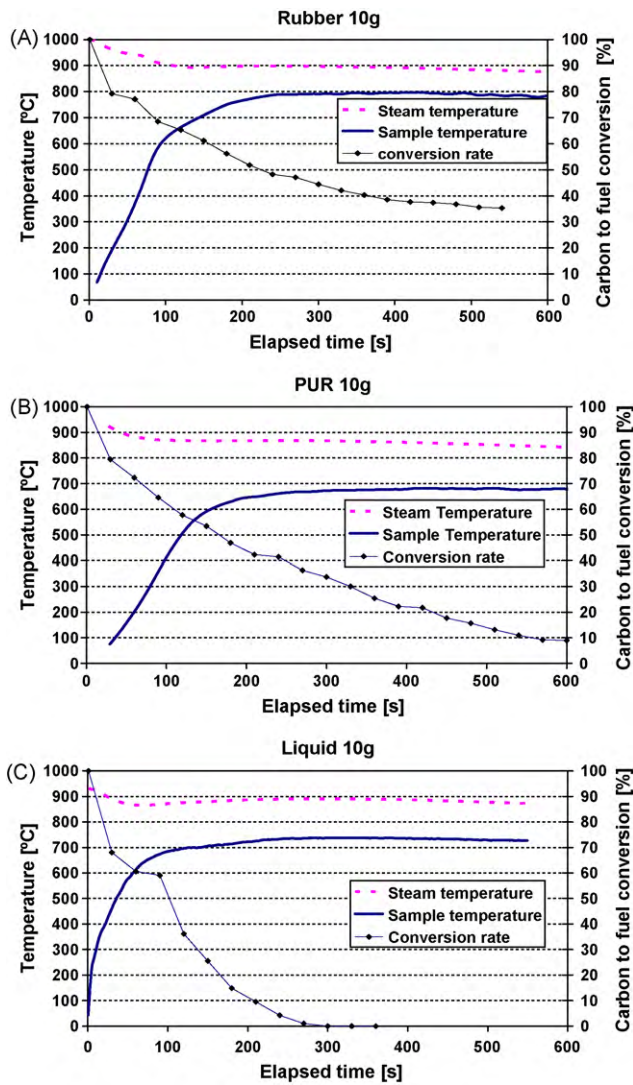


Fig. 4. Dynamic analyses of mass and temperature changes during the gasification experiments with high temperature steam: (A) RUBBER, (B) PUR and (C) Liquid. Steam flow rate 10 g/min. Steam temperature 1000–950 °C.

verted into the fuel. Hence, tar is assumed to be removed from the raw producer gas and fed into the liquid residues from the microwave pyrolysis process. It was anticipated that the conversion of carbon to fuel for solid fractions would not reach 100% in considerable period of time, thus results obtained in a small scale experiment should bring out the more realistic data. A dashed-line frame in Fig. 3 emphasizes the section of the conceptual process which is related to gasification experiments performed, however, in a smaller scale.

3.2. High temperature steam gasification of microwave pyrolysis' residues

3.2.1. Process performance

It was proved that, the higher temperature of gasifying agent is used, the higher conversion of fuel is observed and better quality of producer gas is generated [20,25–27,31]. Fig. 4 presents dynamic changes of masses and temperatures of tested samples exposed to the flow of high temperature steam.

The upper dashed-curve represents the steam temperature entering to the system, which is measured by thermocouple no. 9 in Fig. 4. It also indicates the ambient temperature. The lower increas-

ing curve represents the sample temperature in respect to elapsed time which indicates the heating of sample. This temperature is measured inside the sample bed by thermocouple no. 10 in Fig. 4. The black dot-curve corresponds to the normalized conversion of ash-free solid fuel to gas fuel, described in Eq. (1):

$$C(t, T) = \frac{(m_0 - x_A) - (m_{t,T} - x_A)}{(m_0 - x_A)}, \quad (1)$$

where $C(t, T)$ (kg/kg) is the normalized conversion of the ash-free organic contents of a sample, m_0 , $m_{t,T}$ (kg) are the initial and actual weights of sample; x_A (kg/kg) is an ash content of the initial mass of sample taken from its elemental composition shown in Table 1.

The function expressed in Eq. (1) derives from the common mass loss expression $(m_0 - m_t)/m_0$ widely available in literature (e.g. [30]) and is independent from the ash content in tested material, and therefore it simplifies the comparison between samples containing different amounts of ash. It requires, however, the assumption that the ash is not involved in any reactions resulting in mass change throughout the whole process.

Before materials reach a certain temperature in order to undergo the gasification process, they pass through several thermal processes and transition steps. For solid fuel under high temperature steam condition, one can distinguish processes of: drying/volatilization and pyrolysis. Table 3 gives a brief description of each stage. It can be seen from Table 3 that during mass loss of the sample, at least three separate stages can be identified. Initially, the first stage of drying/volatilization occurred, starting from room temperature to about 130 °C for solid (see Fig. 4A and B) and 200 °C for liquid fuel (see Fig. 4C), respectively. This process lasted for about 30 s. Subsequently, the second stage took place between the temperature 200 and 550 °C. The duration of this process is varied in respect to the type of tested sample; for liquid it underwent rapidly, in less than 50 s, meanwhile for solid fuel it took around 90 s for RUBBER and 130 s for PUR to complete this stage, respectively. During this stage the sample is linearly and rapidly heated. This corresponds to pyrolysis process which undergoes until sample's weight loses about 50% of its total initial weight. The heating rate is almost constant (the sample temperature raises linearly with a time) and varied between: 7 °C/s (420 °C/min) for liquid (vapor), 6.3–6.5 °C/s (390 °C/min) for RUBBER and 4.9 °C/s (290 °C/min) for PUR, as it is shown in Fig. 4C, A and B, respectively. This relatively high contribution of pyrolysis process of the material which had been already pyrolysed via microwave radiation, suggests that the microwave process had not completely de-volatilized the raw samples remaining some of the un-reacted components. This could be a direct effect of microwave heating which is characterized by the variation in microwave absorption for different materials [23]. In addition, differences in heat capacities and heat conductivity among the materials comparing ASR, cause gradients in samples heating rates, which strongly affect the pyrolysis rate. It is, in turn, well known that the heating rate plays a very important role in char formation and its internal structure, and afterwards on reactivity with steam [20,30,31].

During the first and second stage the decreasing trend of the ambient temperature is observed. The high temperature steam in this stage is consumed for heating up the sample, endothermic pyrolysis process and also heat losses.

After pyrolysis the third stage occurring is gasification. This is illustrated in Fig. 4 at the moment when the sample's temperature curve becomes more plateau and the heating rate (dT/dt) tends to go to zero. This process proceeds slower than pyrolysis. The ambient temperature continues decreasing, because steam reforming is an endothermic process, which is presented as Eq. (2):

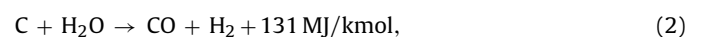
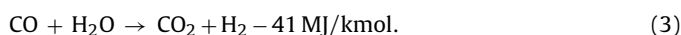


Table 3
Process performance.

Sample	Stage and process name	Duration of stage (s)	Sample temperature (°C)	Mass loss (%)	Heating rate (°C/s)
RUBBER	I Drying/volatilization	0–20	25–150	31	N/A
	II Pyrolysis	20–120	200–700	21	6.3
	III Gasification	100–540	650–800	48	N/A
PUR	I Drying/volatilization	0–30	25–160	16	N/A
	II Pyrolysis	40–150	180–600	28	4.9
	III Gasification	120–600	600–680	56	N/A
Liquid	I Vaporization/volatilization	0–10	0–200	32	20
	II Pyrolysis	20–80	200–620	9	7
	III Gasification	80–300	600–720	59	N/A

Due to the above equation, the ambient temperature reaches minimum. After a while the water gas-shift reaction starts dominating which generates some amount of heat to the system, according to the reaction of Eq. (3):



This can be observed by appearance of a local maximum in the ambient temperature (the upper temperature curve in Fig. 4) after around 300 s of the elapsed time. Simultaneously, the mass loss of sample reaches 55% for RUBBER, 65% for PUR and 100% for Liquid, as it is illustrated in Fig. 4A–C, respectively.

Since pyrolysis is much faster than steam gasification, the whole process was evaluated in two independent steps. One of which was pyrolysis (including drying) and the other one was char gasification. A very fast heating rate of multi-component sample can generate some difficulties in defining the boundary between each of the processes. Some reactions and processes may overlap. Moreover higher heating rates shift the reactions of decomposition toward higher temperatures. This was also observed by Kantarelis [31], who was conducting research on pyrolysis' kinetics of electric and electronic wastes in highly preheated agents. He 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, which affect the carbon matrix and increase its porosity. This also leads to an increase in the reactivity of char. However, there is another phenomenon which takes place during extensive heating; the rearrangement and deformation of char structures can be more intensive, e.g. shrinkage of char can be enhanced which inhibits decomposition. In general it is believed that the overall impact of high heating rates increase the activity for most types of biomass and thus the pyrolysis rate [30], but in some cases the char reactivity slows down, with increasing heating rate. These phenomena were observed by Donaj and Yang [33] who performed series of thermo-gravimetric analysis on ASR char reactivity in oxidative conditions. They indicated that for slower heating rate of 10 K/min the maximum decomposition rate (which corresponds to combustion) was at about 900 K with maximum rate of 40%/min but when the heating rate was of 100 K/min this maximum shifts to 1100 K and the rate decreased to 10%/min.

Nevertheless it is possible to register the sample temperature and its mass change as a function of time and identify each of the process it belongs to. Thus, the dynamic representation of the mass loss and the temperature rise in tested material can generate a useful piece of information about the process performance that takes place during thermal conversion.

3.2.2. Gas composition

The gas composition as the function of residence time is presented in Fig. 5 the rest of the gas is the tracer agent (nitrogen). By adding nitrogen at the constant flow of 0.3 N m³/h and detecting it molar ratio on GC it was possible to calculate the volume flow rate

of generated gases, \dot{V}_G , (dm³/s) and complete the mass balance of the system.

The maximum gas production rate was obtained from 150th to 300th second of the process duration. This corresponds to the second and third stage of the process when both pyrolysis and gasification processes were involved. In this moment both solid-gas and gas-gas phase reactions are present. During this period, the generating gas has the highest H₂, CO and CH₄ content, which yields with the highest lower heating value. Afterwards CO₂ concentra-

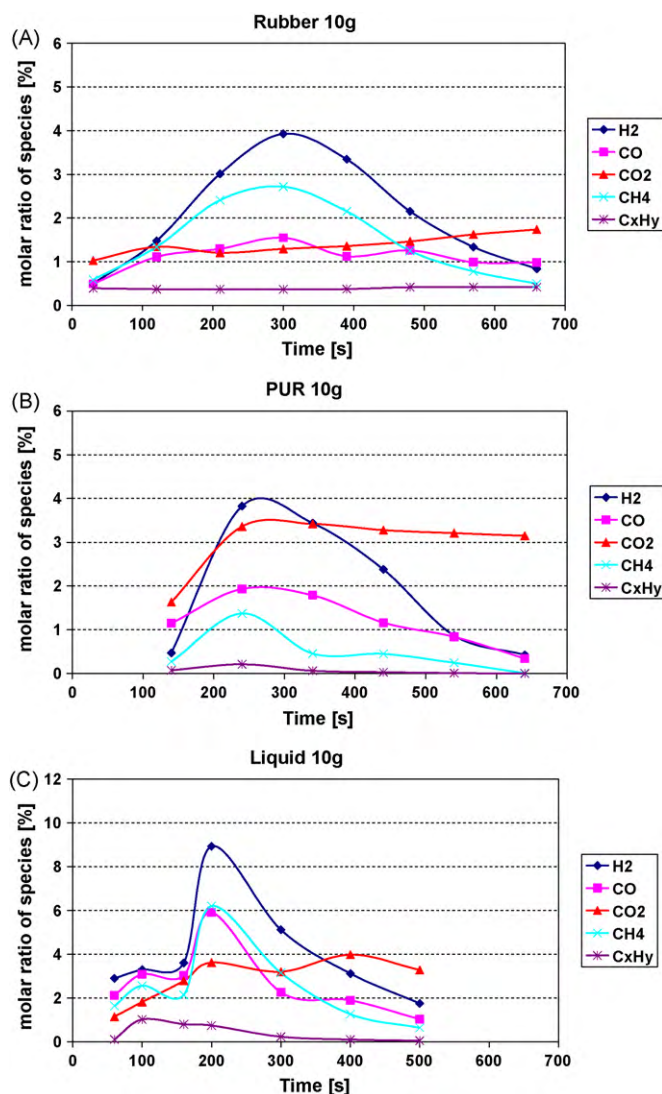


Fig. 5. The gas composition of generated gas after steam gasification vs. residence time. (A) RUBBER, (B) PUR and (C) Liquid.

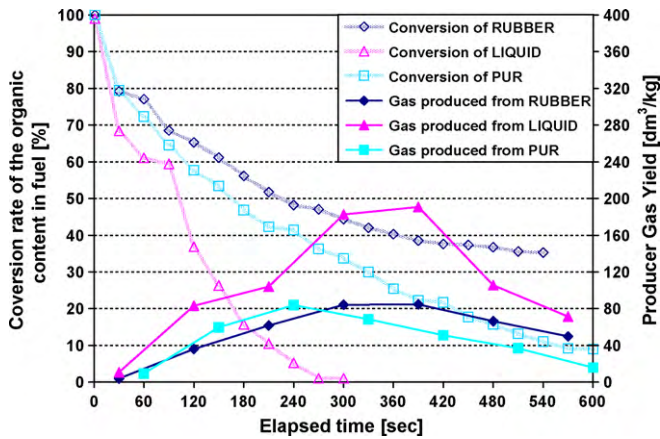


Fig. 6. Conversion of fuel to gas of solid and the volumetric producer gas yield. Steam flow rate 10 g/min Steam temperature 1000–950 °C.

tion increases as a result of water-gas shift reaction which is also indicated as the maximum peak on steam temperature curve in Fig. 4.

Fig. 6 compares the conversion of fuel to gas and the volumetric producer gas yield expressed as a volume of producer gas generation from the unit of carbon content in the fuel as the function of time. It was assumed that the producer gas includes the tar content.

The conversion denotes the highest degree for Liquid 99% followed by PUR 90% and RUBBER 65%. This implicates the low content of organic carbon in ash which, in fact, has been enriched in mineral matter. It is important to point out that the conversion of organic matter to fuel in the current investigations is related only to the char, excluding the reduction of raw ASR's weight via microwave pyrolysis.

The differences in organic matter to fuel conversion rate between tested samples are probably due to differences in char activity and ash content. Both of these factors influence gasification reaction rate and eventually conversion degree. The char structure after microwave pyrolysis is not uniform and the porosity of carbon matrix is not well developed. Wang et al., who conducted research on microwave pyrolysis of pine sawdust, pointed out that with increasing the pyrolysis temperature from 400 to 600 °C the pore size of chars decreased gradually [24]. They also suggested based on SEM that char could melt and deform resulting in shrinking and even closing of pores at higher temperatures. Another reason of decreasing reactivity could be melting of components comprising ash that clog pores of carbon matrix and block the access of reactants to its active sites.

However, some researchers found the catalytic effect of ash on pyrolysis and gasification rates [29,32,34]. Hence, it should also implicate on gasification of ASR's chars. One should notice that in case of ASR that the metal content is highly diversified, therefore it is difficult to predict which of the constituent has a dominating effect; it also differs between the tested samples. Other authors showed that alkali and alkaline earth metallic species can change the catalytic effect with the progress of the gasification [34] and after certain temperature inhibit reaction rate.

Kantarelis et al. [20,31] conducted pyrolysis and gasification experiments of raw Electrical and Electronic Shredder Residues (EESR) from ELV's using highly preheated agents. The pyrolysis experiments were conducted using preheated nitrogen up to 1050 °C and resulted in a hydrogen rich gas generation and solid conversion of 86 wt.% while experiments on gasification with the steam at 1050 °C yielded in a hydrogen rich gas (~45%, v/v) with the conversion of 92 wt.% of the solid material. It is worth to add that EESR has much higher plastic content (mainly PE and PP) reaching

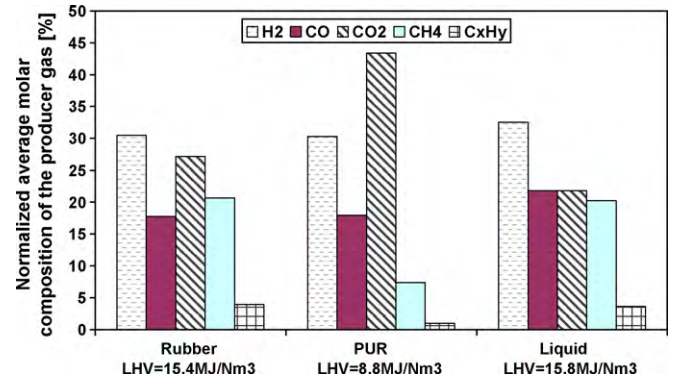


Fig. 7. Normalized, nitrogen-free composition and average LHV of the producer gas.

even 80–90% [20] than compared to ASR which has 10–30% of corresponding fractions. This leads to a conclusion that HTAG of the chars (PUR and RUBBER) has reached the reasonable rate in limited time and can be used as a complimentary method to pyrolysis and in particular microwave pyrolysis.

The specific volume of producer gas generated from a unit of fuel (see Fig. 6) was computed by integrating volume flow rate of producer gas against time, which is illustrated in Eq. (4):

$$v(t_i) = \int_0^{t_i} \frac{\dot{V}_G}{mC(t, T)} dt, \quad (\text{m}^3/\text{kg}), \quad (4)$$

where v is a volumetric producer gas yield (m^3/kg), \dot{V}_G is a volume flow rate of the producer gas (m^3/s), m is an initial mass of sample (kg), $C(t, T)$ is a conversion degree (dependent of time and temperature) of organic matter content in fuel (kg/kg), t_i is an elapse time (s).

Hence, the total volumetric producer gas yield V_t is given in Eq. (5):

$$V_t = \sum_{i=0}^t v(t_i), \quad (\text{m}^3/\text{kg}) \quad (5)$$

It can be seen from Fig. 6 that with decreasing mass of sample the volumetric producer gas yield initially increases reaching maximum after 300–360 s and subsequently decreases. This is a rational behaviour, since the investigated process is a batch type process in terms of fuel supplied system thus gas production reaches some extreme point and afterwards it starts decreasing. The maximum volumetric gas production yield per 1 kg of organic content of liquid fuel were $190 \text{ dm}^3/\text{kg}$ for liquid sample and around $85 \text{ dm}^3/\text{kg}$ for solid samples. After applying Eq. (5), the results, of the total volume of producer gas per kilogram of ash-free basis fuel, yield: $387 \text{ dm}^3/\text{kg}$ from RUBBER, $325 \text{ dm}^3/\text{kg}$ from PUR and $749 \text{ dm}^3/\text{kg}$ from LIQUID.

Fig. 7 shows the normalized gas composition (%) and LHV (MJ/Nm^3) of producer gas.

The experimental products comprise ash rich in metals, and producer gas with the average gas composition of 32, 20 and 20% for H_2 , CO and CH_4 , receptively, with some variation in respect to the fuel. In case of the Liquid sample H_2 :CO was 1.4 with the high content of methane. The H_2 :CO varied from 1.72 to 1.69 mol/mol for RUBBER and PUR, respectively. The average LHV of generated gas was $15.8 \text{ MJ}/\text{Nm}^3$ for liquid, $15 \text{ MJ}/\text{Nm}^3$ for RUBBER and $9 \text{ MJ}/\text{Nm}^3$ for PUR, respectively. The lower value of LHV recorded for PUR was due to the higher content of CO_2 and lower amount of methane and lighter hydrocarbons. In this case water gas steam reaction and steam reforming reactions reduces the content of carbon monoxide and hydrocarbons, and increases the concentration of CO_2 . The CH_4 concentration, varied from 7.4 for PUR to 20% RUBBER and Liquid,

respectively, and contributes significantly in elevating LHV of fuel gas. Taking into account the ash content in PUR which was four times larger than in RUBBER, the carbon conversion for PUR was significantly higher reaching up to 90% vs. 65% for RUBBER. Even in case of PUR, where the CH₄ content was much lower than for other samples, it was still quite high for the equilibrium state. At this experimental condition (steam-to-fuel ratio was 1.38, 950 °C, 1 bar) the following gas mixture should contain 61% of H₂, 23% of CO, 16% of CO₂ without the presence of hydrocarbons [21].

The de-volatilization product generation process and heterogeneous char-steam reaction, referring to mass loss, here will be defined as primary reactions. However, the resulting gases and vapors may undergo further reforming reactions between the generated species and steam, and also those products may undergo further pyrolysis (cracking) process especially when the ambient temperature is higher than a temperature inside the sample. This will refer to secondary reactions. In practice it is very difficult to isolate the primary process from secondary, since that would require a rapidly quenching of generating products to obtain maximum reduction of residence time in hot reaction zone for the primary products. The secondary reactions (e.g. tar formation and the gas-phase reactions) cannot be, however, observed on mass loss curve, but they have a very high contribution to the final gas composition and volumes. Nevertheless it is possible to estimate how much the gas composition registered on GC differs from the expected values obtained from thermodynamical equilibrium for a given condition.

Therefore, the gas composition suggests that mainly primary reactions occurred between steam and fuel and the contribution of secondary reactions in gas phase was not high enough to react with secondary products. In this reactor setup the steam-methane (gaseous hydrocarbons) reforming reaction was not favoured. This leads to a conclusion that most of the reactions proceeded mainly inside the sample basket, and the whole system acted similarly to thermogravimetry analysis (TGA). TGA in fact, which uses very small amounts of sample (<0.1 g), shows the mass changes insensitive to the heat and mass transport phenomena and related mainly to the primary sample decomposition [30]. In case of the current investigation, the composition of generated producer gas is in-between the TGA and the equilibrium. Furthermore, with respect to the gas-phase reactions, the facility used in this investigation can be classified into plug flow reactors, in which the contact time between the gases is relatively short and axial mixing is not observed [35]. The residence time of the secondary products being in the hot reaction zone is too short to react with steam. In addition the lower conversion of solid residues can be explained with a weaker mixing index between the steam and solid phases. That explains why the values of gas composition are quite far from the equilibrium condition, which would show much lower hydrocarbons content at the conditions of experiments. This can also have negative consequences on tar reduction rate, since the concentrations and temperatures of steam are declining fast after passing through the reaction zone and afterwards become probably not sufficient for tar reforming. This problem could be solved by feeding the excess steam to the system or by increasing the residence time for secondary products, however, the last option would require modernization of the existing reactor system. Increasing the contribution of secondary reactions would effect in elevating H₂, CO₂ and volume of producer gas but in the same time the hydrocarbons content would go down reducing LHV of the producer gas.

4. Conclusions

A new concept has been developed for ASR's treatment based on combining both microwave pyrolysis and the HTAG process. This concept has been designed to maximize the conversion of organic

contents of ASR into valuable products (e.g. producer gas), while preserving metals during each step of the process. For the simplification of the model development, it was assumed that the all of organic solid carbon was converted into the fuel. However, the conversion factor required a justification in experimental data.

In order to simplify the comparison between the samples a new conversion function was proposed. This function describes a normalized mass loss of the material independently from its ash content and enables to compare the materials with highly diverse ash content.

The investigations on solid and liquid products after microwave pyrolysis, conducted in a batch-type, lab-scale gasifier using high temperature steam, revealed that the organic carbon to gas conversion was 65, 90 and 100% for RUBBER, PUR and Liquid, respectively. During the experiments it was also found that HTAG of the chars has reached a reasonable rate in limited time and can be used as the complimentary method to pyrolysis and in particular microwave pyrolysis. The total process lasts for about 10 min but the maximum volumetric producer gas yield was reached in about 4–6 min. The volumetric producer gas yield was: 750 dm³ for Liquid, and 320–370 dm³ for PUR and RUBBER per 1 kg of dry ash free bases fuel with the average LHV varied between 8 and 15.8 MJ/N m³.

The results are fairly supportive for the concept for the liquid material, however further investigations of char structure and its reactivity vs. various operation conditions are necessary to perform in case of solid samples. They should lead to getting the optimal operation conditions and to providing more clear benefits and limitations of the considered system as compared to other competitive processes. In addition the system should be tested in continuous operation.

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References

- [1] P. Ferrao, J. Amaral, Assessing the economics of auto recycling activities in relation to European Union Directive on end of life vehicles, *Technol. Forecast. Soc. Change* 73 (2006) 277–289.
- [2] M. Nourredine, Recycling of auto shredder residue, *J. Hazard. Mater.* A139 (2007) 481–490.
- [3] R. Zoboli, G. Barbiroli, R. Leoncini, M. Mazzanti, S. Montessoro, Regulation and innovation in the area of end-of-life vehicles, The European Commission JRC-IPTS and Enterprise DG, March 2000, Milan, Italy. Available at: <http://www.bir.org/efr2/IPTS-ELV-Study-2000.pdf>.
- [4] M.A. Cortes-Pena, L.V. Perez-Arribas, M.E. Leon-Gonzalez, L.M. Palo-Diez, Determination of chlorine and bromine in automotive shredder residues by oxygen bomb and ion chromatography, *Waste Manage. Res.* 20 (2002) 302.
- [5] M.S. Reddy, K. Kurose, T. Okuda, W. Nishijima, M. Okada, Separation of polyvinyl chloride (PVC) from automotive shredder residue (ASR) by froth flotation with ozonation, *J. Hazard. Mater.* 147 (2007) 1051–1055.
- [6] K. Kurose, T. Okuda, W. Nishijima, M. Okada, Heavy metals removal from automotive shredder residues (ASR), *J. Hazard. Mater.* B137 (2006) 1618–1623.
- [7] H.T. Joung, Y.C. Seo, K.H. Kim, Effects of oxygen, catalyst and PVC on the formation of PCDDs, PCDFs and dioxin-like PCBs in pyrolysis products of automotive residues, *Chemosphere* 65 (2006) 1481–1489.
- [8] D. Mirabile, M.I. Pistelli, M. Marchesini, R. Falciani, L. Chiappelli, Thermal valorisation of automotive shredder residue: injection in blast furnace, *Waste Manage.* 22 (2002) 841–851.
- [9] M.K. Harder, O.T. Forton, A critical review of developments in the pyrolysis of automotive shredder residue, *J. Anal. Appl. Pyrol.* 79 (2007) 387–394.
- [10] I. Marco, B.M. Caballero, M.A. Cabrero, M.F. Laresgoiti, A. Torres, M.J. Chomon, Recycling of automotive shredder residues by means of pyrolysis, *J. Anal. Appl. Pyrol.* 79 (2007) 403–408.
- [11] C. Forsgren, Microwave Pyrolysis A New Recycling Tool. IT'07 Conference, May 14–18, 2007 Phoenix, AZ, USA, 2007.
- [12] M. Day, Z. Shen, J.D. Cooney, Pyrolysis of automotive shredder residue: an analysis of the products of a commercial screw kiln process, *J. Anal. Appl. Pyrol.* 37 (1996) 49–67.
- [13] M. Day, Z. Shen, J.D. Cooney, Pyrolysis of auto shredder residue: experiments with a laboratory screw kiln reactor, *J. Anal. Appl. Pyrol.* 51 (1999) 181–200.

- [14] S. Galvagno, F. Fortuna, G. Cornacchia, S. Casu, T. Coppola, V.K. Sharma, Pyrolysis process for treatment of automotive shredder residue: preliminary experimental results, *Energy Convers. Manage.* 42 (2001) 573–587.
- [15] K. Srogi, An overview of current processes for the thermochemical treatment of automobile shredder residue, *Clean Technol. Environ. Policy* 10 (2008) 235–244.
- [16] M. Kondoh, M. Hamai, M. Yamaguchi, S. Mori, Study of gasification characteristics of automotive shredder residue, *JSAE* 22 (2001) 221–236.
- [17] C.F. Cullis, M.M. Hirschler (Eds.), *The Combustion of Organic Polymers*, Oxford University Press, London, 1981 (*J. Polym. Sci.: Polym. Lett. Ed.*).
- [18] P. Donaj, W. Kaminsky, Recycling of polyolefins by pyrolysis in a fluidized bed reactor, in: 17th European Biomass Conference, Paper #OB4.4, June 27–3, 2009, Hamburg, Germany.
- [19] T. Malkow, Novel and innovative pyrolysis and gasification technologies for energy efficient and environmentally sound MSW disposal, *Waste Manage.* 24 (2004) 53–79.
- [20] E. Kantarelis, P. Donaj, W. Yang, A. Zabanitoutou, Sustainable valorization of plastic wastes for energy with environmental safety via High-Temperature Pyrolysis (HTP) and High-Temperature Steam Gasification (HTSG), *J. Hazard. Mater.* (2009), doi:10.1016/j.jhazmat.2009.01.036.
- [21] K. Kubik, Reforming of Car Residues Pyrolysis Products into High-purity Synthetic Gas for Small-scale Electricity Generation, Master Thesis in Energy and Furnace Technology, Royal Institute of Technology, Stockholm, Sweden, 2008.
- [22] P. Donaj, K. Kubik, A. Swiderski, W. Yang, W. Blasiak, C. Forsgren, Assessment of ASR treatment using pyrolysis and reforming of its residues for small scale electricity generation systems, in: IT3 2008, Montreal, Canada, 2008.
- [23] T.J. Appleton, R.I. Colder, S.W. Kingman, I.S. Lowndes, A.G. Read, Microwave technology for energy-efficient processing of waste, *Appl. Energy* 81 (2005) 85–113.
- [24] X. Wang, H. Chen, X. Ding, H. Yang, S. Zhang, Y. Shen, Properties of gas and char from microwave pyrolysis of pine sawdust, *BioResource* 4 (3) (2009) 946–959.
- [25] S. Kalisz, R. Abeyweera, D. Szewczyk, A. Jansson, C. Lucas, W. Blasiak, Energy balance of high temperature air/steam gasification of biomass in updraft, fixed bed type gasifier, in: IT3 Conference, Phoenix, Arizona, May 10–14, 2004.
- [26] C. Lucas, High Temperature Air/Steam Gasification of Biomass in An Updraft Fixed Bed Batch Type Gasifier, Doctorial Thesis in Energy and Furnace Technology Stockholm, Sweden, 2005.
- [27] A. Ponzio, Thermally Homogenous Gasification of Biomass/Coal/Waste for Medium or High Calorific Value of Producer gas Production, Doctorial Thesis, KTH, Stockholm, 2008.
- [28] W. Jangsawang, A. Klimanek, A.K. Gupta, Enhanced yield of hydrogen from wastes using high temperature steam gasification, *J. Energy Resour. Technol.* (2005).
- [29] I.I. Ahmed, A.K. Gupta, Pyrolysis and gasification of food waste: syngas characteristics and char gasification kinetics, *Appl. Energy* 87 (2010) 101–108.
- [30] A.J. Tsamba, Fundamental Studies of Two Selected Tropical Biomass for Energy: Coconut and Cashew Nut Shells, Doctorial Thesis, 2008.
- [31] E. Kantarelis, Thermochemical Treatment of Electric and Electronic Waste for Energy Recovery, Licentiate Thesis in Furnace Technology, Stockholm, Sweden 2009, IRSN: KTH/MSE-9/56-SE+ENERGY/AVH.
- [32] N. Tancredi, T. Cordero, J.R. Mirasol, J. Juan, CO₂ gasification of eucalyptus wood chars, *Fuel* 75 (13) (1996) 1505–1508.
- [33] P. Donaj, W. Yang, Kinetic study of decomposition of ASR residues after pyrolysis in inert and oxidative atmosphere, in: IT3 Conference, May 18–23, 2009, Paper #a42, Cincinnati, OH, USA.
- [34] B. Bayarsaikhan, J.-i. Hayashi, T. Shimada, C. Sathe, C.-Z. Li, A. Tsutsumi, T. Chiba, Kinetics of steam gasification of nascent char from rapid pyrolysis of a Victorian brown coal, *Fuel* 84 (2005) 1612–1621.
- [35] P. Basu, P. Kaushal, Modeling of pyrolysis and gasification of biomass in fluidized beds: a review, *Chem. Prod. Process Model.* 4 (2009) 1 (art 21).