High Temperature Steam Reforming of Solid and Liquid Wastes Generated from Pyrolysis of Automobile Shredded Residue

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Abstract

Presently, there is a growing need of handling wastes generated by disposed vehicles, namely automobile shredder residues (ASR). One solution is microwave pyrolysis by which metals are successfully recycled and by-product such as pyrolysis gas, oil and char are generated. In this work, the treatment of char and liquid product streams from microwave pyrolysis of ASR with high temperature steam (or mixtures of steam with air or oxygen) will be reported. The scope is to produce high quality "syn-gas" that can be used for heat or electricity generation.

The current study is based on the residues generated after microwave pyrolysis. The material tested includes two fractions of solid (char) and liquid (Tar and heavy oils) material. The studies on the gasification process with the use of high temperature steam are carried out on a unique high-temperature air/steam reform reactor at the Royal Institute of Technology (KTH). The steam, generated in the ceramic regenerator, is heated up to 1273K. The gasifier is coupled to a special constructed balance system which is able to record the weight of sample on-line. The thermocouple placed in the sample holder measures the temperature inside the sample.

The heating rate, mass loss, gas composition and lower heating value of syn-gas versus residence time are reported for steam temperatures between 1273 and 1223K. The steam mass flow rate is set to 0.65 kg/h and the sample mass for each run is 10 to 20g.

Nomenclature

ASR	Automobile Shredder Residues
ELV	End-of-Life Vehicles
HiTAG	High Temperature Steam Gasification
GC	Gas Chromatograph
KTH	Royal Institute of Technolgy, 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

1. Introduction

In Europe every year end-of-life vehicles (ELV) generate 8 to 9 mln tonnes of waste [1]. In 2000 the European Commission (EC) enforced Directive 2000/53/EC, which gives guidelines on ELV recycling projection. The objective of the above Directive is to ensure that 85% of ELV's by weight will be recycled by year 2006, increasing to 95% by the year 2015 with additional de-pollution tasks being progressively introduced. Presently, about 75% of vehicle's weight is recovered; mostly metal content – the rest approximately 2.5 mln tonnes (25%wt.) a year is shredded, and creates the fraction of automobile shredded residue (ASR) [2,3]. ASR is a heterogeneous mixture of different types of materials, which consists mostly of plastics, rubber and textiles, while the rest are glass, metals and other species. The exact material or chemical composition of ASR is not easy to find and several authors reported different values [2-16, 19]. These misleading values are because ASR comes from different models, brands, types and year of production of vehicles and that can vary a lot.

Development in advanced plastics and composite materials and improvements in their physical-mechanical properties pushes the car producers to shift from metals towards plastics components. Metals are more and more replaced by lighter plastics [3]. The use of plastic materials has some advantages; i.e. lower production costs, reduction of car's weight, therefore less fuel is consumed. Increasing the content of

plastics in vehicle's weight and obeying the EC targets, creates a growing need of handling wastes generated by disposed vehicles. From ASR it is possible to recycle metals and simultaneously energy and/or chemicals feedstock from organic carbon. This can reduce the consumption of fossil fuels, and therefore decreasing emissions of greenhouse gases into the atmosphere. Due to the heterogonous and complexity in material composition of ASR and extra costs associated with separation [6, 7, 9], most of authors would consider rather thermal treatment method of raw ASR [7-16]. ASR are commonly recovered by combustion [8, 18], pyrolysis [6, 7, 9-15] and gasification [16, 19]. However, before applying thermal methods some pretreatment, should be performed in order to remove or reduce polyvinyl chloride (PVC) content. PVC emits HCl when exposure to heat [4-7]. Chlorides have negative feedback for the thermal processes because their metallic salts are more volatile then oxides or pure metals and they create the problems associated with corrosion of the facility. Combustion seems to be the simplest method of dealing with ASR, but it creates problems of high heavy metals content in fly ash, due to oxidative and high temperature condition taking place within the process [4, 5, 8]. Pyrolysis, which is one of the most promising methods of ASR treatment, has been widely studied [9-15]. During this process, carried out in an inert atmosphere with the absence of oxygen, the high energy free radicals are generated. They crack the polymer molecules into smaller compounds. Therefore wide range of hydrocarbons in solid, liquid and gaseous form, as well as some small amount of water and CO_2 is generated [16, 17]. Recently, several pyrolysis techniques have been reported in the area of ASR: microwave pyrolysis [11], screw kiln pyrolysis [10, 12, 13, 14]. The product distribution shifted from condensate to volatile products when the pyrolysis is conducted in higher temperatures [17, 18]. However, above 700°C the secondary reaction occurs, which yields in aromatic compounds responsible for formation of polycyclic aromatic hydrocarbons (PAH), and subsequently this leads to increase in tar formation. Pyrolysis of ASR generates high amounts of charcoal that can even reach even 50% of total product distribution [10-14]. Gasification is an alternative option for recycling of ASR [16, 19]. The gasification process is conducted with the limited oxidative condition during which syn-gas is forming. A gasified agent could be air, steam, CO_2, or mixture of them) and gasification temperatures are higher then for pyrolysis. The gasification of ASR was studied in various conditions and experimental setup [16].

In this work, the products after microwave pyrolysis of ASR which are char and liquid, are reformed using high temperature steam. The scope is to produce high quality "syn-gas" that can be used for heat or electricity generation. The high temperature agent gasification (HTAG) where the agent is steam, air or air/steam mixture and the feedstock is biomass and wastes, and coal have been widely studied [20-23]. In this process the gasifying agent is heated up to temperature above 1000°C and provides all necessary heat in order to conduct gasification. This results in high conversion of fuel to gas, higher LHV and lower tar content compared as in conventional gasification. The technique mentioned above will be used for the first time for the reforming of solid and liquid residues after pyrolysis.

2. Methodology and Experimental Setup

The sample characterization is presented in Table 1. Three different types of materials have been tested (see Table 2). Two of these samples were in solid form and one was a liquid. Each was residue after micro wave pyrolysis of ASR. Polyurethanes and textiles were removed form the rest of ASR fraction before treated with microwave pyrolysis, and de-volatilized separately. Therefore, two streams of solid residues were generated. They were indicated as "Rubber" and "PUR". The liquids yielding in both pyrolysis processes were mixed together to create the "Liquid" fraction. Rubber consists of different particle size, thus it was pulverized prior to run an experiment, meanwhile PUR was used as received in a "flake" form. The 4th experiment was the mixture of liquid and Rubber 9/1 ratio (w/w), which corresponds to the fraction streams generated during microwave pyrolysis. The "Rubber" sample has a high carbon content relatively low ash content, high LHV. From the elemental composition "Rubber" is comparable to coal. The "PUR" sample has very high ash content reaching to almost 50%wt. Both solid materials have relatively low volatile and very low moisture content as it was expected due the fact the both materials derived after pyrolysis. In the liquid product it was found high water content around 40%, which significantly decrease the LHV of liquid fuel. The LHV of fuel was calculated via Boi's formula [24].

A unique high-temperature air/steam reforming batch-type reactor at KTH was used for the studies. The general view of this facility is showed in Figure 1. In the beginning the facility is heated up by combustion of natural gas (4). The ceramic honeycomb accumulates the heat from the combustion that afterwards is used for gasification. In this facility, high temperature steam is generated by a honeycomb regenerator located in the facility (5). The balance located over the facility (16) records the mass loss of sample during the process. The generated gas passed through the gas piping-cleaning units and it was analyzed by the micro GC. As a tracer gas the nitrogen was used. The nitrogen coming from the sample was neglected.

Table 1. The proximate and ultimate analysis of tested material.

Proximate analysis	Units	Rubber	PUR	Liquid
Ash	%wt.	9.11	49,74	0.044
Volatile matter	%wt.	20.3	27,67	99
Moisture	%wt.	0.9	3,34	43
Lower Heating Value LHV [24]	MJ/kg	32.44	14.98	14.68
Ultimate analysis /dry basis/				
Carbon	%wt.	84.58	38,76	47.19
Hydrogen	%wt.	2.82	2,67	3.13
Nitrogen	%wt.	0.12	3,58	4.1
Oxygen	%wt.	2.23	3	45.41
Sulphur	%wt.	1.01	1,18	0.034
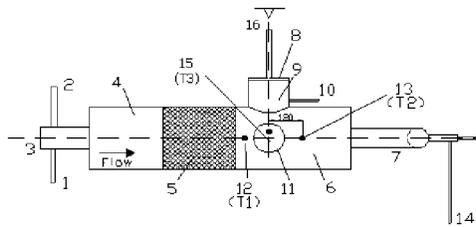
Figure 1. Small lab scale batch type gasifier.

Table 2. The number and parameters of experiments

No of Exp.	Type of sample	Mass of sample	Steam Temperature
1	Rubber	10 g	1273 -1223K,
2	PUR	10 g	1273 -1223K,
3	Liquid	10 g	1173 -1123K,
4	Lquid + Rubber 9:1	10 g	1173 -1123K,
5	Rubber	20g	1273 -1223K,

The mass flow rate of steam was fixed at 0.65 kg/h and temperature was set up between 1173 - 1273 K. The conversion rate was calculated according to the formula:

$$\alpha = 1 - \frac{m_{in} - m}{m_{in} - m_r} \tag{1}$$

where m_{in}, m and m_r are the initial, actual and final mass of the sample, respectively.

3. Results and Discussion

Figure 2 shows the dynamic change of temperatures and mass of sample in respect to elapsed time. The graphs correspond to 1st, 2nd, 3rd and 5th runs of the experiment. The upper (pink) curve represents the steam temperature entering to the system, which is measured by the thermocouple T1 (no. 12) in Figure 1. It also indicates the ambient temperature. The lower (blue) curve represents the heating of sample which is measured inside the basket by thermocouple T3 (no 15) in Figure 1. The derivative of sample temperature over time gives the value of heating rate (tan θ). The black dot-curve corresponds to the conversion rate. In all analyzed cases it can be observed the heating rate proceeds in four recognizable stages. Initially, the first stage of drying is occurred, starting from room temperature till about 130°C for solid and 200°C for liquid fuel, respectively. This process lasts about 30 seconds. Subsequently, the second stage is running between the temperature 200-550°C. The duration of this process is varied in respect to type of tested
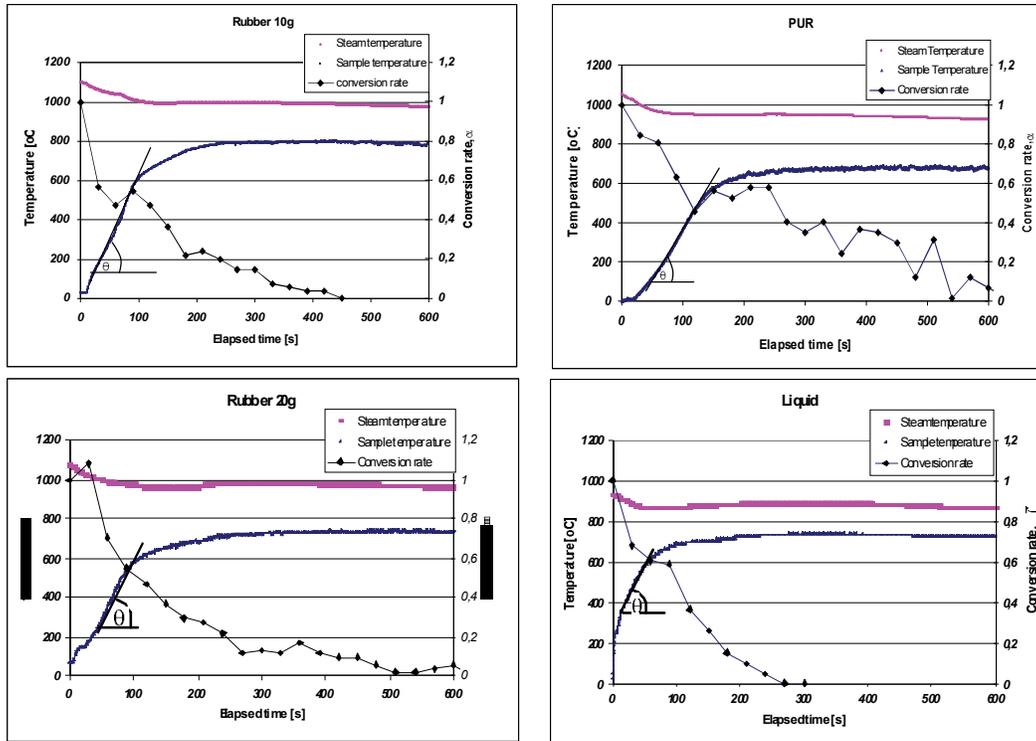
Figure 2. Dynamic analyses of mass and temperature changes during the gasification experiments with high temperature steam. From the slope of the line (tanθ) it can be calculated the heating rate for pyrolysis process. Steam flow rate 0.65 kg/h. Steam temperature 1273-1223K.

sample; for liquid it underwent in less than 50 seconds, meanwhile for solid fuel it took around 90 and 100 second for Rubber of initial weight 10 and 20 g and 130 second for PUR to complete this stage, respectively. During this stage the sample is heated very fast, the pyrolysis process of sample undergoes and the sample's weight loses about 50% of total mass loss. The heating rate (tan θ) is almost constant and it is varied between 7 ^{o}C/s (420 ^{o}C/min) for liquid, 6.3-6.5 ^{o}C/s (390 ^{o}C/min) for rubber and 4.9 ^{o}C/s (290 ^{o}C/min) for PUR, respectively. During the first and second stage it is also observed the decreasing trend of the ambient temperature. The pyrolysis is an endothermic process so the sample consumes the heat accumulated in the steam and ambient. After pyrolysis the third stage occurred. It can be observed when the sample's temperature curve becomes more flat and the heating rate can be described as linear function of time. This stage corresponds to the gasification of char (fixed carbon). This process is slower then the pyrolysis. The ambient temperature continues to decrease, because steam reforming is an endothermic process, which carries out as follows:

$$C + H_2O \rightarrow CO + H_2 \qquad + 131 \text{ MJ/kmol}$$

and finally reaches a minimum. Afterwards, the 4th stage starts proceeding. During the 4th stage the water gas-shift reaction starts dominating which generates some amount of heat to the system, accordingly to the reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad - 41 \text{ MJ/kmol}$$
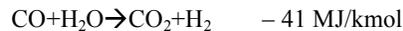
This can be observed by the appearance of a local maximum in the ambient temperature (the pink curve) in around 300th second of the elapsed time. Simultaneously, the mass loss reaches 100% for liquid and 85% for Rubber and 65% for PUR sample of total conversion rate, respectively.

The analysis of mass loss gives the basic knowledge about the conversion of solid or liquid fuel. However, it does not provide any useful information about the secondary reactions that are taking place during pyrolysis and gasification, i.e. tar formation, gas phase reaction. Most of these reactions are carried out in a gas phase. The gas composition as the function of residence time is presented in Figure 3. The rest of the gas is the tracer agent (nitrogen). By adding nitrogen it was possible to get the volume of generated gas. The time demanding thermal analysis of sample coupled with gas composition of generating gas and mass loss can better describe the process fundamentals. The maximum gas production rate was obtained between 200-300th sec. of the process duration. This corresponds to the 3rd stage of the

process when gasification process is involved. In this moment both solid - gas and gas - gas phase reaction are preset. During this period, the generating gas has the highest H_2, CO and CH_4 content, which yields with the highest lower heating value. Afterwards CO_2 concentration increase as the results of water gas shift reaction which is also indicated as the maximum peak on steam temperature curve in Figure 2.

Figure 4 compares the mass loss as the function of time for all analyzed cases. Due to the high temperature of steam no much tar and heavy hydrocarbons have been generated. For "rubber" the conversion varied from 25% for sample of 20g to approx 50% for sample of initial sample weight of 10g, respectively. The conversion of liquid sample was much larger than the solids one; therefore the total gas volume was 4 times higher when the gasified fuel was liquid material, which shows in Figure 5. The maximum gas production was obtained between 200th - 300th second of each experiment run.
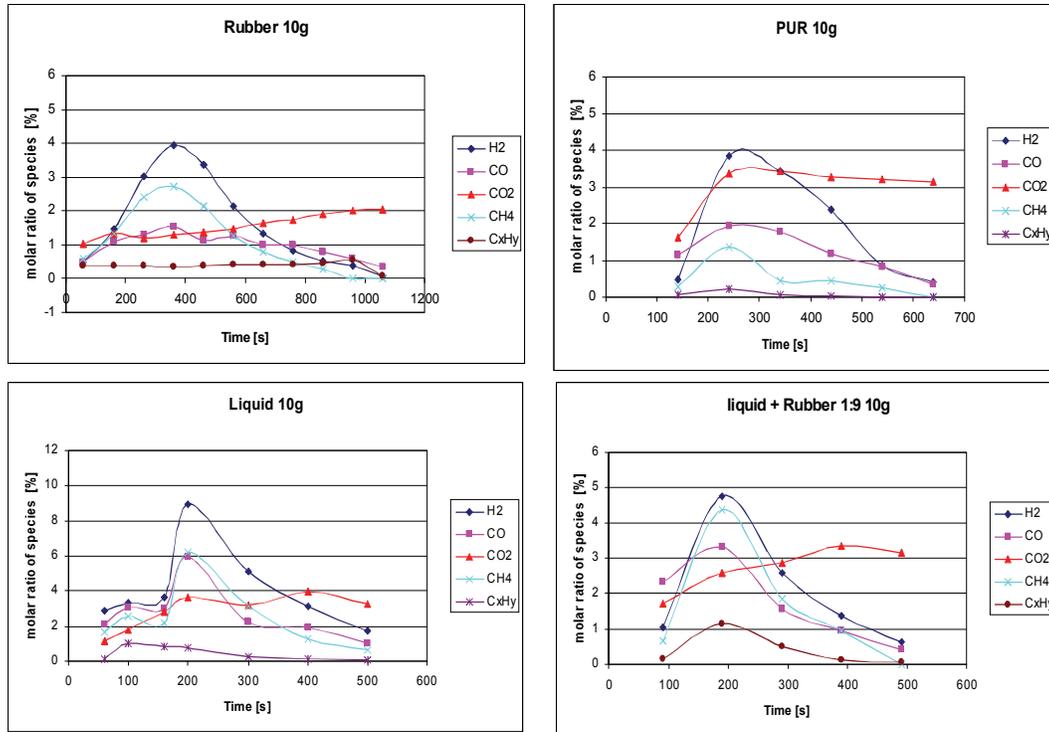
Figure 3. Gas composition of generated gas after steam gasification versus residence time.
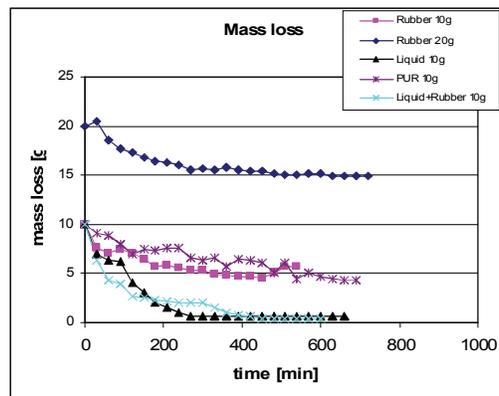
Figure 4. Mass loss of solid and liquid residues after pyrolysis. Steam flow rate 0.65 kg/h. Steam temperature 1273-1223K.
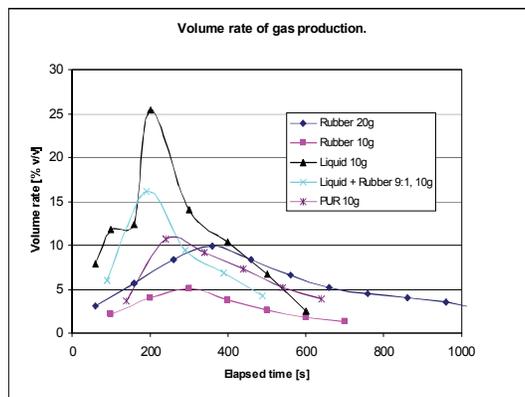
Figure 5. Volume rate of gas generated. Steam flow rate 0.65 kg/h. Steam temperature 1273-1223K.
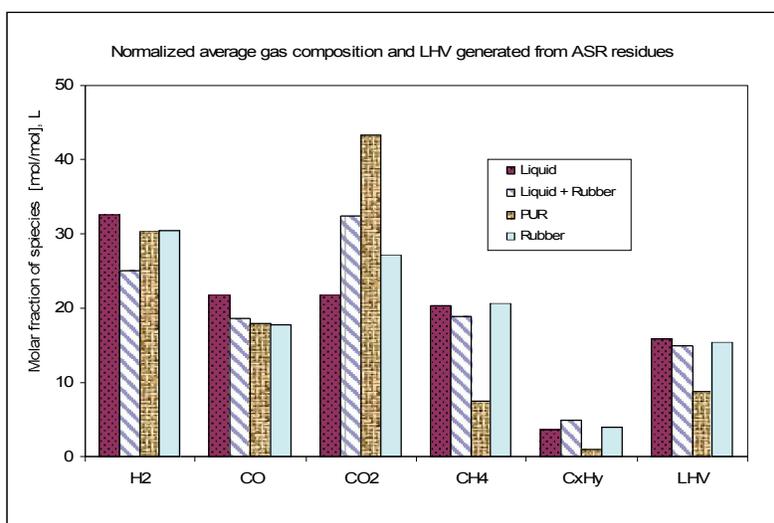
Figure 6. Normalized integrated gas composition and LHV.

Figure 6 shows the normalized integrated gas composition and LHV. It can be seen that the best gas quality in terms of heating value was obtained for liquid and liquid + Rubber experiments. For these experiments the gas volume was also the highest. However, the mixture of Liquid and Rubber has slightly worse results in terms of composition and lower heating value of generating gas, than the pure Liquid. The poorest performance was obtained for PUR. It also indicated the highest CO_2 concentration and the lowest average heating value of the gas. The H_2:CO mol/mol ratio varied from 1,72 and 1,69 for Rubber and PUR to 1,4 for Liquid, respectively. The high content of methane generating both from Rubber and PUR contributes to increasing of lower heating value of these gases. Comparing PUR to Rubber it was noticed slightly higher mass loss of PUR about 55%. However, taking into account the ash content in PUR which was four times larger than in Rubber, the conversion of carbon into fuel for PUR was significantly higher. The lower conversion of solids residues can be explained with the weaker mixing index between the steam and solid phases.

4. Conclusions

Pyrolysis of ASR and other heterogeneous plastic mixture (electric cable residues, tiers) can be one solution for metals recovery and fuel generation. The residues after pyrolysis can be therefore utilized as the feedstock for steam gasification. From by-product after pyrolysis with the usage of steam gasification it is possible generate valuable product, like syn-gas, that can be used either for heat and/or electricity generation or for chemical feedstock.

High Temperature Steam Gasification can be a useful method for treatment non-volatile, persistent, heterogonous residues which still contain some organic carbon structure like tar and char coal.

The best gas quality in terms of heating value was obtained for liquid and liquid + Rubber experiments. For these experiments the gas volume was also the highest. The LHV coming out for Rubber was also high due to the high methane content, but the volume of gas was much lower, because of the poor conversion rate. The poorest performance was obtained for PUR. It also indicated the highest CO_2 concentration and the lowest average LHV of the gas.

The time demanding thermal analysis of sample coupled with gas composition of generating gas and conversion rate can better describe the process fundamentals and build the more complete picture of process performance.

Acknowledgments

Bibiography

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