



Sustainable valorization of plastic wastes for energy with environmental safety via High-Temperature Pyrolysis (HTP) and High-Temperature Steam Gasification (HTSG)

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ARTICLE INFO

Article history:

Received 15 September 2008
Received in revised form 8 January 2009
Accepted 9 January 2009
Available online 19 January 2009

Keywords:

Shredder residues
Plastic wastes
Steam gasification
Pyrolysis
H₂
Syngas
Sustainable waste management

ABSTRACT

In the present study the energetic valorization of electric cable shredder residues (mixed plastics) has been investigated. Thermochemical conversion by means of High-Temperature Steam Gasification (HTSG) and High-Temperature Pyrolysis (HTP) was studied. The effects of temperature and reaction time – process parameters – were investigated. Comparison of the results showed that HTSG seems a more suitable process in terms of produced syngas quality (64%, v/v and 13 MJ/Nm³) than HTP because of higher H₂ yield and lower tar content.

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1. Introduction

The amounts of mixed plastic wastes have been increasing steadily in the recent years and a question is rising up about sustainable disposal management of these materials. Sustainability as a multidisciplinary topic includes technological challenges. Technology holds threats for sustainability because on one hand interferes to the ecosystem extracting resources, depleting both natural reserves and species, including human, and on the other hand, waste generation from production processes or post consumer products waste is a threat both for environmental and human future. So a technique involving energy generation and simultaneous waste minimization is a way for natural energy resources relief, energy conservation and waste management.

With the current industrial practice, thermal disposal and especially incineration, is a desired and a viable alternative and is often used in industrialized countries, but is on the back foot of a more popular option, landfilling which is at present the most common disposal method in EU. However, new commission directive on landfilling will put an end to this option in the years to come [1].

Thus, exploiting plastic waste, which theoretically have a great fuel value when polyolefins are considered, for energy or chemicals, has become an interesting option either as in co-processing with coal [2], biomass [3] or as standalone feedstock [4,5]. Much research has been carried out on plastics, mainly on pyrolysis for feedstock recycling. As far plastics mixtures are concerned automobile shredder residue (ASR) is gaining the lion's share of research. Studies on pretreatment, emissions during thermal treatment and potential uses [6–13] of ASR have been carried out because the disposal of end-of-life vehicles (ELVs) has become a very important issue. Little is known as far as electric cable shredder residue is concerned even though residues of electric and electronic devices are increasing dramatically.

The dominating thermal method of treating such waste – mass-burn grate incineration – has drawbacks as well hazardous emissions and harmful process residues. Unlike other fossil fueled incineration plants, waste to energy (WtE) plants have significantly lower energy efficiencies (13–24%) due to lower steam temperatures, fouling and slugging. Apart from these problems, acidic gases such as HCl, SO_x, NO_x, HF and VOC's (such as polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins and dibenzofurans PCDD/Fs) which are harmful, are emitted. Moreover, solid residuals of the final process constitute a serious problem due to their heavy metal content [14].

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Nomenclature

ECSR	Electric Cables Shredder Residue
HTP	High-Temperature Pyrolysis
HSTG	High-Temperature Steam Gasification
WtE	Waste to Energy
VOC	Volatile Organic Compounds
PAH	Polycyclic Aromatic Hydrocarbons
PCB	Polychlorinated Biphenyls
PCDD/F	Polychlorinated Dibenzo Dioxins/Furans
PVC	Polyvinyl Chloride
LHV	Lower Heating Value
HHV	Higher Heating Value

To-date technologies have to deal with these problems, to be more energy efficient, environmental friendly and economically attractive. Thermo-chemical treatment is an ideal way to transform such kind of waste into energy and simultaneously into an environmentally harmless and less voluminous substance, resulting in a more sustainable and effective waste management.

Thermochemical treatment (pyrolysis and gasification) and especially gasification is a very attractive option as it reduces and avoids corrosion, reduces emissions by retaining the alkali metals (except mercury and cadmium), sulphur, chlorine, PCDD/F and thermal NO_x formation due to lower temperatures and reducing conditions. In addition, slagging gasification may provide for destruction and vitrification of hazardous compounds [14]. The produced gas of these processes can be used in many applications such as lime and brick kilns, metallurgical furnaces, as raw material syngas, Fisher Tropch synthesis and so on, providing higher efficiencies.

Pyrolysis can also be considered as a chemical recycling process due to the cracking of the long polymeric chains into smaller molecules of the same chemical structure. However, the absolute value of recycling plastic waste is mainly based on the desired product. On the other hand, heterogeneity and thus differences in composition, even in samples of the same residue-waste, make them difficult to be compared with their pure components thermal behavior, as interactions among the latter and impurities, during treatment are taking place. Furthermore, the presence of heteroatoms such as chlorine and bromine are undesirable, as these elements distribute over the products and their elimination is a major consideration in developing processes for mixed plastics.

The research work presented in this paper comprises of two parts; in the first part HTP of ECSR is investigated, followed by HTSG in the second part.

2. Materials and methods

2.1. Material

The electric cables residues that have been studied were provided by the Swedish Company, STENA Recycling AB. This sample is from the light fraction of production cables by Draka Nässjö.

Raw material, prior to its use, was pretreated in order some important compounds to be removed/recovered.

Firstly, the raw material shredded to a particle size of 5–10 mm and most of its containing copper was removed (Cu < 1%). Cu removal is important because apart from its recovery, due to its presence, polychlorinated biphenyls (PCB) can be formed [15]. It is known that Cu presence in the fly ash has a catalytic effect on PCDD/F formation, also known as de-novo synthesis of PCDD/F and maximum formation occurs at about 300 °C [16].

Table 1

Ultimate and proximate analysis of ECSR on dry basis.

Proximate Analysis			
Moisture			0.24 wt%
Ash			13.98 wt%
LHV			32 MJ kg ⁻¹
Ultimate Analysis			
C	67.64 wt%	Pb	35.9 ppm
H	9.48 wt%	Ni	7.2 ppm
S	0.001 wt%	Cr	10.7 ppm
O ^a	21.75 wt%	Cd ^b	nd
N	0.07 wt%	Mn	44.5 ppm
Cl	0.17 wt%	Al	5171 ppm
Zn	99.2 ppm	Fe	925 ppm
Cu	2564 ppm		

^a Calculated by difference.

^b Not detected.

After the first pretreatment step, the copper free cables underwent wet separation, where PVC content separated from the light part of the waste. PVC removed in order of HCl formation [17] and corrosion problems to be avoided. In addition, PVC presence increases heavy metal load and contributes to the formation of PCDD/Fs [18]. The total chlorine content in the raw material was less than 1%. The remaining material consists mainly of Polyethylene (PE) with some crosslinked PE (PEX).

The raw material was naturally dried for 3 days at 25 °C because its moisture content was 13.36 wt%. Afterwards ultimate analysis of the sample followed. By ultimate analysis, chemical formula of the raw material can derive. The ultimate and proximate analyses on dry basis are listed in Table 1. Thus, chemical formula of ECSR was CH_{1.68}O_{0.24}. Nitrogen content is an important factor to be assessed because toxic hydrogen compounds can be formed during pyrolysis. Such compounds are hydrogen cyanide and ammonia [19]. As shown in Table 1, nitrogen content is very low and therefore HCN and NH₃ are difficult to be formed. Important cable components are polyolefins (mainly polyethylene PE and polypropylene PP) [20].

In each of the experimental run about 30 g of sample was used.

2.2. Experimental set-up

The experiments took place at Royal's Institute of Technology (KTH) – Division of Energy and Furnace Technology – laboratories in Stockholm, Sweden. The experimental facility, employing a fixed bed batch reactor, is represented in Fig. 1.

The reactor employed was 1000 mm long with an inner diameter of 100 mm. A ceramic honeycomb was placed just before a basket where the sample was fitted. The experimental procedure required a heating up phase where methane was burned inside the reactor in order to produce the heat needed for each experimental run. The ceramic honeycomb was used as a heat carrier. When a temperature of about 100–150 °C above the desired temperature was achieved, the methane flow was stopped and a transient period was beginning. During transient period nitrogen in the case of pyrolysis or steam in the case of steam gasification began to flow inside the reactor and heated up by the hot honeycomb attaining a nearly constant temperature. During that transient period a temperature decrease of about 100 °C was observed. After temperature stabilization the sample was placed inside the reactor by a support shaft where the basket is screwed. During experimental phase temperature was monitored by several thermocouples and no temperature variations greater than ±15 °C were observed. At the end of each experimental run, the basket was removed from the reaction chamber and it was cooled by nitrogen (Fig. 1). The major portion of the

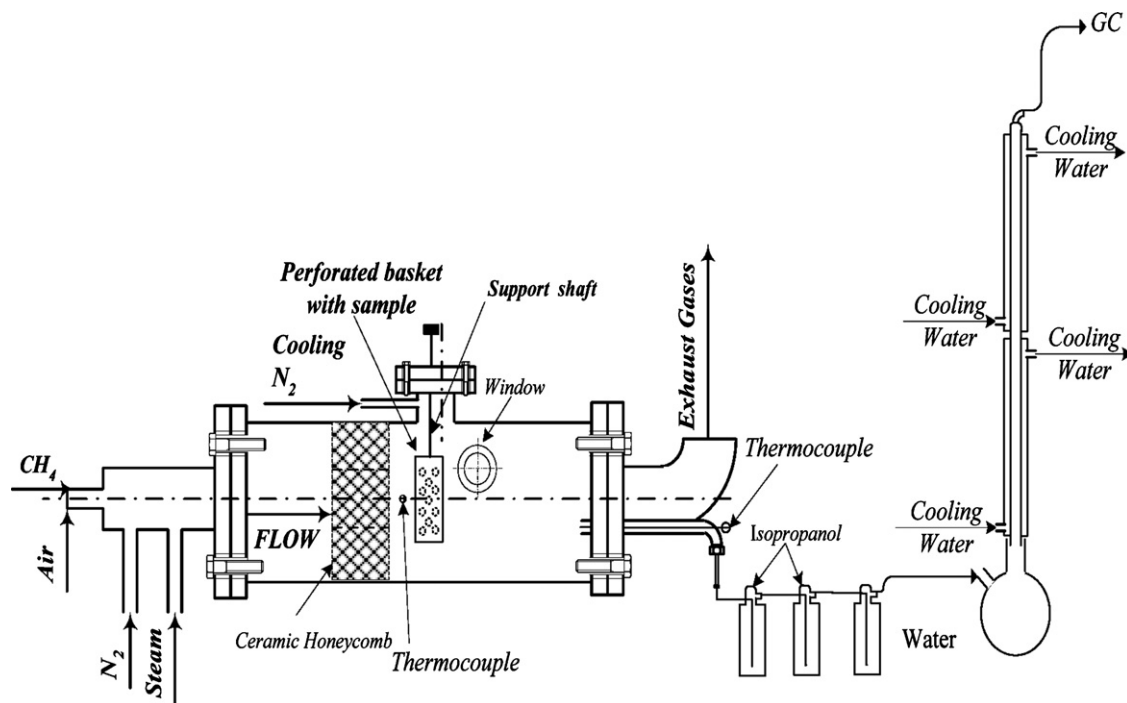


Fig. 1. High temperature pyrolysis/steam gasification facility.

flue gases was driven to a chimney, while a small quantity passed through a sampling line in order to be analyzed. The sampling line comprised of two gas washing bottles filled with isopropanol in order to capture the tar content and one filled with water to remove any particle that might be present in the gases mixture. At the same time produced gas was cooled by two heat exchangers. Orsat analysis was used for detection of O_2 , N_2 , CO , CO_2 , H_2 , CH_4 , C_2H_2 , C_2H_4 and C_2H_6 .

The flue gas composition was firstly determined by using an on-line Maihak MULTOR610 gas analyzer for $CO/CO_2/O_2$ using the Non-Dispersive Infrared (NDIR) method. In order to measure O_2 concentration in the gas sample the M&C Analysentechnik PMA 25 analyzer was used. Additionally, it was equipped with a paramagnetic detector. The data from the analyzer filled in the information gap from the use of a GC. The analyzer also validated results obtained from the GC. The GC used was a Varian micro-GC CP4900. It is a two columns portable micro-GC equipped with a thermal conductivity detector. The carrier gases used were argon and helium respectively on a MOLSIEVE 5A column and a PORAPLOT column. The temperatures on the columns were kept at $90^\circ C$ and $40^\circ C$ and a constant pressure of 25 psi.

Tar analysis performed using the Solid Phase Adsorption (SPA) method developed at KTH [21].

3. Results and discussion

3.1. Effects of temperature and reaction time on sample mass loss and gas composition during ECSR HTP

Pyrolysis experiments took place at a temperature range of 700 – $1050^\circ C$. The sweeping gas used in pyrolysis runs was nitrogen and the flow rate applied was of $0.5\text{ m}^3\text{ h}^{-1}$. This flow rate was determined in order the gas sample not to be much diluted in nitrogen. Less flow rate was not applicable due to technical constraints of the experimental set up. Thermal degradation of waste carried out at high temperatures ($>700^\circ C$) and produced gas, an

olefin mixture (C_1 – C_4) and aromatic compounds mainly benzene, toluene and xylene as also reported by van Kasteren and Slapak [18]. Generally, long reaction times applied due to low heat transfer coefficient of plastic waste. As depicted in Fig. 2 temperature and reaction time increase had a positive effect on plastics conversion. The maximum mass conversion during pyrolysis (88.6 wt% of dry sample) achieved at $1050^\circ C$. It has to be noticed that at longer than maximum reaction times presented here, no further reactions are taking place. This has been validated by the GC analysis.

The gases produced during pyrolysis were H_2 , CO , CO_2 , CH_4 and light hydrocarbons (C_2H_2 , C_2H_4 and C_2H_6 joined as C_mH_n). The composition of the produced gases during time gives an idea of a probable degradation mechanism of the waste.

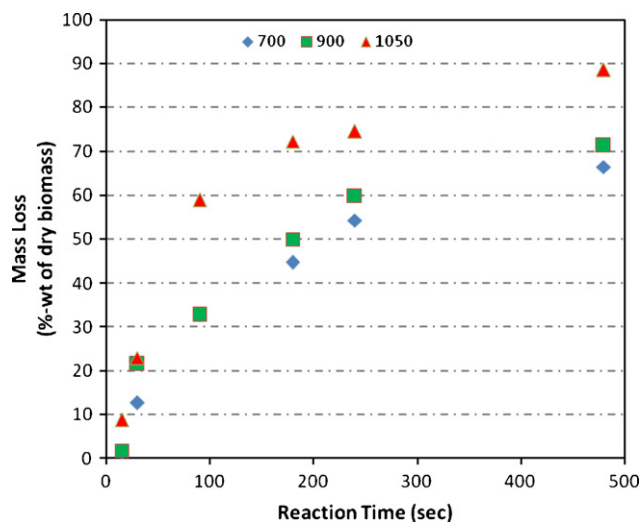


Fig. 2. Effect of temperature and reaction time on mass loss of ECSR HTP.

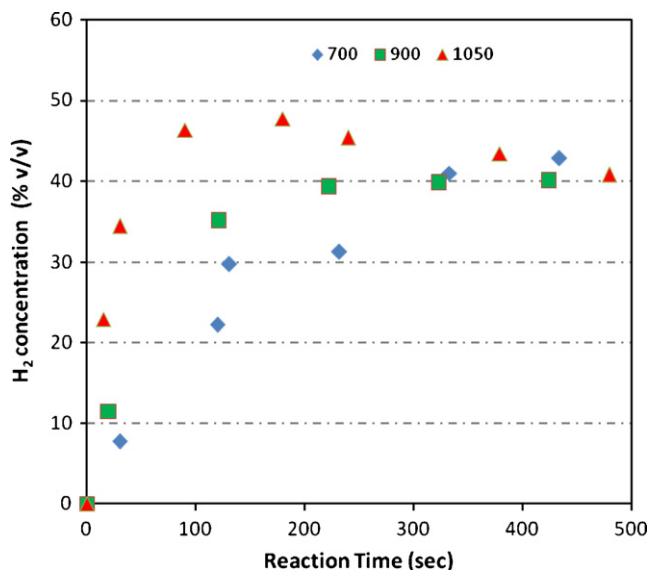


Fig. 3. H₂ concentration in produced gas of ECSR HTP at various temperatures and reaction times.

Figs. 3–7 depict the production of these gases in relation to temperature and reaction time. It is clear that with temperature and reaction time increase, H₂ production favored (Fig. 3) with the production rate being proportional to temperature. Most of the H₂ production occurred during the first stage (short reaction time) of pyrolysis. Increasing trends at short reaction times also observed for CH₄ and C_mH_n production (Figs. 6 and 7) and this is due to the degradation mechanism. The most common mechanism is that of the random scission of the polymeric chain [22] where the polymer is broken up randomly, producing chains of various lengths of smaller molecules, resulting in the production of volatile matter with or without double bonds. According to this mechanism smaller molecules are formed at the initiation of the degradation which take part in cyclization reactions and also degrade to form light hydrocarbons. After this stage, these cyclic compounds and hydrocarbons are thermally cracked to produce simpler molecules such as CO and CO₂ and this is vindicated by their trends during time as

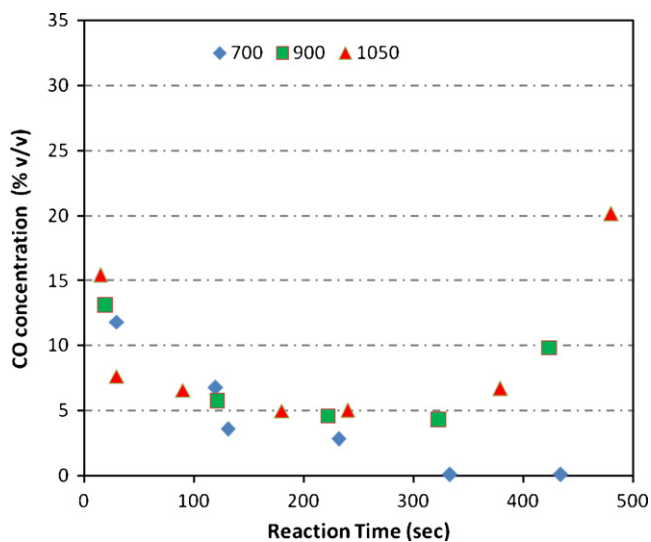


Fig. 4. CO concentration in produced gas of ECSR HTP at various temperatures and reaction times.

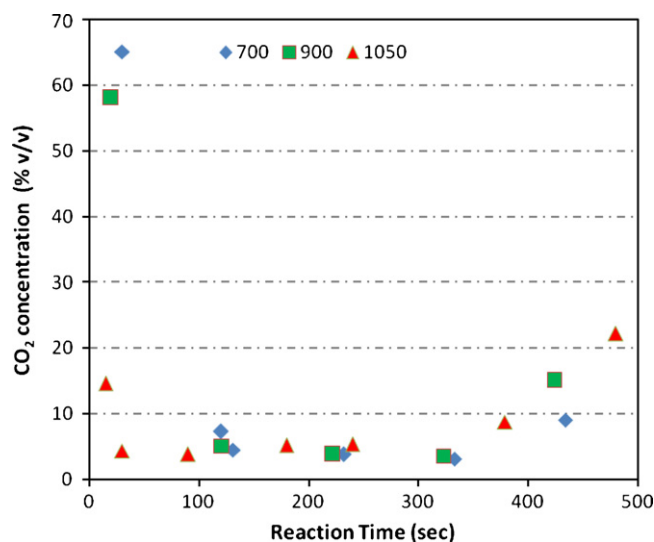


Fig. 5. CO₂ concentration in produced gas of ECSR HTP at various temperatures and reaction times.

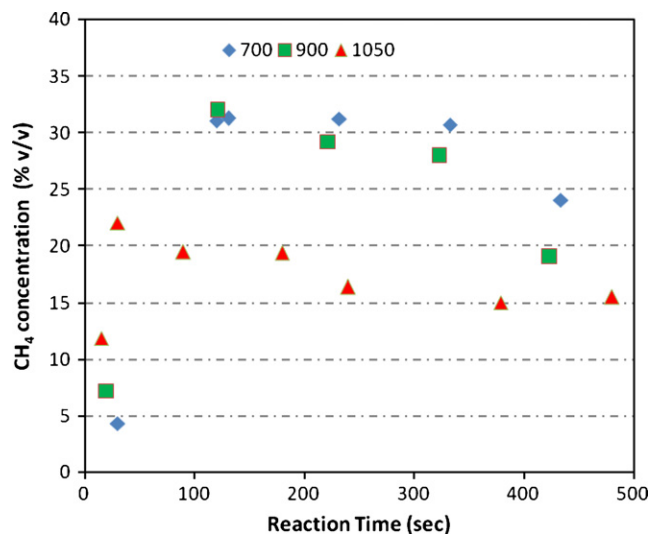


Fig. 6. CH₄ concentration in produced gas of ECSR HTP at various temperatures and reaction times.

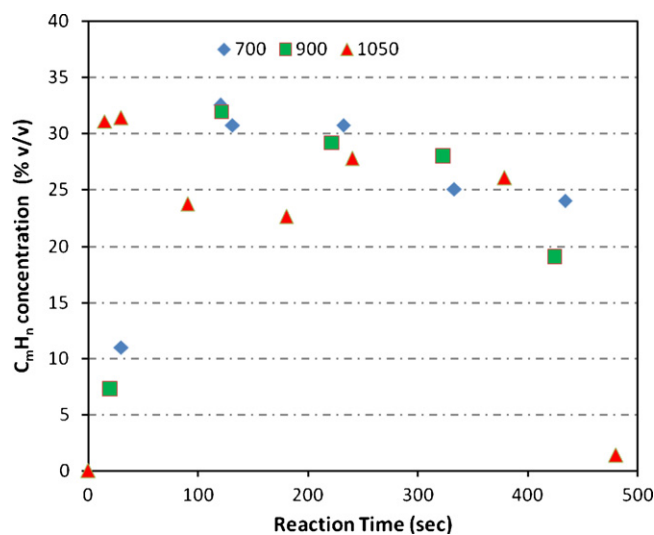
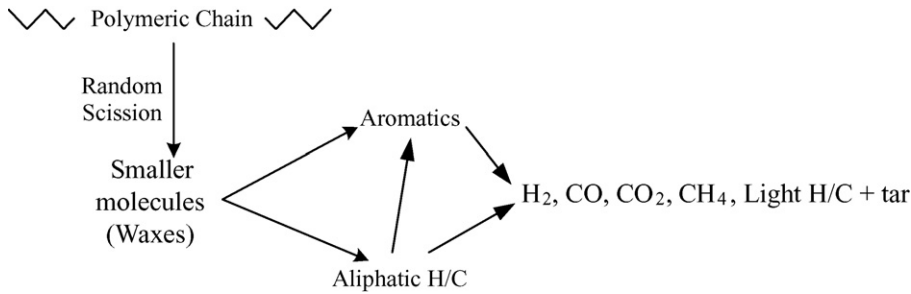


Fig. 7. C_mH_n concentration in produced gas of ECSR HTP at various temperatures and reaction times.

shown in Figs. 4 and 5.



It has to be mentioned that as temperature increased, lower amounts of CH_4 and C_mH_n produced while greater amounts of H_2 , CO and CO_2 emitted. This is due to methane and C_mH_n decomposition and tar cracking.

As temperature increased, different tar compounds formed because of different pyrolysis conditions. Milne et al. [23] classified the tar in three categories:

1. Primary pyrolysis products produced at low temperature operation and are always fragments of the original material.
2. Secondary pyrolysis products, characterized by phenolic peaks.
3. Tertiary products that include methyl derivatives of aromatics (alkyl products) and condensed tertiary products that include benzene, toluene, naphthalene, etc. These compounds, which have a higher molecular weight, are produced at higher reaction severity and are the precursors of particulate matter.

Generally primary tars can react to secondary tars by further reactions at the same temperature and to tertiary tars at high temperature.

In this work it was obvious that temperature favored tar cracking and thus it is a tar production limitation factor. Another factor that favored tar elimination might be the metal content of the raw material which acted as a catalyst in tar cracking reactions. 80–90 wt% of tar is comprised of benzene, xylene, toluene and naphthalene, as shown in Table 2.

With temperature raise, decrease in xylene and toluene content observed due to further cracking. As far as naphthalene and benzene are concerned, an increase observed until 900°C due to cyclation reactions occurring above 850°C [24] and cracking of polycyclic molecules that produced the 'simpler' poly-aromatic naphthalene and mono-aromatic benzene. Further temperature increase resulted in cracking of these molecules.

3.2. Effects of temperature and reaction time on sample mass loss and gas composition during ECSR HTSG

Temperature of experimental runs of steam gasification was of the same range as in pyrolysis with a constant steam flow rate of 0.6 kg h^{-1} . As shown in Fig. 8 maximum conversion of $\sim 92\text{ wt}\%$ of dry sample was attained at 1050°C and maximum reaction time with conversion being proportional to temperature. Most of the

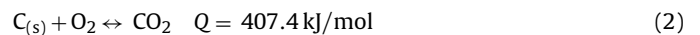
Table 2
Tar analysis of ECSR HTP.

Compound	700°C	900°C	1050°C
Benzene (mg/Nm^3)	2184.27	2287.67	348.74
Toluene (mg/Nm^3)	924.14	523.66	62.15
m/p-Xylene (mg/Nm^3)	201.13		
o-Xylene (mg/Nm^3)	324.38	228.93	19.26
Naphthalene (mg/Nm^3)	164.70	188.58	13.77
2,4-Xylenol (mg/Nm^3)	76.91	27.53	3.76
Unknown (mg/Nm^3)	1124.48	443.64	52.32

(1)

devolatilization of the sample occurred during the first seconds. In order to explain the permanent gases evolution, the following reactions between gases, steam and gases steam and carbon (char) and carbon with gases are considered [24].

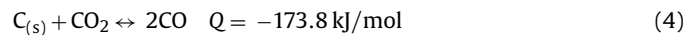
Oxidation



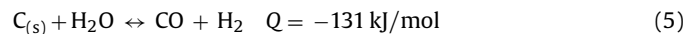
Partial Oxidation



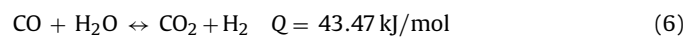
Boudouard reaction



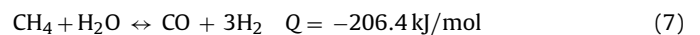
Steam carbon reaction



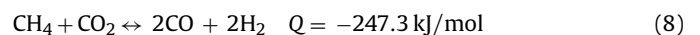
Water gas shift reaction



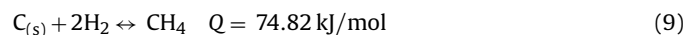
Methane Steam reforming [25]



Methane Dry reforming [26]



Methanation [26]



Temperature rise had a favorable impact on H_2 production as shown in Fig. 9, due water gas shift reaction (6) and reactions (5), (7)

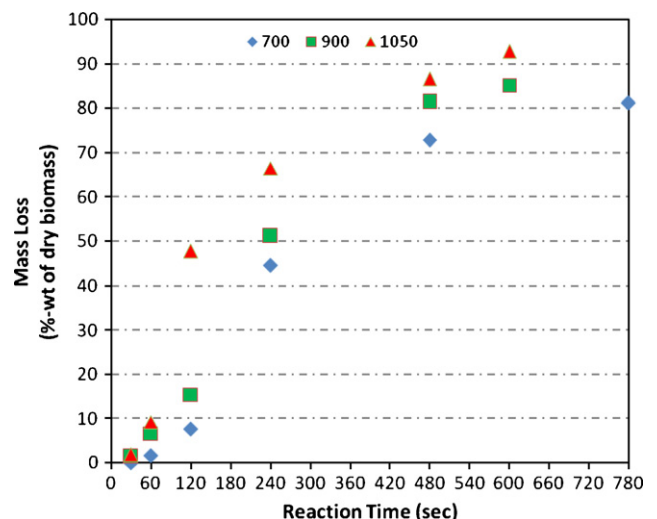


Fig. 8. Effect of temperature and reaction time on mass loss of ECSR HTSG.

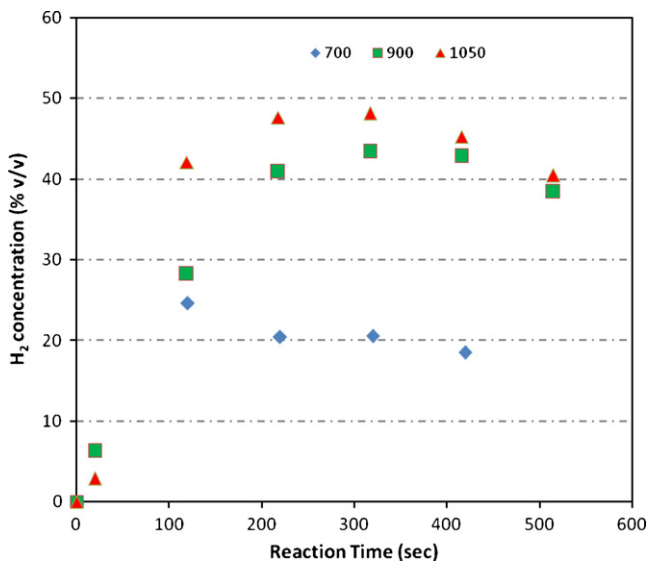


Fig. 9. H₂ concentration in produced gas of ECSR HTSG at various temperatures and reaction times.

and (8), where according to Le Chatelier's principle, H₂ production is favored. At longer reaction times H₂ concentration in the produced gas decreased slightly probably due to methanation reaction (9).

CO concentration (Fig. 10) in the produced gas increased rapidly in the first seconds due to the partial oxidation reaction (3) but with further reaction time increase water gas shift reaction took place to consume CO. At temperatures of 900 °C and 1050 °C after the decrease phase of CO concentration, an increase observed because of methane steam reforming (reaction (7)) where methane consumed to form hydrogen and carbon monoxide, and this can also be shown in Fig. 12 which represents CH₄ concentration in the produced gas. Another factor that favored CO production is temperature increase over 830 °C where Boudouard reaction (4) is more important than water gas shift reaction [27]. This can also be explained by the fact that at 700 °C consuming of CO observed at longer reaction time with parallel increase of CO₂ (Fig. 11). Hydrocarbon cracking observed with temperature increase as shown in Fig. 13.

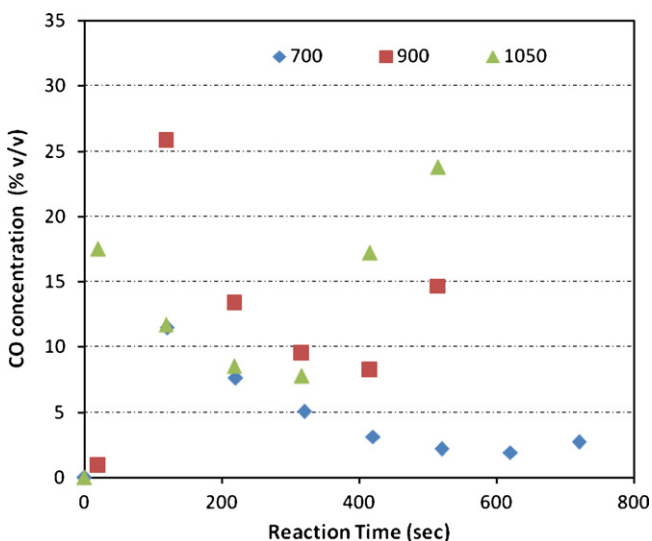


Fig. 10. CO concentration in produced gas of ECSR HTSG at various temperatures and reaction times.

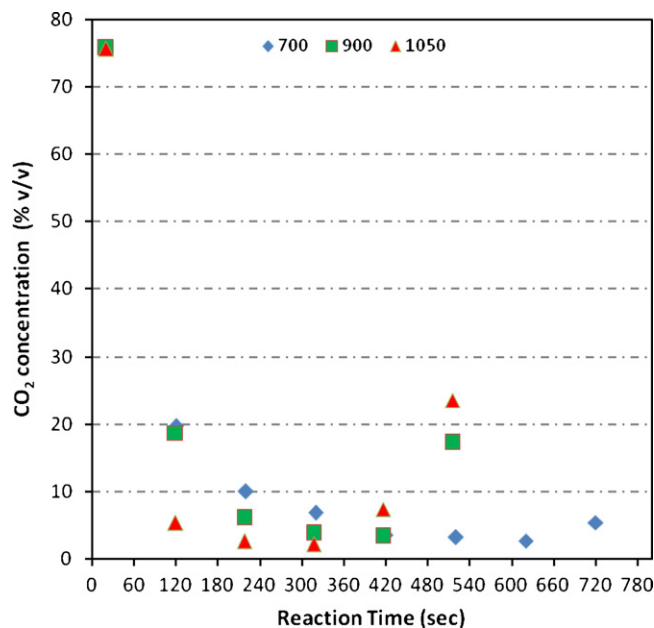


Fig. 11. CO₂ concentration in produced gas of ECSR HTSG at various temperatures and reaction times.

CO/CO₂ ratio seemed to follow the same trend in the investigated temperature range, achieving a maximum value at medium reaction times with this peak obtaining a greater value with temperature increase (Fig. 14). This also shows the importance of the Boudouard reaction over the water gas shift reaction over the temperature of 830 °C; where the ratio is lower than one.

The major factor of tar reduction was temperature. Due to increased reaction temperature, secondary reactions occurred in the gas phase which converted oxygenated tar compounds to light hydrocarbons, aromatics, oxygenates and olefins subsequently forming higher hydrocarbons and larger PAH in tertiary processes.

As also quoted by Malkow [14], who gives description of gasification processes that can handle plastic waste mixtures, high carbon conversion can be achieved under high temperature with low tar

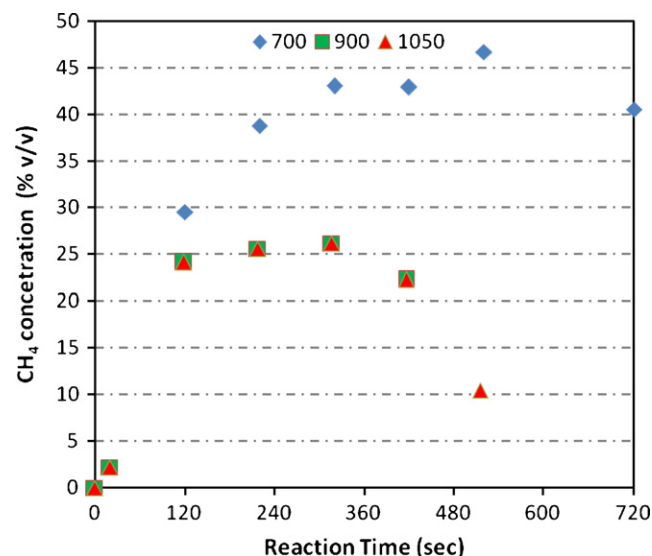


Fig. 12. CH₄ concentration in produced gas of ECSR HTSG at various temperatures and reaction times.

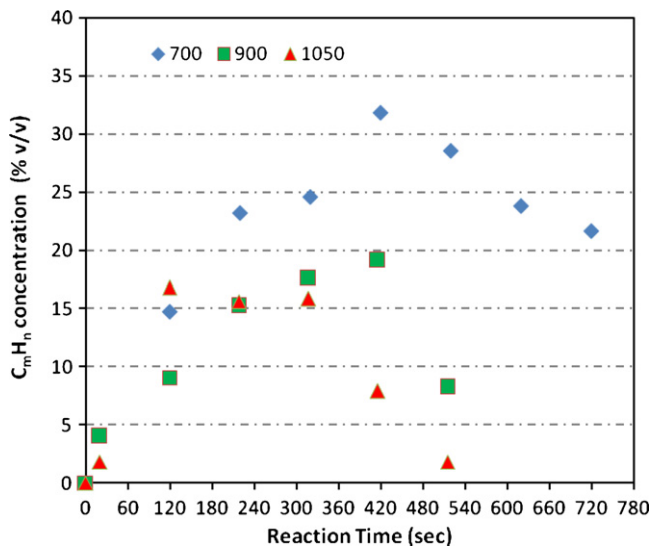


Fig. 13. C_mH_n concentration in produced gas of ECSR HTSG at various temperatures and reaction times.

production. Tar cracking and steam reforming occurs under the presence of steam and metals such as Ni which is present in the raw material [28]. Much research has been carried out on benzene and toluene (major tar components) steam reforming on commercial Ni-based catalysts [29].

In order to simplify the model, steam reforming of toluene can be described by the following reactions:

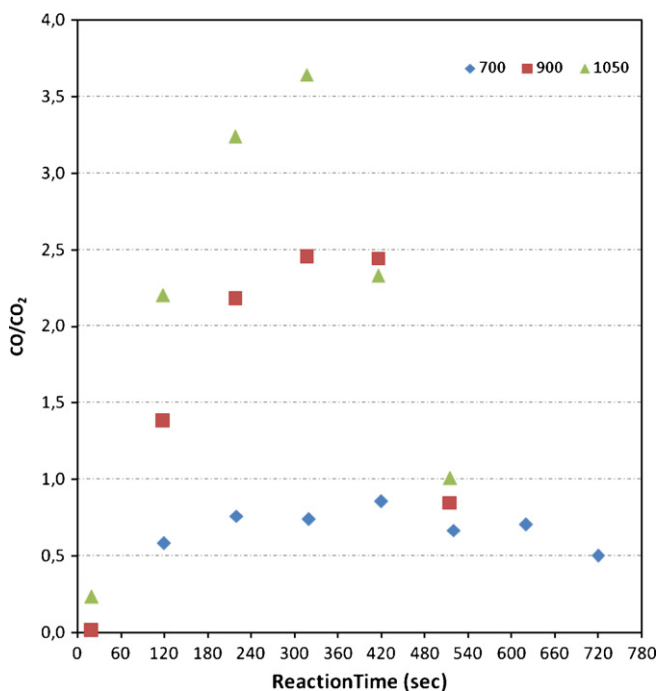
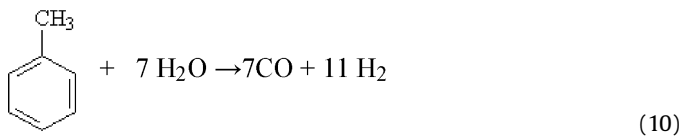
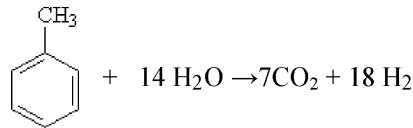


Fig. 14. CO/CO₂ ratio for ECSR HSTG at various temperatures and reaction times.

Table 3
Tar analysis of ECSR HTSG.

Compound	700 °C	900 °C	1050 °C
Benzene (mg/Nm ³)	1120.81	869.59	94.55
Toluene (mg/Nm ³)	266.60	92.64	23.96
m/p-Xylene (mg/Nm ³)	27.71	7.50	
o-Xylene (mg/Nm ³)	98.88	51.66	12.74
Indene (mg/Nm ³)	21.26	10.87	
Naphthalene (mg/Nm ³)	134.81	115.29	8.04
Biphenyl (mg/Nm ³)		7.73	
Acenaphthylene (mg/Nm ³)		6.31	
2-Methylnaphthalene (mg/Nm ³)	12.88		
Phenanthrene (mg/Nm ³)	14.45	13.62	
Phenol (mg/Nm ³)	1.57	3.61	0.11
o-Cresol (mg/Nm ³)		0.72	
p-Cresol (mg/Nm ³)		0.22	
2,4-Xylenol (mg/Nm ³)	14.52	9.56	0.59
Unknown (mg/Nm ³)	36.51	10.66	

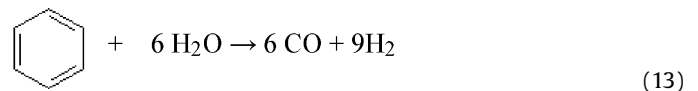


The main problem of these steam-reforming reactions is that of carbon formation according to the reaction:



The toluene steam reforming reactions (10) and (11) thermodynamically can be favored at temperatures higher than 435 °C and 350 °C, respectively. On the other hand carbon formation reaction is favored at temperatures lower than 650 °C thus, the most favorable conditions for carrying out the toluene reforming reaction, in order to avoid carbon formation, are above 650 °C [30].

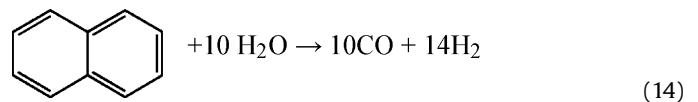
As far as benzene steam reforming over Ni-catalysts is concerned, the following reaction takes place:



According to Coll et al., steam-reforming reaction when Ni-based catalysts are employed, is carried out at temperatures between 650 °C and 900 °C [31].

As shown in Table 3 there is a rapid decrease of benzene comparing with other tar compounds which is probably due to lower activation energy of benzene steam reforming reaction also quoted by Coll et al. [31].

Naphthalene reforming reaction is the most difficult to occur during tar reforming [32].



The temperature increase from 700 °C to 1050 °C resulted in reforming over 90% of these compounds that were present at 700 °C. Benzene, Toluene, o-Xylene and Naphthalene, which are the major tar compounds, decrease observed due to temperature rise was 91.56%, 91.01%, 87.11% and 94.04% respectively.

3.3. Comparison between ECSR HTP and HTSG

Following the above discussion, the question about the most preferable method for energy recovery from ECSR rises. Comparing the two methods it has been found that higher conversion (~92 wt%) achieved at 1050 °C and reaction time of 600 s during HSTG comparing to HTP (~88 wt% at 1050 °C)

Table 4
Char elemental analysis.

	HTP at 1050 °C	HSTG at 1050 °C
C	18.67 wt%	21.81 wt%
H	1.2 wt%	1.43 wt%
S	0.088 wt%	0.004 wt%
N	0 wt%	0 wt%
Cl	3.63 wt%	2.48 wt%
Zn	554 ppm	562.5 ppm
Cu	42156 ppm	20164 ppm
Pb	nd	22.98 ppm
Ni	2716 ppm	4432 ppm
Cr	4259 ppm	8177 ppm
Cd	nd	nd
Mn	459 ppm	695 ppm
Al	105516 ppm	64022 ppm
Fe	13700 ppm	39490 ppm

Elemental analyses of char produced at temperature of 1050 °C both during pyrolysis and steam gasification are presented in Table 4. The carbon content in both cases (18% during HTP and 21% during HSTG) was way lower than Shenkel's and Guyot's [33] regulation norms for fixed carbon of charcoal, where char is enlisted in two categories A and B according to carbon content. In order the char to belong in categories A or B, the carbon content must be at least 76% and 69% respectively [33].

A drawback of pyrolysis process is the high tar content in the produced gas which creates the need of further processing, as it

Table 5
Tar tolerance for gas engines and turbines.

Application	Allowable tar concentration	Reference
IC Engine	<10 mg Nm ⁻³	[34]
	Up to 30 mg Nm ⁻³	[35]
Gas Turbine	0.05–0.5 ppm	[36]
	0.5 mg Nm ⁻³	[36]

does not meet the standards for the allowable tar content. Indeed, the tar content in HTP's produced gas is way above the limits for use in internal combustion engines (ICE) and gas turbines, while steam gasification produced a raw gas almost suitable for use in ICE. Tar tolerance for gas engines and turbines are listed in Table 5. Dilution of the produced gas in the sweeping gas is another factor to take into consideration in order to use pyrolysis for syngas or H₂ production contrary to steam gasification where no additional sweeping was used. On the other hand, the energy demand for steam generation in steam gasification is a factor that decreases the overall energy efficiency of the process.

In order to evaluate the gas as a potential fuel, attention has to be turned to syngas concentration in the produced gas. The strong reducing activity of produced gas mixture containing syngas with a concentration over 80% (v/v) makes it suitable for application in iron sponge production [37].

Syngas concentration in the produced gas increased at higher temperatures and longer reaction times with HTSG achieving

Table 6
Produced gas characteristics of ECSR HTP and HTSG.

Pyrolysis							
700 °C							
Reaction time (s)	30	120	131	232	333	434	
Syngas (% v/v)	19.52	28.99	33.33	34.09	41.08	42.88	
H ₂ /CO	00.65	03.26	8.24	11.00			
LHV (MJ Nm ⁻³)	10.88	35.08	34.46	34.50	31.41	28.55	
HHV (MJ Nm ⁻³)	11.20	36.70	36.24	36.31	33.40	30.31	
900 °C							
Reaction time (s)	121	222	323	424			
Syngas (% v/v)	40.75	43.85	44.04	49.87			
H ₂ /CO	06.13	08.50	09.25	04.05			
LHV (MJ Nm ⁻³)	52.51	53.73	64.78	73.61			
HHV (MJ Nm ⁻³)	56.21	57.62	70.65	81.34			
1050 °C							
Reaction time (s)	15	30	90	180	240	379	480
Syngas (% v/v)	38.32	42.09	52.88	52.71	50.37	50.09	60.92
H ₂ /CO	01.49	04.50	07.02	09.52	09.01	06.49	02.03
LHV (MJ Nm ⁻³)	28.46	32.57	27.91	27.12	29.09	27.50	13.38
HHV (MJ Nm ⁻³)	29.35	34.08	29.56	28.79	30.60	28.92	14.80
Steam gasification							
700 °C							
Reaction time (s)	120	220	320	420	520	620	720
Syngas (% v/v)	36.07	28.00	25.57	21.63	21.55	22.86	32.43
H ₂ /CO	02.14	02.68	04.05	05.94	08.93	11.00	11.00
LHV (MJ Nm ⁻³)	24.06	31.82	33.89	38.01	37.23	35.79	31.83
HHV (MJ Nm ⁻³)	25.69	33.73	35.97	40.03	39.42	38.18	33.99
900 °C							
Reaction time (s)	119	218	317	416	515		
Syngas (% v/v)	54.05	54.24	52.86	51.04	53.08		
H ₂ /CO	01.09	03.06	04.56	05.21	02.62		
LHV (MJ Nm ⁻³)	18.59	24.53	26.26	27.31	18.90		
HHV (MJ Nm ⁻³)	19.86	26.28	28.11	29.18	20.49		
1050 °C							
Reaction time (s)	20	119	218	317	416	515	
Syngas (% v/v)	20.38	53.80	56.18	55.90	62.43	64.16	
H ₂ /CO	00.16	03.60	05.57	06.18	02.63	01.70	
LHV (MJ Nm ⁻³)	04.46	25.33	25.32	25.61	20.07	12.26	
HHV (MJ Nm ⁻³)	04.60	27.09	27.24	27.57	21.83	13.47	

to produce larger amounts than pyrolysis (64%, v/v and 61%, v/v respectively). The decreasing trend in syngas concentration observed at 700 °C in steam gasification, is due to the fact that water gas shift reaction (reaction (5)) is more favorable than Boudouard reaction (reaction (3)) at temperatures below 830 °C. The produced gas characteristics are listed in Table 6.

H₂/CO ratio is an indicator of potential uses of syngas and thus its value is of great importance. H₂/CO values between 1 and 2 make produced gas suitable for methanol synthesis whereas for ratios about 1 oxo-synthesis is the most suitable application for the produced gas. Fischer Tropsch synthesis process is suitable when ratios are equal to 2. It is reported that values near the stoichiometric needed is more cost effective for internal combustion engines as well as fuel cells [38].

H₂/CO ratios obtained during pyrolysis show similar trends at 900 °C and 1050 °C whereas at 700 °C H₂/CO ratio tends to infinity due to inexistence of CO in the produced gas. CO inexistence is a result of the scission mechanism proposed above, where heat provided to the waste is insufficient to crack bigger molecules to simpler ones. Higher H₂/CO achieved at 1050 °C and equaled to 9.5 at medium reaction times. Further increase in reaction time seemed to be against high H₂/CO ratios because of CO concentration increase in the produced gas. As far as steam gasification is concerned, relatively lower ratios obtained contrary to pyrolysis. At 700 °C, increasing trends observed with reaction time increase to reach a maximum value of 11. At 900 °C and 1050 °C same trends observed, with longer reaction time resulting in lower ratios due to Boudouard reaction.

Another factor used to assess thermodynamic efficiency of the process is the heating value of the produced gas. Lower heating (LHV) and higher heating (HHV) value of the produced gas of both processes calculated using the following correlations:

$$\text{LHV} = (30 \cdot [\text{CO}] + 25.7 \cdot [\text{H}_2] + 85.4 \cdot [\text{CH}_4] + 151.3 \cdot [\text{C}_m\text{H}_n]) \cdot 4.2 / 1000 \text{ MJ/Nm}^3; [39,40].$$

$$\text{HHV} = (12.75 \cdot [\text{H}_2] + 12.63 \cdot [\text{CO}] + 39.82 \cdot [\text{CH}_4] + 63.43 \cdot [\text{C}_m\text{H}_n]) / 100 \text{ MJ/Nm}^3; [41].$$

where [H₂], [CO], [CH₄] and [C_mH_n] are the molar fractions in the produced gas.

High calorific values are obtained at medium reaction times due to the high C_mH_n concentration in the produced gas. Further reaction time increase had a negative effect because of CH₄ and C_mH_n decrease. It has to be noticed that in pyrolysis the molar fraction is nitrogen free which means that reduced heating values are expected due to dilution.

4. Conclusions

In this paper high temperature pyrolysis and high temperature steam gasification of electric cables shredder residues have been carried out, in a fixed bed batch type reactor at KTH laboratories – Division of Energy and Furnace Technology – in Stockholm, Sweden.

After experimental data assessment, it has been revealed that apart from temperature, reaction time is an operating variable of great importance as it determines the product distribution both in pyrolysis and steam gasification.

Higher sample conversion achieved during HSTG (92 wt%) comparing to HTP (88.6 wt%). However, in both cases low carbon content of the resulted solid residue makes it inappropriate for further exploitation as a solid biofuel or activated carbon precursor.

Syngas concentration in the produced gas increased proportionally to temperature with HTSG achieving a syngas concentration of 64% (v/v) at 1050 °C, while in HTP a syngas concentration of 61% (v/v) achieved at the same temperature. However, the real concentration of the resulting pyrolysis gas had a lower concentration due to N₂ dilution.

Pyrolysis as a method for syngas and/or H₂ production has several limitations due to the high tar content which has to be handled.

Tar concentration in the produced gas was relatively higher in HTP than in HTSG (500 mg Nm⁻³ comparing to 140 mg Nm⁻³ obtained at HTSG at 1050 °C) where steam-reforming reactions taking place. In both cases temperature raise was major factor of tar cracking. Longer reaction times were in favor of olefins cracking and reforming resulting in maximization of syngas production.

Comparing HTP and HTSG processes, the exploitation of ECSR for energy generation is preferred by means of HTSG due to the significant lower tar content, good quality product (syngas) thus its use in commercial scale.

Concluding, thermochemical treatment of ECSR by means of HTSG seems as a very attractive alternative for sustainable waste management. Furthermore apart from the energy recovery and environmental discharge another factor that promotes the use of ECSR thermochemical treatment is the avoided landfilling costs contributing to viability of such a venture.

Acknowledgments

The authors would like to thank STENA Recycling AB for providing the sample and the European Union for funding this work under the frame of the SUSPOWER Project. Authors are also thankful to A. Martin and A. Swiderski, whose help and contribution were essential for completing this work. Finally, authors would like to acknowledge the financial support from Swedish Research Council (contract No. 70398901).

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