Steam Gasification Process of Chlorine-rich Shredder Granules: Experiments and Flow-sheeting Modelling for Process Evaluation and Scale-up

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Gasification technology is gaining more and more importance, due to its engineering property of energy conversion of feedstock material into valuable gaseous process fuel. Using waste material the gasification process appears even more interesting, mostly when an ecological drawback like the production of low-pH and chlorine-rich syngas is turned into a substantial advantage. This is given when the acid gas is used for particular applications such as steel scrap preheating and simultaneous surface cleaning before its utilisation in steel plants.

In this paper a lab-scale steam gasification process for the production of a chlorine-rich gas is presented. The produced syngas shows an interesting heating value as well as adequate chlorine content for its utilisation in the mentioned application.

The overall process has been evaluated by means of flow-sheeting models to assess its performances in comparison with alternative solutions. Models are intended to calculate mass and energy balances as well as to evaluate the optimum process operating conditions considering the downstream utilisation of the syngas. Results of the models are presented in comparison with experimental data. Finally an outlook is given with regard to possible model applications as guidelines for process scale-up and optimisation.

1. Introduction

To encourage the efforts improving the rate of reuse and recovery of End of Life Vehicles (ELV), the European Parliament has passed the Directive 2000/53/EC. The regulations have been coming into effect in two steps at 2006 and 2015. In the first step the Directive 2000/53/EC regulates that new vehicles and vehicles built after 1979 shall be reused and recovered by at least 85 % mass, whereof a percentage of 5 % mass of thermal treatment has not to be exceeded. The second step of the Directive determines that the rate of reuse and recovery shall be by at least 95 % mass, whereof a percentage of 10 % mass- of thermal treatment has not to be exceeded (Directive 2000/53/EC). Currently, the average rate of their use and recovery in EU-27 states is around 85 % mass, which requires to step down one of the Directive 2000/53/EC. However, to accomplish the goal of the second step of the Directive 2000/53/EC in 2015, it is necessary to develop new economical and ecological process technologies to increase the recovery rates of auto shredder residues (ASR).

Applications of the gasification technology are well described in (Hamel et al., 2007) and the gasification of wastes and ASR is well known from (Filippis et al., 2003). Some advantages of the gasification process are the lower generation of environmentally harmful elements like dioxins, NO_x and SO_x in comparison to the direct combustion of solid fuels and in addition to the higher achievable conversion rates (Hein et al., 2012). Furthermore the generation of a calorific gas opens widespread opportunities of downstream applications e.g. electricity generation, hydrogen production, gas synthesis, and the direct use in fuel cells (Weil et al. 2005).

One of the main problems of ASR gasification is the formation of acid hydrogen chloride (Slapak et al., 2000). The researchers Borgianni et al. 2002 and Shahid et al. 2011 investigate the dechlorination of ASR or poly-vinyl-chloride (PVC) containing waste using a gasification process. During the thermal treatment of a chlorine-rich fuel more than 99.5 % of Cl is released at 350 °C (Zevenhoven et al., 2002). Zevenhoven et al. (2002) describe in their experiments that the amount of Cl in the solid residue is less than 0.1 %, i.e. the PVC has released approximately 99.5 % of its chlorine at 305 °C. The most researchers use the dechlorination behavior of PVC to separate chlorine and to reduce the chlorine amount in the process gas and separate it from the residual gas stream.

The purpose of the present paper is to describe a gasification process intended to generate a chlorine-rich low-pH gas for direct use in downstream processes, e.g. in steel scrap preheating processes with simultaneous surface cleaning through acid zinc removal. Therefore the generation of chlorine during the gasification of "chlorine rich auto shredder granular" (SG+) has been investigated and a gasifier model for process scale-up has been developed with the software Aspen Plus®, a powerful commercial software for modelling and simulation of chemical processes. The software has been used extensively in literature concerning simulation of biomass processing and gasification technology (Porzio et al., 2012) as well as simulation of processes in the steel industry (Porzio et al., 2011). The model is intended to calculate energy and mass balances of the gasification process in order to estimate the syngas composition and yield for comparison of the process performances with alternative processing routes, e.g. pyrolysis or gasification of ASR, in order to guarantee a homogeneous heating of the steel scrap and simultaneous surface zinc removal.

2. Experimental and process modelling

The main focus of the gasification investigations is on the product gas composition and yield. The experimental work is conducted at 700 °C, 800 °C and 900 °C, with steam as gasification agent and nitrogen as inert carrier gas. Experimental work has been done with a steam to fuel ratio of around 0.4.

2.1 Lab-scale gasifier and fuel properties

The atmospheric fixed/fluidized bed reactor with a cylindrical bed diameter of D = 53 mm and a cylindrical enlargement of D=113 mm as freeboard is operated up to temperatures of more than 900 °C. The bed consists of silica sand (98.8 % SiO_2) with a particle size between 0.5 mm and 0.71 mm. The reactor is equipped with an air pre-heater and two radiant electrical heaters. For steam gasification an additional steam injection below the distributor plate is fixed. The temperatures are measured on-line below the gas distributor, in the bed and in the freeboard. For analysis of the components CO_2, O_2, CO, CH_4, SO_2, H_2, C_xH_y gas samples are extracted at the top of the reactor.

Table 1 Physical and chemical properties of Shredder Granules + heavies; *calculated (Eq(1));
**recalculated from oxygen content of char, db = dry base

Sample	(av.)	(1)	(2)	(3)	unit
Bulk density	530	530	530	530	g/dm^3
Particle size	2-10	2-10	2-10	2-10	mm
Humidity (raw)	1.32	< 0.01	2.1	1.86	% mass
Ash (db)	31.6	31.0	32.5	31.3	% mass
Volatiles (db)	69.1	69.0	68.7	69.5	% mass
Fixed-C (db)	n.m.	n.m.	n.m.	n.m.	% mass
HL(raw)	17.2	15.5*	18.4*	17.7*	MJ/kg
Carbon (db)	39.5	37.5	41.4	39.6	% mass
Hydrogen (db)	5.1	4.6	5.5	5.3	% mass
Nitrogen (db)	2.95	1.9	3.3	3.6	% mass
Oxygen (db)	15.2	19.3**	13.2**	13.0**	% mass
Sulphur (db)	1.0	1.2	0.6	1.3	% mass
Chlorine (db)	3.8	3.1	4.0	4.4	% mass

An analysis of the investigated feedstock SG+ is summarized in Table 1. The content of carbon, hydrogen and ash varies only slightly. Content of carbon deviates from 37.5 % mass to 41.4 mass and content of hydrogen varies from 4.6 % mass up to 5.5 % mass. The content of ash ranges from 31 % mass to 32.5 % mass, which is consistent with the ash residues after gasification processing. A greater variance of around 1.3 %mass is obvious regarding the content of chlorine. The particle size of fuel lies in a range of 2 -1 0

mm. SG+ contains fractions of aluminium and copper which potentially originate from cables or electrical connectors.

In consequence of different measurement methods a slight measuring error of up to 3 % becomes obvious regarding chemical properties. The denoted oxygen values are calculated from the oxide compositions in the ash and ranges from 13 % mass to around 19 % mass. For recalculating the lower heating value of SG+ the formula of Boie (Eq(1)) was used.

$$LHV_{fuel} = 34.8 \cdot C + 93.9 \cdot H + 10.5 \cdot S + 6.3 \cdot N - 10.8 \cdot O - 2.44 \cdot w \tag{1}$$

2.2 Description of gasification model

The Aspen Plus® gasification flowsheet is based on four different equilibrium reactors (minimising free Gibb's energy) each represents a different gasifier zone. In the first one, the "neck" of the gasifier, the feedstock is provided together with steam, which contributes as gasification medium. According to the experimental system configurations superheated (180 °C) steam is fed with a ratio of 0.4 kg_{steam}/kg_{fuel}. The feed material has a calculated LHV of 19.05 MJ/kg, which is slightly higher than the measured one.

The reactor is kept under isothermal conditions without any addition of air. Products from the first reactor are then separated and the gases proceed to an isothermal high-temperature gasifier, while the solids are discharged at the reactor bottoms. Since it has been assumed that the pilot-scale gasifier has a circulating bed design, the solids from the bottoms are brought to an adiabatic reactor (supplied with air as a combustive agent) from which ashes and inert bed materials are circulated back into the gasifier.

The gasifier model is shown in Figure 1. The gasifier neck and bottoms are operated under isothermal conditions (700 °C and 550 °C respectively), the gasifier temperature is varied according to the experimental part between 700 °C and 900 °C, while the combustor is operated adiabatically.

3. Results and discussion

3.1 Experimental work

Table 2 shows the system configurations and a summary of the output averaged process gas properties. To compare the experimental results the gas concentrations are specified as H_2O and N_2-free. While carbon monoxide (CO) and methane (CH_4) fluctuate slightly, the concentration of hydrogen (H_2) increases significantly and a decreasing of higher hydrocarbons (C-Org.) with an increasing temperature becomes obvious. Increasing of H_2 and decreasing of hydrocarbons reveals better conditions for the homogenous water-gas-reaction. Analogues to the product gas yield and the alteration of the gas composition, higher temperatures result in a slightly decreasing carbon residue.
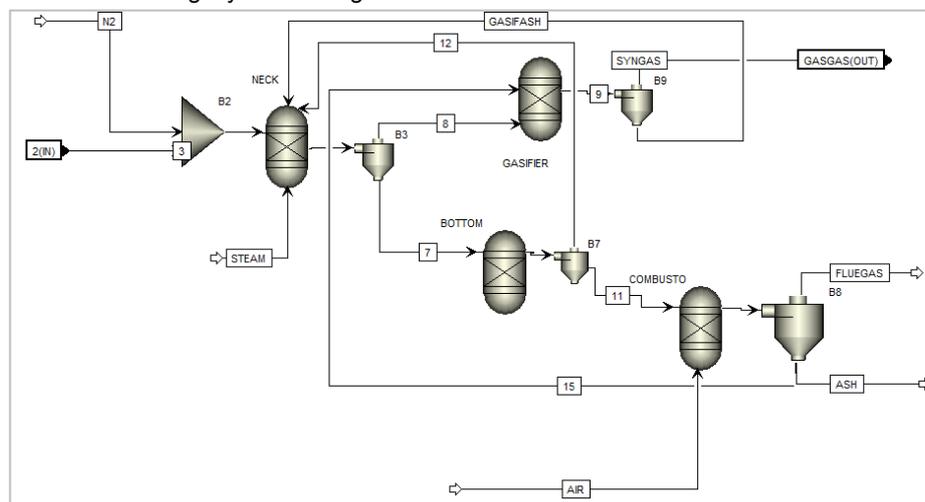
Figure 1: Flowsheet of the Aspen Plus gasifier model

After gasification the coke residue is cooled down with nitrogen and removed from the gasifier. The content of coke residues remains almost constant at all temperatures and lies in region of around 30 % mass based on the fuel input. The chlorine content of coke varies between 4 % mass at 900 °C and 6.4 % mass at 700 °C. This corresponds to values of around 1.2 - 1.8 % mass regarding the fuel input at 900 °C to 700°C. In comparison to the experimental results of Zevenhoven et al. (2002), who investigated the release of chlorine during the pyrolysis of PVC, the Cl concentrations in the coke are substantially higher.

It may indicate that a high amount of the contained chlorine is bonded in temperature stable inorganic salts.

LHV_{pg} of the gas varies only slightly. The highest LHV_{pg} of around 19 MJ/m$^3_{sv}$ was observed at a gasification temperature of 700 °C due to a higher amount of organic carbon. For analyzing the experiments the mass differences between the input of chlorine and the value of chlorine in the coke residues were compared. For recalculating the content of chlorine in the process gas it was assumed that overall chlorine is present as gaseous hydrogen chloride (HCl). The recalculation based on the average fuel composition SG+ (av.) (shown in Table 1) results in a HCl value a range of around 2 % vol up to 4 vol.-% in the dry and nitrogen free product gas.

3.2 Process modelling

Flowsheeting simulations have been carried out following the experimental system configuration, in order to estimate the syngas composition and the flow-rate which can be used in a subsequent processing step. In particular, the temperature of the gasifier has been adjusted as well as the steam to fuel ratio. Results of the simulation show a good prediction of the system behaviour, both in terms of gas yields (see Figure 2) and trends in the syngas composition. The model overestimates the hydrochloric acid concentration in the syngas, showing an increase in the error with the increase in the gasification temperature. The average content of HCl is in fact equal to 3.6 % vol, 0.5 %vol. higher than the average experimental results. On the other hand, the calculated syngas heating value is slightly underestimated by the model given the different calculation methodology (nitrogen and steam are not excluded from the calculation of the heating value in the model), leading to an average LHV of 14.6 MJ/m$^3_{sv}$, around 4 MJ/m$^3_{sv}$ lower than the one in the experimental part.

3.3 System up-scale concerning chlorine production

The prediction of the syngas quality is of particular importance in the assessment of a possible process scale-up, as well as for comparison with alternative fuel processing technologies such as pyrolysis. A direct comparison among different technologies is beyond the scopes of the present work. However, an estimate on the process needs can be carried out with regard to a pilot plant that uses the syngas for simultaneous scrap preheating and surface cleaning in a dedicated shaft before its utilisation in a steelmaking furnace. Therefore the hot flue gas of combusted chlorine-rich producer gas is conducted in a shaft reactor, which is filled with zinc-coated scrap. The heat and the chlorine-rich acid atmosphere in the reactor lead to zinc evaporation and to formation of zinc chloride. Downstream process options for zinc recovery through chemical separation are well known.

Table 2: Experimental system configuration and average outgoing process gas properties; n.m. = not measured; sv = standard volume; sd = standard deviation; **calculated from carbon content of coke based on fuel input mass; ***residue measured after gasification process based on fuel input mass

Fuel	SG+ (av.)	SG+ (av.)	SG+ (av.)
Temperature (°C)	700	800	900
Steam to fuel ratio kg$_{steam}$/kg$_{fuel}$	0.41	0.44	0.42
Fuel flow rate (kg$_{fuel}$/h)	0.1	0.1	0.1
Average product gas composition (H2O- and N2-free) and further gas properties			
HCl (Vol.-%)*	3.76	3.2	2.4
C-Org. (C$_3$H$_8$) (Vol.-%)	9.0	6.1	7.1
CO$_2$ (Vol.-%)	26.5	22.8	18.4
H$_2$ (Vol.-%)	27.9	34.2	39.7
CO (Vol.-%)	18.7	18.8	20.0
CH$_4$ (Vol.-%)	14.1	14.9	12.4
Average gas yield (L$_{(sv)}$/kg$_{fuel}$)	346.9	497.7	679.8
Carbon residue (mass$_{fuel}$-%)**	2.3	1.1	0.8
Coke residue (mass$_{fuel}$-%)***	32.08	28.91	28.36
Lower heating value (MJ/m$^3_{sv}$)	18.8	17.1	17.9

Simulations have been carried out in order to consider treatment of a batch of 50 t of zinc-coated steel scrap. The zinc content is around 1.6 % by weight in scrap, bringing the total amount of zinc to be removed to 0.8 t. The removal of zinc by means of hydrochloric acid happens at a molar ratio of 1:2, i.e. 2 mole of HCl is required to react with 1 mole of ZnO. However, an amount of 2.2 moles HCl/mole ZnO has been taken into account (i.e. 10 % excess), so around 27 kmol (or 986 kg) of HCl in the syngas are required. However, the driver for syngas production is the preheating energy requirement: considering that

the energy required to preheat a ton of steel to 600 °C (optimum preheating temperature) is of about 100 kWh, and assuming a preheating furnace efficiency of 75 %, the specific energy requirement is of about 133 kWh/t scrap.
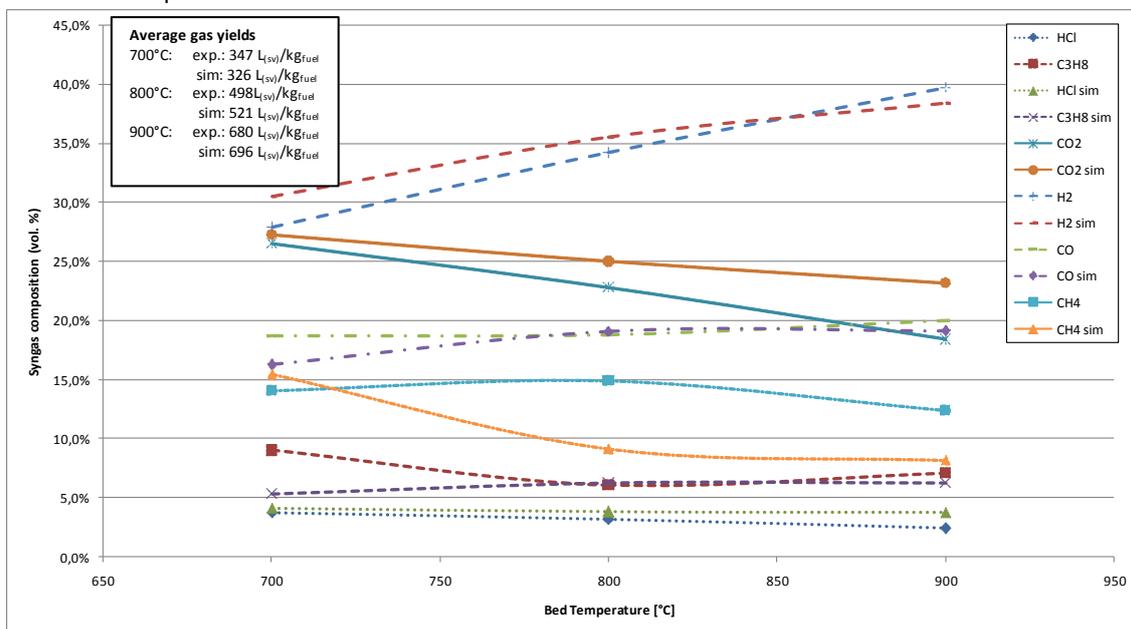
Figure 2: Syngas compositions (vol.-%) at gasification temperatures of 700 °C, 800 °C and 900 °C, experimental and simulation data

Therefore, for preheating a batch of 50 t, 24 GJ would be necessary. To satisfy such an energy demand, the simulation resulted in a production of around 1,880 m^3_{sv} of syngas at an LHV of 12.8 MJ/ m^3_{sv}. The utilisation of about 5.4 t of SG+ is required to generate such an amount of gas. However, since the gas chlorine concentration has been estimated to be around 3.1 % vol, only about 110 kg of HCl would be supplied in such a case. Due to the fact that around 0.99 t of HCl are required for the ZnCl2 – formation the lack of Cl however has to be balanced by an additional hydrochloric acid source. Optimisation of process models as well as inclusion of alternative processing routes in the modelled system will be object of future work in order to estimate the best trade-offs in operating conditions and include an economic assessment to the analysis.

4. Conclusions

Political directives and economic aspects are leading to a growing interest in effective methods for recycling of wastes. Especially the automotive sector is encouraged to improve the rates of reuse and recovery of ELV according to the Directive 2000/53/EC.

In the present paper the gasification of ASR has been investigated with the aim to produce a chlorine-rich process gas for usage in downstream processes, e.g. scrap preheating with simultaneous surface cleaning before charge in EAF. Therefore, lab-scale gasification of chlorine-rich ASR fraction has been performed and a process model has been developed with the software Aspen Plus® in order to simulate gas yield and composition produced during the experiments. During the gasification tests a calorific low-pH gas with chlorine contents in a range of around 2 % vol at 900 °C up to 4 % vol at 700 °C was experimentally verified. By comparison of experimental and simulation data the results of process modelling have shown that simulations can be used to estimate the gas yield and composition in different operating conditions. For considering a possible process scale-up the preheating with simultaneous surface cleaning of a batch of 50 t scrap was calculated. Using an amount of about 5.4 t of SG+ the required heat could be generated from the process gas. However an amount of around 0.88 t of HCl is required from an additional hydrochloric acid source.

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