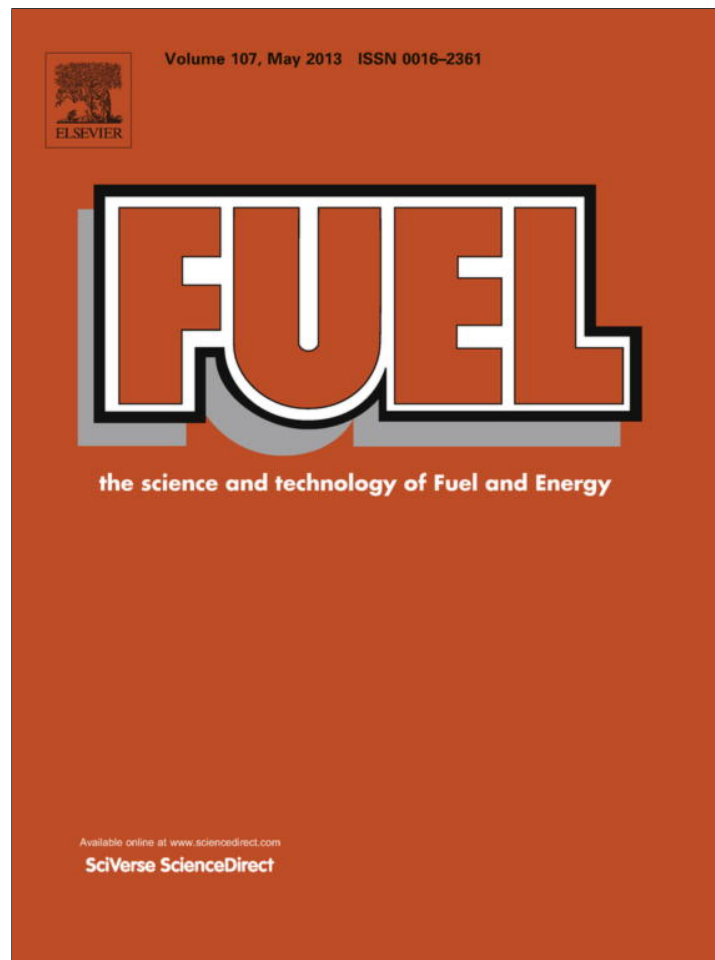


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Conversion of mixed plastic wastes in a dual fluidized bed steam gasifier

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H I G H L I G H T S

- ▶ Steam gasification of plastic materials in a dual fluidized bed pilot plant.
- ▶ The product gas from PE is rich in CH₄ and C₂H₄.
- ▶ The polymer mixtures behave differently from the pure substances.
- ▶ Mixtures interact strongly, higher gas yield and enhances reforming reactions.
- ▶ Extensive tar formation.

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Steam gasification of plastic materials was studied in a dual fluidized bed gasification pilot plant (DFB). Several types of plastics, which are available in large amounts in waste streams, were investigated: PE, PP, and mixtures of PE + PS, PE + PET and PE + PP. It was found that the product gas from PE was rich in CH₄ and C₂H₄ and had a LCV of 25 MJ/N m³. About 22% of PE was converted to the monomer C₂H₄. Different mixtures of PE with other polymers showed, that the concentrations of CH₄ and C₂H₄ increased with an increasing proportion of PE and that they were the main decomposition products of PE. The product gas from pure PP contained more CH₄ and less C₂H₄ compared to the product gas from PE. The polymer mixtures behaved differently from the pure substances. Significantly more H₂ and CO were generated from PE + PP and PE + PS. It can be assumed that the decomposition products of the two polymers in the mixture interacted strongly and alternately influenced the gasification process. More water was converted, so the gas production increased. The reforming reactions were enhanced and yielded H₂ and CO at the expense of CH₄ and C₂H₄. The mixture of PE + PET differed from the other polymers because of the high oxygen content of PET. Thus, 28% of CO₂ were measured in the product gas. By contrast, CO₂ was in the range of 8%, when oxygen-free polymers were gasified and CO₂ was only produced from reactions with steam. Gasification of polymers resulted in significantly high tar loads in the product gas in the range of 100 g/N m³. The GCMS analysis of tars showed that tars from polymers mainly consisted of PAH and aromatics. Naphthalene was the most important tar compound.

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1. Introduction

Modern societies generate more and more plastic residues every year as the quantity of disposable commodities increases. In 2007, 10% of the municipal solid waste in Austria consisted of

plastics [1]. Different methods of plastic waste treatment are possible: disposal at landfill sites, thermal recovery or mechanical recycling. The European Union aims to enhance the recycling of waste streams and gives priority to prevention and recycling over recovery and disposal in the waste hierarchy [2]. Owing to initiatives for selective collection, 35% of plastic residues have been recycled in a material-sensitive way in Austria in 2008. In the countries of EU27, the share of material-sensitive recycling of plastics amounts to 30% [3]. Most commonly plastic residues are disposed of with the mass of municipal solid waste in waste incineration plants. Gasification and pyrolysis are interesting approaches for the thermal treatment of plastic residues, because they offer high conversion efficiency and recovery of the chemical

Abbreviations: comb., combustion; DFB, dual fluidized bed; ER, equivalence ratio; EU 27, 27 member states of the European Union; gasif., gasification reactor; GCMS, gas chromatograph with mass spectrometer; LCV, lower calorific value; PAH, polyaromatic hydrocarbons; PE, polyethylene; PET, polyethylene terephthalate; PP, polypropylene; PS, polystyrene; S/C, steam-to-carbon ratio.

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Nomenclature

C_xH_y	sum of C_2H_6 , C_3 - and C_4 -gaseous hydrocarbons (vol.%)	$P_{bed,in}$	power of bed material coming into the gasification reactor (kW)
λ	excess air ratio (kg/kg)	$P_{bed,out}$	power of bed material leaving the gasification reactor (kW)
\dot{m}	mass flow (kg/h)	$P_{fuel,combustion}$	power of fuel fed to the combustion reactor (light fuel oil at pilot plant) (kW)
$\dot{m}_{carbon, feedstock}$	mass flow of carbon in the feedstock (kg/h)	$P_{feedstock}$	power of feedstock inserted into the gasification reactor (PE, PP, etc.) (kW)
$\dot{m}_{H_2O, consumed}$	mass flow of water consumed in gasification reactions (kg/h)	SPC	specific power of combustion (kW/kW)
$\dot{m}_{H_2O, feedstock}$	mass flow of water in the feedstock (kg/h)	SPG	specific power of gasification (kW/kW)
$\dot{m}_{H_2O, fluidization}$	mass flow of fluidization steam fed to the gasification reactor (kg/h)	X_{H_2O}	water conversion (%)
$\dot{m}_{O_2, available}$	mass flow of oxygen available in the combustion reactor (kg/h)	X_{PE}	PE conversion to ethylene (%)
$\dot{m}_{O_2, stoichiometric}$	mass flow of oxygen required for stoichiometric combustion in the combustion reactor (kg/h)	vol.%	concentration based on volume $m^3/m^3 * 100\%$
$\dot{m}_{PE, feedstock}$	mass flow of PE in the feedstock mixture (kg/h)	wt.%	concentration based on weight $kg/kg * 100\%$
$N m^3$	volume at 273.15 K and 101,325 Pa (m^3)		
P	power (kW)		

energy of the plastic material. The gas generated in these processes can be used further for chemical synthesis processes.

Extensive studies are available in the literature on feedstock recycling of plastics carried out in reactors of different types and scales. Many researchers have focused on pyrolysis or catalytic processes. Kaminsky et al. investigated fluidized bed pyrolysis of various materials, for example mixed plastic waste from households, polyethylene (PE) [4] or polyethylene terephthalate (PET) [5]. The aim of this process was the production of monomers for polymer synthesis. The composition of the pyrolysis gas was strongly influenced by the feedstock and the fluidization media. The main pyrolysis products of PE were olefins, such as C_2H_4 and C_3H_6 and methane. Pyrolysis of PET also yielded acids, among them benzoic acid and terephthalic acid, that decreased with an increase in the pyrolysis temperature. Serrano et al. tested specialized catalysts in a small screw kiln reactor for the catalytic degradation of PE. The focus of the work was the production of usable liquids from polymers. Due to the reactor design the production of gases was considerably low. Thermal degradation of PE without catalysts yielded hydrocarbons in the boiling range of gasoline and middle distillates. The catalysts influenced the product distribution and significantly increased the amount of gasoline in the product [6,7]. Marcilla et al. also investigated catalysts for degradation of PE and used a small fixed reactor [8]. They reported the formation of C_3 - and C_4 -hydrocarbons as the main products of thermal degradation. The use of catalysts enhanced the formation of C_4 - and C_5 -compounds. The reaction mechanisms that generate the different products of pyrolysis processes have been described by Bockhorn et al. The reactions of PE and polypropylene (PP) are radical chain reactions, and are described in [9]. The reactions of polystyrene (PS) can be found in [10].

Gasification processes of plastic materials are the topic of many research activities. Numerous co-gasification studies of plastics, coal and/or biomass have been carried out in bubbling fluidized bed gasifiers. Pinto et al. gasified different mixtures of PE and pine wood with steam [11]. With an increase in PE in the mixture, higher gas yields were achieved and more H_2 , CH_4 and C_xH_y , but less CO and CO_2 were formed. The highest share of PE in the mixture was 60%. In another study, Pinto et al. investigated mixtures of coal, PE and pine wood and used air and steam as the fluidization agent [12]. A total of 10% PE in a mixture with coal increased the concentration of CH_4 and C_xH_y , and more tar was also generated. Pohorely et al. [13] reported gasification of PET and coal. They used a bubbling fluidized bed reactor fluidized with 10% oxygen in bulk nitrogen. They stated that PET was far more reactive than coal

and thus consumed rapidly the available free oxygen. Therefore, coal decomposed more slowly with less contact to O_2 and more bottom char was formed compared to coal gasification. In the product gas from PET and coal, more benzene, C_2H_4 and tar were found. Ruoppolo et al. gasified pellets made of PE and pine wood with a mixture of air and steam [14]. Compared to the gasification of pine, more CH_4 and more tar were measured. Mastellone et al. [15] investigated air gasification of mixed plastic waste, coal and wood in order to determine the influence of the different constituents of the mixtures. Plastics increased the gas yield and the tar formation. As the product gas was richer in CH_4 and light hydrocarbons, the lower calorific value of the product gas increased. All these co-gasification studies show that gasification of plastic materials enhances the formation of CH_4 , light hydrocarbons and tar and increase the gas yield.

There have also been some studies on the mono-gasification of plastic materials in bubbling fluidized bed gasifiers. The use of plastic materials in gasification processes caused some difficulties. Several authors reported problems with the feeding system, the formation of large amounts of fine black powder [11], as well as char depositions and catalyst deactivation [7,8,16].

Mastral et al. [17] compared pyrolysis and air gasification of PE in a lab-scale gasifier. At 850 °C, the main products of PE were C_2H_4 and aromatics, which were found to be independent of the atmosphere in the gasifier. CO and CO_2 were produced only during gasification via reactions with the gasification agent. Arena et al. [18] and Mastellone and Arena [16] gasified recycled PE with air and Sancho et al. [19] and Xiao et al. [20] carried out gasification tests with PP waste in an air-blown gasifier. As different inert and catalytic bed materials were used, the results of these studies differ much, however some similarities can be stated. Air gasification is a suitable conversion technology for PE and PP to yield a product gas with a lower calorific value of approximately 6 MJ/N m^3 . The product gas composition strongly depends on the bed material and the amount of fluidization air (the equivalence ratio; ER). The tar formation has been reported to be minimized by in-bed catalysts.

Recently, two-stage gasification processes have been developed for plastic materials; Wu and Williams investigated hydrogen production from several types of polymers and waste [21] in a two-stage fixed bed gasifier. In this reactor, polymers were pyrolyzed first and the pyrolysis gas was further converted by catalytic steam reforming. Kim et al. used a two-stage fluidized bed reactor [22] in order to reduce the tar formation during the gasification of mixed plastic waste.

Besides these investigations at laboratory scale, there are also several industrial gasifiers, where plastic residues are used as feedstock. Mixtures of plastic residues and other fuels are gasified in air blown large scale circulating fluidized bed gasifiers in Lahti [23], Rüdersdorf [24] and Grève-in-Chianti [25]. The new gasification plant in Lahti recently started operation on refuse-derived fuels, which consist mainly of plastics and paper [26]. Automotive shredder residues and other plastic waste are used as feedstock for a pyrolysis plant coupled to the boiler of a hard coal power plant [27]. However, there have been no detailed studies on the gasification behavior of these plastic wastes.

The literature cited above primarily describes how plastic materials are converted by air blown bubbling fluidized bed gasification, whereas the number of publications on the mono-gasification of plastics is limited. Only little information is available on steam gasification.

This paper presents the results of a study on steam gasification of plastic materials in a dual fluidized bed gasifier. Several types of plastics, which are available in large amounts in waste streams, were investigated in a 100 kW pilot plant: PE, PP, mixtures of PE + PS, mixtures of PE + PET and mixtures of PE + PP. The gasification characteristics of the materials were analyzed and the mass and energy balances of the process are established. Special focus was placed on the conversion of PE and PP to their monomers in the product gas as well as on tar formation.

2. Dual fluidized bed gasification

Since the 1990s, steam blown dual fluidized bed (DFB) gasification technology has been subject of scientific studies at Vienna University of Technology [28,29]. The basic principle of the DFB reactor is shown in Fig. 1. Gasification and combustion take place in separate reactors, which are thermally connected by a circulating bed material. Feedstock is inserted in the gasification reactor, where it reacts with steam and forms the product gas. Some ungasified char remains and it is transported to the combustion reactor with the bed material. Char is combusted with air and thus the bed material is heated up. The bed material is separated from the flue gas stream, returns to the gasification reactor and supplies the heat for the endothermic gasification reactions. Two different gas streams are yielded: product gas and conventional flue gas.

The gasification system was originally designed for the thermal conversion of biomass aiming at the generation of high quality product gas. Steam is used as the fluidization and gasification agent in the gasification reactor of the DFB system and, therefore, the product gas has a high hydrogen content (>40%) and a moderate lower calorific value of 12–14 MJ/N m³, when wood is gasified. The DFB gasification process was demonstrated successfully in 2001 with the first industrial sized plant in Güssing (Austria). It

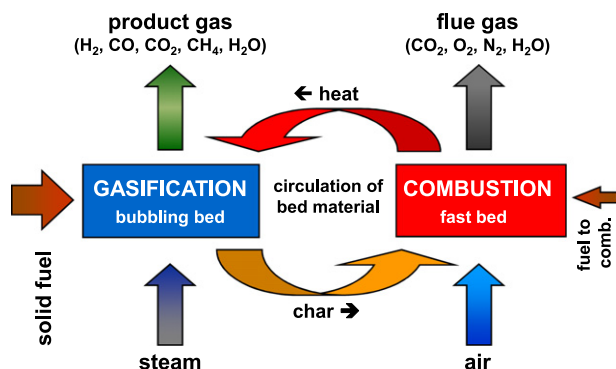


Fig. 1. Basic principle of the dual fluidized bed gasification technology.

has since exceeded an operation time of approximately 60,000 h. Further information on the demonstration plant is available in [30,31]. Several industrial gasifiers based on this technology are in operation or under construction by now, for example in Oberwart (Austria), Villach (Austria), Senden/Neu-Ulm (Germany), and Gothenburg (Sweden). In industrial gasifiers, the product gas is used for electricity production in a gas engine, as well as for heat supply e.g. for district heating grids. Due to steam gasification, the product gas is also well-suited for chemical syntheses of interesting products. Various research activities at the locations of the gasification plants in Güssing and Oberwart focus on the production of hydrogen, Fischer–Tropsch diesel [32], synthetic natural gas [33], and other chemicals [34].

3. Materials and methods

3.1. Pilot plant

Industrial DFB gasifiers mainly operate with wood chips from the forestry industry. However, alternative feedstock for these gasifiers are in increasing demand by operators. At Vienna University of Technology, a 100 kW pilot plant is operated for scientific purposes. It is similar in design to industrial DFB gasifiers and it is an essential tool for further development of the DFB gasifier and evaluation of new feedstock. Fig. 2 provides a schematic illustration of the pilot plant.

The pilot plant is equipped with several gas-tight hoppers for feedstock storage and feeding. Usually, the material is inserted directly into the fluidized bed by the screw conveyor of hopper 1. On top of the gasification reactor, a special hopper for plastics has been installed, hopper 3. There the screw conveyor transports the feedstock to a downpipe. The downpipe conically increases in diameter and has a water-cooled jacket in order to prevent melting of the plastic material while feeding. The feedstock falls through the downpipe onto the fluidized bed.

Gasification takes place in a bubbling fluidized bed, which is generated by superheated steam. The temperature in the center of the fluidized bed amounts to 850 °C. Olivine is used as bed material, because it shows moderate tar cracking activity and has good

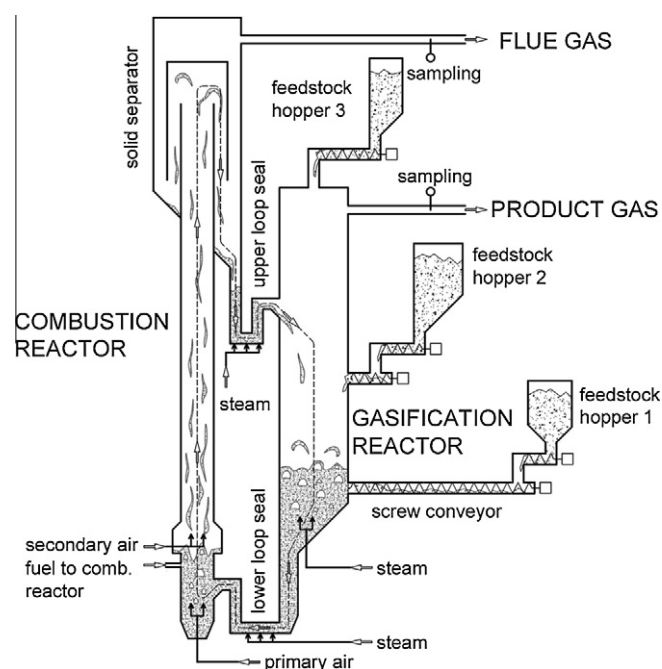


Fig. 2. Schematic illustration of the 100 kW gasification pilot plant.

mechanical stability [35]. As different feedstock are investigated in the pilot plant, the bed material is disposed of after each experiment and fresh material is used. Thus, it is ensured that all feedstock are tested in the same environment. The gasification and the combustion reactor are connected by loop seals. The loop seals are fluidized with steam, so that the transport of solids is promoted and gas leakage between the two reactors is efficiently prevented.

The combustion reactor is fluidized with air. It is injected in two stages: primary air at the bottom of the reactor, where a dense fluidized bed is formed, and secondary air at a higher level in order to transport particles to the top of the reactor. In the combustion reactor, heat is generated via char combustion for the gasification reactions. In addition to char from the feedstock, some other fuel is inserted into the combustion reactor to control the temperature in the gasification reactor. In industrial gasifiers, tars and char from the product gas and other combustible streams are recycled to the combustion reactor for this purpose. In the pilot plant, light fuel oil is used instead of recycled streams. If no fuel is added to the combustion reactor, the temperature in the gasification reactor is moderated according to the energy demand of the gasification reactions and the amount of char transported into the combustion reactor together with the bed material. The bed material is heated by combustion; the temperature difference between the combustion and the gasification reactor amounts to 40–60 °C on average. Bed material is precipitated from the flue gas stream and is returned to the gasification reactor. There, it supplies heat for the endothermic gasification reactions.

Fig. 2 does not present downstream equipment. After leaving the gasifier, the product gas is cooled in a heat exchanger to approximately 250 °C and is then sampled for analysis. Product gas and flue gas are mixed and combusted in a post-combustion chamber with air. A cyclone removes particles before the gas reaches the stack.

3.2. Measurement equipment

Extensive measurement equipment and automatic data recording are provided at the pilot plant. The main product gas components, H₂, CO, CO₂, CH₄ and O₂, are analyzed online with a Rosemount NGA2000 device. C₂H₄, C₂H₆, N₂ and the sum of gaseous C₃- and C₄-hydrocarbons are measured with a Syntech Spectras GC 955 gas chromatograph, which samples every 20 min. Flue gas from the combustion reactor is also analyzed continuously. CO, CO₂, O₂, NO and SO₂ are measured by a Rosemount NGA2000.

An impinger bottle method is used for tar measurement, which was developed at the Vienna University of Technology. It is based on the conventional tar protocol, but has been adapted for the product gas from steam gasification. Toluene is used as tar absorbent. It is immiscible with water, therefore water, dust, entrained char, and tar content of the product gas can be analyzed using a single sample. Two different methods of tar analysis are applied: gravimetric tar and GCMS tar measurement. Gravimetric tars are weighed after vacuum evaporation of the solvent; they comprise mostly tars with a high molecular weight. A GCMS device (gas chromatography with mass spectrometer) is used to measure the content of 50 different tar species of medium molecular weight in the product gas. The measurement ranges of the two techniques overlap, therefore, both values are given. A further description of tar measurement is available in [36].

3.3. Mass and energy balances with IPSEpro

The process simulation tool IPSEpro is used for the evaluation and validation of the process data which are measured in the experiments. IPSEpro offers stationary process simulation based on flow sheets. The software uses an equation-oriented solver

and contains a comprehensive model library for gasification plants, which was developed at Vienna University of Technology. It is described in detail in [37]. The mass and energy balances of the experimental runs are computed with IPSEpro. For this purpose, measured data from stationary operation of the pilot plant are used. An over-determined equation system is formed which is solved by the Method of Least Squares. More information about this procedure can be found in [38]. The reconciled solution best describes the actual operation of the pilot plant within the limits of the model.

4. Feedstock

Several types of plastics, which are available in large amounts in waste streams, were investigated in this study: PE, PP, mixtures of PE + PS, mixtures of PE + PET and mixtures of PE + PP. These polymers are typically used for the production of foils and other types of packaging for consumer goods. Most commonly, polymers are used in mixtures (blends) to adjust the properties of the product. Hence, three different mixtures of PE and other polymers were gasified, which are listed in Table 1. The mixtures were based on mass and represent frequently used polymer blends. Polystyrene (PS) is used for packaging in the form of foils or foams. The main application of PET is the production of beverage bottles. For the experiments, the mixture of PE and PP, and the mixture of PE and PET were made of granulates of the pure substances. The mixture of PE and PS was in the form of flakes that were waste material from a foil production process. In addition to these mixtures, mono-gasification of PE and PP was also carried out using virgin polymers in order to investigate the conversion process in more detail and to provide a basis for comparison. Pure PE and PP were provided by the manufacturer Borealis Polyolefine GmbH Austria in the form of granulates.

Table 2 presents the proximate and ultimate analysis of the pure substances and the mixtures. The main constituent of PP, PE and PE + PS was carbon. The carbon content amounted to approximately 86% and the hydrogen content to about 14%. PET also contained a significant amount of oxygen. Therefore, the lower calorific value (LCV) of PE + PET was significantly lower than the LCV of the other polymers. The polymers contained virtually no water. The concentrations of sulfur and chlorine were also below the detection limit. All pure substances and their mixtures did not contain ash, except for PE + PS, which was waste material from a production process. Traces of nitrogen were found in all polymers. The content of volatiles allows a first assessment of the devolatilization and gasification behavior of the fuels. In general, polymers are highly volatile materials. Virtually no solid residues (char and ash) remained, when PE and PP were heated in an atmosphere of nitrogen. Some solid residue was found when PE + PS was heated that was mainly ash. PE + PET had a slightly lower content of volatile matter than PE, PP and PS. As virtually no ash was present in PE + PET, char remained after devolatilization.

5. Results and discussion

5.1. General reactor performance

During the gasification tests the main parameters of the DFB pilot plant were kept constant to allow for the comparison of the

Table 1
Pure substances and polymer mixtures.

		PE	PP	PE + PET	PE + PS	PE + PP
Share of PE	wt.-%	100	0	20	40	50
Share of other polymer	wt.-%	0	100	80	60	50

Table 2

Proximate and ultimate feedstock analysis.

		PE	PP	PE + PET	PE + PS	PE + PP
Lower calorific value	kJ/kg	43,379	43,419	26,337	39,787	43,399
Ash	wt.-% (dry)	<0.1	<0.1	<0.1	1.46	<0.1
C	wt.-% (dry)	85.84	85.86	66.89	87.18	85.85
H	wt.-% (dry)	14.07	13.91	6.06	11.12	13.99
O	wt.-% (dry) ^a	<0.01	0.13	26.67	0.08	<0.01
N	wt.-% (dry)	0.09	0.10	0.08	0.16	0.10
S	wt.-% (dry)	<0.005	<0.005	<0.005	<0.005	<0.005
Cl	wt.-% (dry)	<0.005	<0.005	<0.005	<0.005	<0.005
Volatile matter	wt.-% (dry)	>99	>99	95.46	98.55	>99

^a O calculated as the sum to 100%.**Table 3**

Data from DFB reactor operation.

		PE	PP	PE + PET	PE + PS	PE + PP
Fuel mass flow	kg/h	7.5	7.5	13.6	7.9	7.5
Fuel power	kW	90.4	90.5	99.5	87.3	90.4
Feeding position ^a	-	Top	Top	Top	Bed	Top
Bed material	kg	100	100	100	100	100
Bed pressure ^b	mbar	78	84	75	72	71
Gasification temp.	°C	852	855	852	855	835
Steam fluidization	kg/h	15.0	15.0	16.3	14.2	15.0
Steam-to-carbon ratio	kg/kg	2.3	2.3	1.8	2.1	2.3
Combustion temp.	°C	895	911	890	907	887
Primary air	N m ³ /h	4.6	4.1	4.2	4.2	5.0
Secondary air	N m ³ /h	49.7	48.7	49.8	49.2	55.7

^a Bed ... feeding from hopper 1, top ... feeding from hopper 3.^b Pressure relative to atmosphere.

materials. Important data from stationary operation of the pilot plant for all test runs were averaged and are presented in Table 3.

The nominal fuel power of the DFB pilot plant amounts to 100 kW, which was applied for gasification of PET. However, for the other polymers the fuel power was reduced to 90 kW. These polymers are likely to generate product gas with a high calorific value, which is combusted in the post-combustion chamber of the pilot plant together with the flue gas after analysis. The fuel power of the post-combustion chamber is limited; therefore the fuel power of the gasification reactor was reduced. Usually, hopper 3 in Fig. 2 is used for feeding plastic materials due to the water-cooled chute. The mixture of PE + PS had to be fed directly into the fluidized bed from hopper 1 because of the size and shape of the flakes. The necessary mass flow could not be achieved with the screw of hopper 3. All other polymers and mixtures were thrown onto the fluidized bed from hopper 3. A total of 100 kg of olivine was used in the gasification plant as bed material. The particle size distribution of the bed material ranges from 0.4 to 0.6 mm. The steam-to-carbon ratio was in the range of 2.1–2.3 kg/kg. This ratio relates the mass flows of the fluidization steam and the fuel water to the mass flow of carbon of the fuel according to Eq. (1). In order to maintain circulation and sufficient fluidization of the fluidized bed, a minimum amount of steam is required, which cannot be further reduced. During gasification of PE + PET, a lower S/C ratio of 1.8 kg/kg was possible due to the lower concentration of carbon in this polymer.

$$\frac{S}{C} = \frac{\dot{m}_{\text{H}_2\text{O, fluidization}} + \dot{m}_{\text{H}_2\text{O, feedstock}}}{\dot{m}_{\text{Carbon, feedstock}}} \quad (1)$$

The combustion reactor is fluidized with primary and secondary air usually in the range of 4.5 N m³/h and 50 N m³/h, respectively (Table 3). During gasification of PE + PP, the amount of secondary air was increased to about 56 N m³/h, but the influence of the increase in secondary air on the whole process considered to be small.

Fig. 3 shows the pressure and temperature profiles of the 100 kW pilot plant. In this figure, average data of gasification of PP is used as an example. Temperatures and pressures were measured at the same measurement points. Their locations are shown in the schematic of the pilot plant. Pressure measurements along the reactor are an indicator of the bed material distribution and the fluidization conditions in the gasification system. Most of the bed material is present in the bubbling bed of the gasification reactor, where the pressure was highest. The bed material moves from the gasification reactor towards the areas of lower pressure in the lower loop seal and the combustion reactor. In the combustion reactor, the bed material is distributed sparsely over the height in a fast fluidized bed. The pressure is lower there. A denser zone is formed in the bottom area. The pressure at the exit of the gasification reactor is slightly higher than atmospheric pressure, because the product gas has to overcome the pressure drop of the product gas heat exchanger, which is located downstream of the gasification reactor. Table 3 lists the pressure at the lowest point in the bubbling bed for all experiments (at 0.2 m measured from the lower loop seal). It averaged 76 mbar relative to atmosphere. In all experiments the pressures remained stable with standard deviations in the range of 1–3 mbar.

The temperature profile shows the different temperature levels in the DFB reactor. The reference gasification temperature was measured at the position of the in-bed feed point at a height of 0.8 m. This temperature was adjusted to 850 °C during stationary operation of the DFB gasifier. Table 3 lists the gasification temperature, which was actually achieved during the test runs. During the gasification of PE + PP it was only 835 °C, which will be discussed further as a part of the energy balance in 5.7. In the combustion reactor, temperature increases due to combustion of residual char and fuel for combustion. The reference combustion temperature, which is given in Table 3, was measured at a height of 0.4 m, where the secondary air was injected into the reactor. The combustion temperature exceeded the gasification temperature by 40–60 °C in the experiments. The temperature profile shows a hot spot in the freeboard region of the gasification reactor. There, the hot bed material returns from the combustion reactor. In all experiments, the temperatures in the DFB gasifier remained constant with standard deviations in the range of 3–7 °C.

5.2. Product gas composition

Fig. 4 illustrates the product gas composition yielded from the different materials. The standard deviation of the measured values is also shown in the diagram. The deviations were mainly based on the varying degree of filling of the screws used for fuel feeding. However, the differences in product gas composition between the experiments were significantly large, so that the deviations were still small enough to be negligible. The main gasification products of PE and PP were H₂, CH₄ and C₂H₄. Gasification of PE

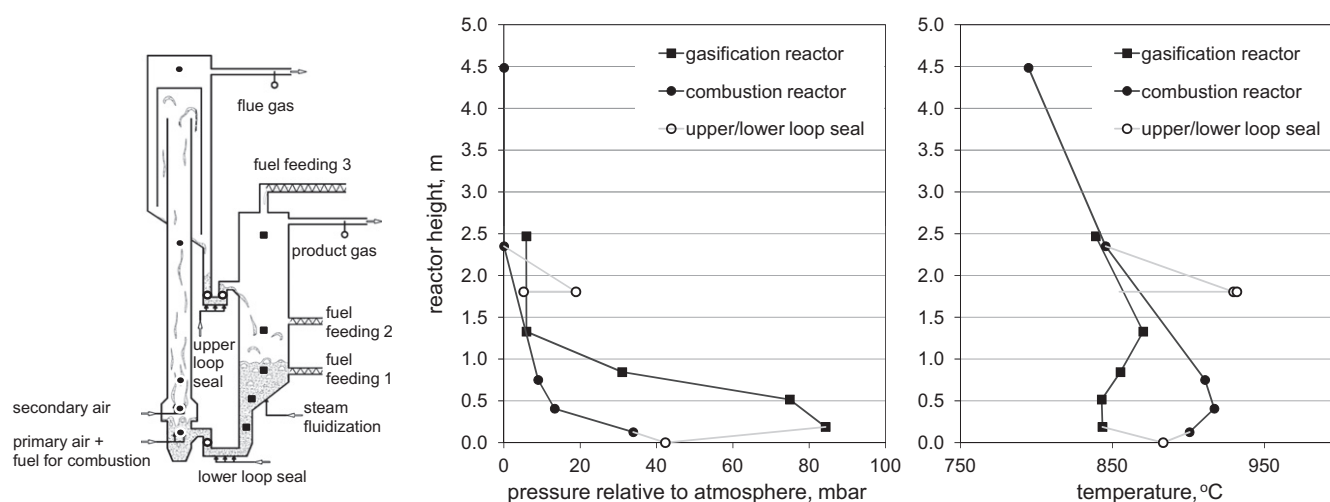


Fig. 3. Temperature and pressure profile of gasification of PP in the 100 kW pilot plant.

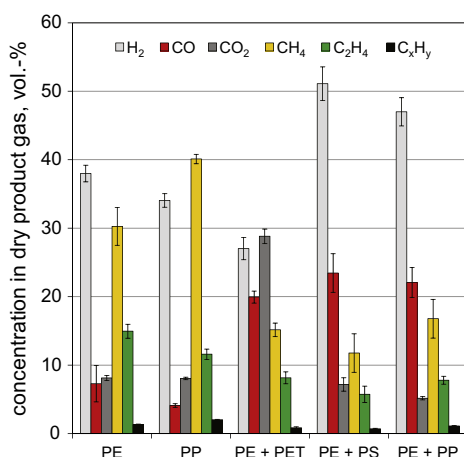


Fig. 4. Product gas composition from pure substances and mixtures.

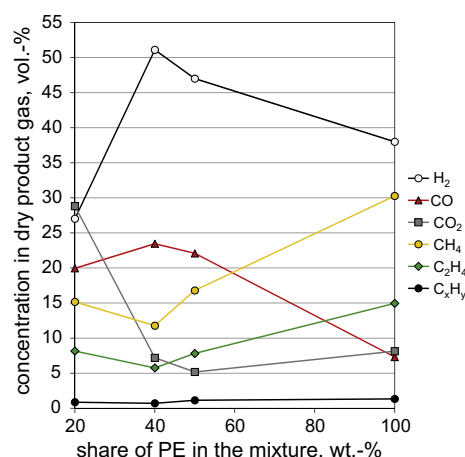


Fig. 5. Influence of PE content in the mixtures on gas composition.

resulted in a high concentration of the monomer C_2H_4 , while PP yielded a higher concentration of CH_4 and less C_2H_4 . PP contains a methyl group in the constitutional repeating unit, which apparently favored the formation of CH_4 , a stable gaseous product. The CO and CO_2 content were in the range of 5–10% during gasification of PE or PP. As neither polymer contains oxygen, CO and CO_2 were the reaction products of carbon with steam.

In contrast, the mixture of PE + PET contained about 27% of oxygen and the product gas consisted of about 50% of CO and CO_2 . The S/C ratio was significantly lower than during the gasification of the other polymers. When wood is gasified, an increase in S/C ratio increases the yield of H_2 and CO_2 and lowers the concentration of CO and CH_4 [39]. If PE + PET behaved similarly to wood, even more CO_2 would have been yielded at a higher S/C ratio.

The mixtures of PE + PS and PE + PP yielded the highest concentrations of H_2 in the range of 50%. The concentrations of CO were relatively high (20%), although there was no oxygen in the mixtures of PE + PS and PE + PP. The reaction of carbon with steam forms CO and H_2 is also produced from steam. Thus, an increase in CO and H_2 occurs together and indicates more interaction with steam. This is also supported by the decrease in CH_4 and C_2H_4 compared to pure PE. C_xH_y is the sum of C_2H_6 and the gaseous C_3 - and C_4 -hydrocarbons, which was in the range of 1%.

5.3. Influence of PE content on the gas composition

In Fig. 5 the product gas composition is plotted versus the share of PE in the mixtures. As PE is mixed with different polymers, the figure shows a global trend rather than a strict relationship. The mixture of 20% PE and PET contained oxygen, which resulted in a significantly different product gas composition. However, higher shares of PE increased the concentration of CH_4 and C_2H_4 and decreased the concentration of CO, which shows that CH_4 and C_2H_4 were the main decomposition products of PE.

5.4. Gas production

Several key parameters characterize gas formation, which are summarized in Table 4. The specific gas production relates the dry product gas volume flow and the mass flow or the energy content of the fuel. The mass-based specific gas production is, therefore, highly influenced by the energy density of the material. The mass-based specific gas productions of the pure substances were lower than those of the mixtures, except for PE + PET, which had a lower LCV and required a greater mass flow. The energy-based specific gas production eliminates the influence of the LCV of the feedstock. Gasification of the mixtures yielded higher concentration of H_2 and CO than the gasification of PE or PP. When PE or

Table 4
Key parameters for gas production.

		PE	PP	PE+PET	PE+PS	PE+PP
Specific gas production	N m ³ /kg	1.2	1.0	1.0	1.9	2.1
Specific gas production	N m ³ /kW	0.10	0.08	0.14	0.17	0.18
Lower calorific value (LCV)	MJ/N m ³	25.8	27.2	16.4	17.0	19.4
Water conversion	%	11.4	8.0	22.7	31.1	27.4

PP was gasified as virgin polymer, it resulted in CH₄ and C₂H₄ rich product gases. Larger gaseous molecules led to lower gas production from a fixed quantity of substance.

The LCV of the gas was also calculated. Tar and dust were not considered in the calculation. Due to higher concentration of CH₄ and C₂H₄, the LCV of the product gas from PE or PP amounted to about 26 MJ/N m³. The product gas from PE + PET had a lower LCV because of the formation of 28% CO₂ which dilutes the gas and does not contribute to the LCV. The product gas from PE + PS and PE + PP had a LCV in the range of 18 MJ/m³, because more H₂ and CO were formed compared to gasification of pure PE or PP. The concentrations of CH₄ and C₂H₄ decreased, which would have increased the LCV.

The water conversion (X_{H_2O}) describes the ratio of water consumed by the gasification reactions and water supplied to the gasification reactor in the form of steam and fuel water; Eq. (2). The steam mass flow and the amount of fuel water were measured values. The amount of water consumed by the gasification reactions resulted from the mass and energy balance calculated with IPSEpro.

$$X_{H_2O} = \frac{\dot{m}_{H_2O,consumed}}{\dot{m}_{H_2O,fluidization} + \dot{m}_{H_2O,feedstock}} \cdot 100\% \quad (2)$$

The water conversion shows the interaction with the gasification agent, similar to CO and CO₂ formation for oxygen-free polymers. Lower values were found for pure substances compared to the mixtures. It can be explained by the thermal decomposition mechanism of polymers that is mainly based on radical chain scission. The polymer chain breaks into smaller molecules, which leads to a variety of molecules that continue to react further. The detailed degradation mechanisms of PE, PP and PS are described by Bockhorn et al. in [9] and [10] and are comprised of random chain scission and beta scission of radicals. Pyrolysis of PE yields mainly linear alkanes and alkenes, in contrast to PP, which predominantly produces alkenes [9]. When pure PS is pyrolyzed, the main product is the monomer styrene [10]. PET is decomposed by scission of the alkyl-oxygen bond into acetaldehyde, CO, CO₂ and water when heated [40]. When mixtures of polymers were gasified, it is likely that a larger variety of radicals was available. These radicals interacted with the steam and enhanced the formation of the smaller molecules such as H₂ and CO.

5.5. Tar formation

Tars are condensable higher hydrocarbons and are undesired byproducts of gasification. When the product gas is cooled to lower temperatures, tars condense and form depositions on heat exchangers and other downstream equipment of the gasifier. Usually, tars have to be removed prior to product gas utilization in gas engines or syntheses processes. Therefore, the tar concentration in the product gas has important consequences on the design of the gasification process and in particular on the gas cleaning equipment.

In the DFB gasifier, a low concentration of tars is achieved, when woody biomass is gasified. The tar content ranges from 2 to 6 g/N m³ of gravimetric tar and 5–15 g/N m³ of GCMS tars. In order

to eliminate the influence of the gas yield, the tar concentration is referred to the fuel input of the DFB gasifier. Concentrations <1 g/kW h wood of gravimetric tar and 1–3 g/kW h wood of GCMS tars are produced on average. More information on tar formation during the gasification of wood can be found in [41,42]. Figs. 6 and 7 illustrate the tars, dust and char contents measured during the gasification of plastic materials. The tar content was markedly high: 4–8 g/kW h of gravimetric tars and 10–15 g/kW h of GCMS tars. Considerably high concentrations of tars also have been found by others authors, who compared the gasification of plastics to coal or biomass in co-gasification studies [13,14,18,43].

The mixture of PE + PP was an exception, yielding a significantly lower tar content of 1 g/kW h of gravimetric tar and 4.5 g/kW h of GCMS tars. As described by Bockhorn et al. in [9], PE decomposes in linear alkanes and alkenes, whereas PP predominantly produces alkenes. Apparently, the mixture of decomposition products of PE and PP interacted with each other and enhance the reforming reactions. This might result in markedly lower tar formation than during the gasification of the pure substances.

There were virtually no incombustible solids (dust) in the product gas. As the polymers contained almost no ash, the dust mainly consisted of entrained bed material. In general, only a small amount of char was entrained with the product gas flow, which is related to the volatile nature of the polymers. However, some

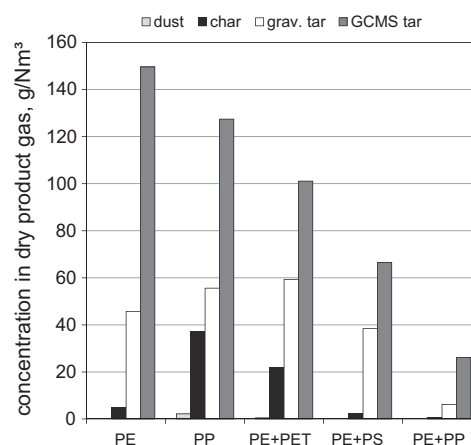


Fig. 6. Concentration of tars, dust and char in dry product gas (g/N m³).

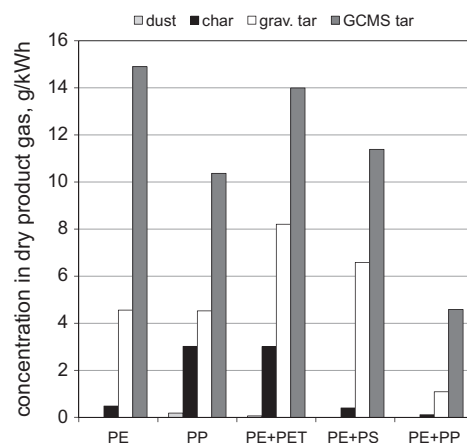


Fig. 7. Concentration of tars, dust and char in dry product gas (g/kW h_{fuel}).

char entrainment occurred during the gasification of PP and PE + PET.

According to Figs. 6 and 7, there was no significant influence of the feeding position on tar formation. PE + PS was fed directly into the fluidized bed. In this way the volatiles flow through the fluidized bed and can have more contact with the catalytic bed material than during on-bed feeding. Thus, the tar content could be lower during in-bed feeding. However, the concentration of tars during the gasification of PE + PS did not differ much from the other materials, so no significant influence can be attributed to the feeding position.

A total of 50 different tar species were assessed by GCMS. For better comparison, they were grouped according to their chemical functionality based on [36]. Table 5 lists the substance groups and their constituents. The tars generated during the gasification of polymers were mainly comprised of PAH and naphthalenes as shown in Fig. 8. Roughly 10% of tars were aromatic compounds, such as phenylacetylene, styrene or mesitylene. Virtually no phenols or furans were found in the GCMS tar.

Tar formation is influenced by the process conditions, such as the gasification agent, temperature and bed material, but also strongly depends on the nature of the feedstock. For biomass gasification, the mechanisms of tar formation are described in detail by several authors, for example by Milne et al. [44], Elliott [45] or Devi [46]. Milne et al. distinguished four different groups of tars: primary, secondary and tertiary tars, which are either methylic or condensed aromatics. Primary tars are formed rapidly at low temperatures and are based on the main constituents of wood: lignin,

Table 5
Tar substance groups.

Group	Substance
Phenols	Phenol, 2-methylphenol, 4-methylphenol, 2,6-methylphenol, 2,4-methylphenol, 2,5-methylphenol, 3,5-dimethylphenol, 2,3-dimethylphenol, 3,4-dimethylphenol, 2-methoxy-4-methylphenol, catechol
Furans	Benzofuran, 2-methylbenzofuran, dibenzofuran
Aromatics	Phenylacetylene, styrene, mesitylene, 1-H indene, 1-indanone
Naphthalenes	Naphthalene, 2-methylnaphthalene, 1-methylnaphthalene
PAH	Biphenyl, acenaphthylene, acenaphthene, flourene, anthracene, phenanthrene, 4,5-methylphenanthrene, 9-methylanthracene, flouranthene, pyrene, benz[a]anthracene, chrysene, benz[b]flouranthene, benz[k]flouranthene, benz[a]pyrene, benz[g,h,i]perylene, indeno[1,2,3-cd] pyrene, dibenz[a,h]anthracene

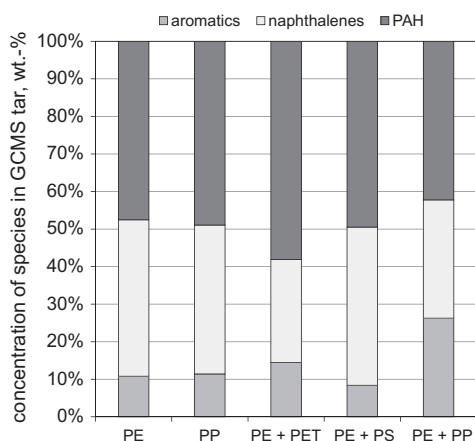


Fig. 8. Concentration of species in GCMS tar.

cellulose and hemicellulose. Secondary tars consist of phenols and olefins. Tertiary tars are formed at higher temperatures from primary and secondary tars and are methylic or condensed aromatic ring systems. The most important tar compound is naphthalene [44].

As mentioned beforehand, thermal decomposition of polymers is mainly based on a radical chain scission mechanism, where the polymer chain breaks into smaller molecules. They vaporize if they are gaseous at the prevailing temperature. Depending on the type of material, thermal decomposition of polymers also comprises the formation of char. All the considered feedstock are thermoplastics, which are charring materials similar to wood [40].

Although the pyrolysis products of polymers differ a lot from wood and comprise large linear hydrocarbons, the tars which were formed during gasification were similar to tar from wood and were mainly aromatic and condensed ring systems. Naphthalene was the most important tar compound, which is also true for wood as reported for example in [36,41]. About 50% of the tars from polymers were PAH, which are also called recombination or high temperature tars. They were not present in the original feedstock, but formed from devolatilization products (primary and secondary tars). The most important tar species are given in Table 6. The sum of the substances in Table 6 amounts to more than 90% of the GCMS tars. PE, PP and PE + PS produced rather similar GCMS tars. Although styrene is the main pyrolysis product from pure PS, only small amounts of styrene were measured during gasification of PE + PS. It seems that styrene continues to react to larger compounds within this feedstock mixture. It is worth noting that PE + PP formed styrene, which did not occur during gasification of pure PE or pure PP. In general, the mixture of PE + PP yielded lighter tar compounds compared to tars from the pure substances. This strongly indicates that the mixtures behaved differently and the decomposition products alternately influenced each other. PE + PET formed large amounts of biphenyl, which is an example of the combination of two benzene radicals.

5.6. Carbon balance

Carbon is inserted into the gasification reactor and is converted into four possible products in the DFB gasifier, which appear in Fig. 9. Carbon either reacts to carbonaceous product gas com-

Table 6
Concentration of species in GCMS tar.

		PE	PP	PE + PET	PE + PS	PE + PP
Aromatics	Styrene	wt.% 7	7	9	4	19
	1H indene	wt.% 4	4	4	4	7
Naphthalenes	Naphthalene	wt.% 40	38	26	41	30
PAH	Acenaphthylene	wt.% 15	19	8	12	11
	Anthracene	wt.% 14	15	19	22	20
	Phenanthrene	wt.% 4	2	1	1	1
	Biphenyl	wt.% 3	4	20	5	2
	Pyrene	wt.% 3	2	1	2	2
	Fluorene	wt.% 2	1	1	1	2

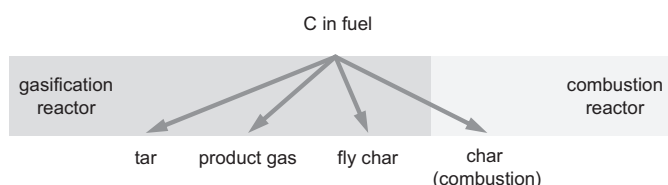


Fig. 9. Pathway of carbon in the DFB reactor.

pounds, such as CO, CO₂, and CH₄ or is present in the form of tar or char in the product gas. In the DFB gasifier, ungasified char from gasification is transported to the combustion reactor by the circulating bed material. There, it is combusted with air and supplies the heat for the endothermal gasification reactions. In this way, carbon is also present in the combustion reactor in the form of char for combustion.

The carbon balance was calculated with IPSEpro using the measured values from stationary operation of the pilot plant. As there was no measurement of the char composition available either in the product gas or in the combustion reactor, it was assumed that char consists of 8% hydrogen and 92% carbon similar to polyaromatic hydrocarbons. It was also assumed, that no char was transported back to the gasification reactor. Fig. 10 shows the carbon distribution for the tested materials. A large quantity of carbon was bound in tar, which considerably reduced the share of carbon in the product gas. The lowest tar value was found during the gasification of PE + PP; thus the share of carbon in the product gas amounted to 82%. Although the amount of volatiles in polymers was virtually 100%, the calculation showed that some char was available for combustion. It was in the range of 10% except for PE + PS, where more char (17%) was transported to the gasification reactor.

Char formation from polymers is also described by other researchers. Mastellone and Arena gasified recycled PE in an air-blown bubbling fluidized bed gasifier with olivine [16]. They reported that 65–85% of carbon is converted to product gas depending on the amount of air used as gasification agent (equivalence ratio; ER). The product gas had an average LCV of 6 MJ/N m³, was rich in H₂, CO, and N₂ and contained low concentrations of CH₄ (5%) and C₂H_m (1%). No tar was measured in the product gas after syngas treatment. The remaining carbon from PE formed a carbonaceous layer on olivine during gasification, which was documented by X-ray spectroscopy analysis. Carbon depositions on the catalyst are also reported by other authors [7,8].

It might be that a similar layer was formed on the olivine in the DFB gasifier. According to [40], thermoplastics, such as the polymers used in the experiments, also form char during thermal decomposition. In the DFB gasifier, bed material coated with a carbonaceous layer can be regenerated in the combustion reactor. The layer is burnt there and clean material returns to the gasification reactor. The amount of char entrained by the product gas flow was comparably low. This also indicates that char is more likely to be attached to the bed material than to be present as a char particle.

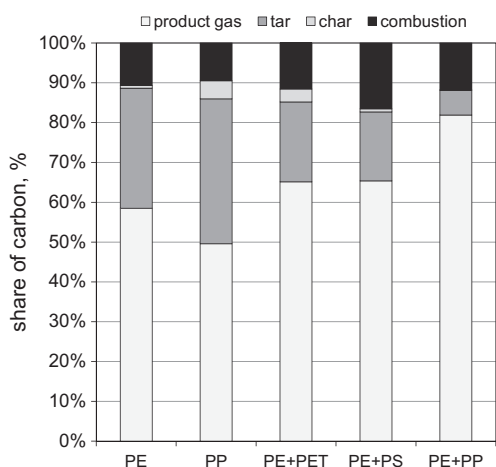


Fig. 10. Distribution of carbon in the DFB reactor for pure substances and mixtures.

5.7. Energy balance of the DFB gasifier

Fig. 11 illustrates the energy streams in the DFB gasifier during the gasification of PE. The ingoing streams into the gasification reactor are plastics, steam and hot bed material from the combustion reactor. Product gas, tar and char leave the gasification reactor, as well as bed material with residual char from gasification that is transported to the combustion reactor. Fuel for combustion and air are also fed into the combustion reactor. Flue gas and hot bed material leave the combustion reactor. Due to the high operation temperature of the system, the bed material is the largest energy stream in the DFB gasifier.

The combustion of residual char and fuel for combustion controls the gasification temperature. In industrial gasifiers, tars and char from the product gas and other combustible streams are recycled to the combustion reactor for this purpose. In the pilot plant, light fuel oil is used instead of recycled streams. Thermal losses are also included in Fig. 11. In the 100 kW pilot plant, heat losses to the environment are much higher compared to any industrial plant because of the quality of the insulation and the disadvantageous volume-to-surface ratio of the pilot plant. In industrial plants, heat losses are more or less negligible.

Three energy streams were selected to describe the energy distribution between the two reactors of the DFB gasifier: char for combustion, fuel fed to the combustion reactor and the in- and out-going bed material. The other energy streams did not change significantly comparing the different experiments, because the operation conditions (temperatures and mass flows of air and steam) were kept in a comparable range (Table 3).

Residual char for combustion was calculated from the mass and energy balance. The specific power of gasification, SPG, Eq. (3), describes the power consumption of the gasification reactions. The circulating bed material delivers heat to the gasification reactor, which is mainly determined by the temperature difference of the in and outgoing bed material. A part of the heat is used to cover the thermal losses of the gasification reactor and to heat the fluidization steam from approximately 250 °C to the gasification temperature of 850 °C. The remaining power is consumed by the gasification reactions. The specific power of combustion, SPC, is calculated from the fuel fed to the combustion reactor. The measured fuel demand of the combustion reactor is corrected for the heat losses of the pilot plant to obtain a rough estimation for an industrial plant, Eq. (4). All values refer to the fuel power of the gasification reactor and are compiled in Table 7.

$$SPG = \frac{P_{\text{bed,in}} - P_{\text{bed,out}} - P_{\text{losses,gasif.}} - P_{\text{heat,steam}}}{P_{\text{feedstock}}} \quad (3)$$

$$SPC = \frac{P_{\text{fuel,combustion}} - P_{\text{losses}}}{P_{\text{feedstock}}} \quad (4)$$

The specific power of combustion was considerably higher for polymers compared to biomass. This is mainly due to the high content of volatile matter in the polymers. Thus, comparably less char was available for combustion. The gasification of polymer mixtures (PE + PS, PE + PP) required more specific power of combustion, but also more specific power of gasification compared to pure substances. Apparently, the interaction of the polymers and the water conversion enhanced endothermal reactions. PE + PET differed from the other mixtures. It required less power of gasification and combustion, which might be attributed to the oxygen bonds in the PET polymer that are very reactive.

During gasification of PE + PP the specific power of combustion was the highest reaching a value of 0.30. The maximum amount of fuel was fed to the combustion reactor in order to adjust the gasification temperature to 850 °C. Because of limitations in the pilot plant the fuel mass flow could not be increased further. In order

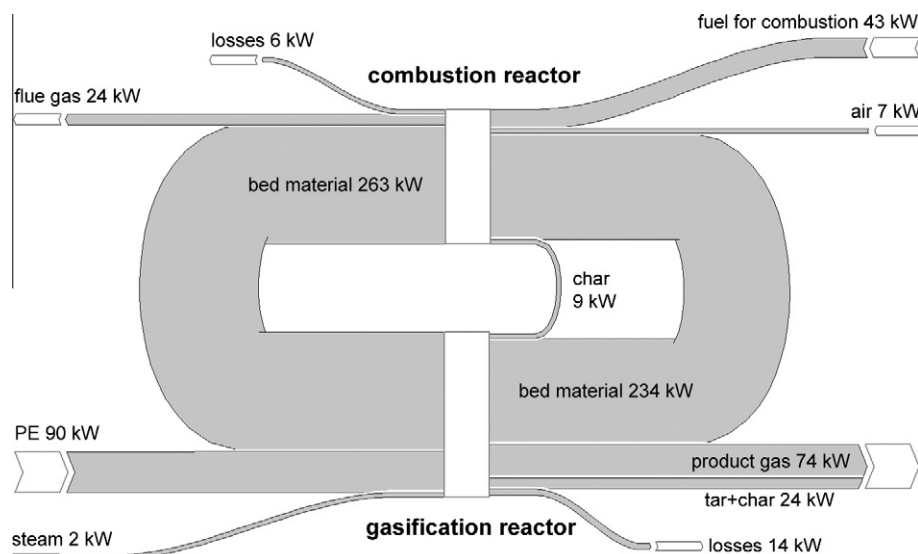


Fig. 11. Energy streams in the DFB gasifier for gasification of PE.

Table 7
Reaction parameters for energy streams in the DFB gasifier.

	PE	PP	PE + PET	PE + PS	PE + PP
Specific power of gasification	kW/kW 0.07	0.06	0.06	0.15	0.11
Char for combustion	kW/kW 0.10	0.09	0.13	0.16	0.11
Specific power of combustion	kW/kW 0.25	0.25	0.18	0.27	0.30
Excess air ratio ^a	kg/kg 1.13	1.13	1.13	1.01	1.13

^a Calculated.

to ensure complete combustion, the secondary air flow was raised to about 56 N m³/h. The combustion temperature was the highest of all experiments at 911 °C (Table 3). Despite all that, only a gasification temperature of 835 °C was reached.

$$\text{Excess air ratio } \lambda : \lambda = \frac{\dot{m}_{\text{O}_2, \text{available}}}{\dot{m}_{\text{O}_2, \text{stoichiometric}}} \quad (5)$$

The excess air ratio λ of the combustion reactor is also given in Table 7. The excess air ratio relates the oxygen supply of the combustion reactor to the oxygen demand of stoichiometric combustion of char and fuel for combustion. It amounted to 1.13 during the experiments except for the gasification of PE + PS. It was lower, because comparably more char was transported to the combustion reactor (Fig. 10). The specific power of combustion of PE + PS was in good agreement with the other polymers. As the amount of carbon in the combustion reactor increased at constant air fluidization, the excess air ratio decreased to 1.01.

5.8. Influence of temperature on gasification of PP

The influence of gasification temperature was investigated with pure PP. Table 8 shows how the performance at lower temperatures differed from gasification at 850 °C. At lower temperatures, less product gas was generated. As product gas flows through the fluidized bed, it also serves as a fluidization agent. Thus, steam fluidization was increased slightly to compensate for the lower gas formation and to maintain the fluidized bed in a comparable state, when the gasification temperature decreased. Fig. 12 shows the influence of gasification temperature on the product gas composition. At higher temperatures, the concentration of C₂H₄ and higher hydrocarbons, C_xH_y, decreased.

Table 8
General reactor performance (temperature variation with pure PP).

	640 °C	760 °C	850 °C
Gasification temperature	°C 642	759	855
Combustion temperature	°C 754	856	911
Steam fluidization	kg/h 16.6	15.3	15.0
Steam-to-carbon ratio	kg/kg 2.6	2.4	2.3

amounted to 36% at 640 °C. In contrast to that, the sum was reduced to 21% at 850 °C. The CH₄ content increased between 640 and 760 °C and decreased then. The H₂ content increased steeply as did the CO and CO₂ concentrations. This indicates that more reactions occurred with steam at higher temperatures and also the reforming of larger carbonaceous molecules into smaller ones was favored. At lower temperatures, a significant amount of gaseous compounds were produced, which could not be analyzed by the measurement equipment at the pilot plant. These compounds

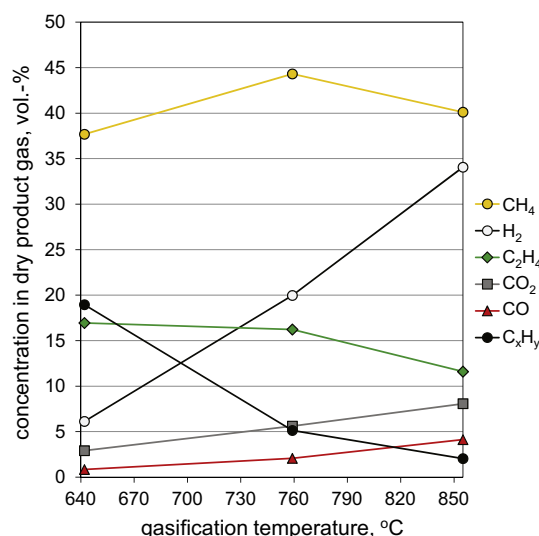


Fig. 12. Influence of gasification temperature on gasification of PP.

were benzene, toluene and the like. At 850 °C, the sum of the measured gaseous compounds was close to 100%, but this value was lowered to 93% at 760 °C and to 83% at 640 °C. Because of this gap, the mass- and energy balances for 640 °C and 760 °C were not as reliable as for the other experiments at 850 °C and should be interpreted as trends rather than as strict values.

A decrease in the tar content was observed with a reduction in the gasification temperature, which is illustrated in Fig. 13. It is possible that benzene, toluene and other undetected compounds occurred in higher concentrations at 640 °C, which could increase the tar content with a decrease in gasification temperature. The detailed composition of the GCMS tars is shown in Fig. 14. At 640 °C a small amount of furans was formed, which are similar to secondary tars from biomass. With an increase in temperature, they disappeared. The amount of aromatic tars diminished and the PAH content rose to almost 50% at 850 °C.

Table 9 presents the influence of gasification temperature on important reaction parameters. At 640 °C the specific gas production was the lowest; it increased with an increase in the gasification temperature. The lower calorific value likewise decreased, as the concentration of C₂- and C₃-hydrocarbons in the product gas declined. In general, reactions proceed faster at higher gasification temperatures. The increase in water conversion showed a more intensive interaction with steam. More power was also consumed by the gasification reactions, which can be explained by enhanced

endothermal reforming reactions of C₂-, C₃- and C₄-hydrocarbons. More power for combustion was required with increase in temperature to maintain the higher temperature in the gasification reactor, although more char for combustion is available.

5.9. Conversion to monomers

According to Fig. 5, the monomer of PE, C₂H₄, was an important gasification product of PE. Fig. 15 shows the extent of PE conversion to C₂H₄. The PE conversion was calculated as the ratio of C₂H₄ in the product gas to PE in the polymer mixture, Eq. (6). When 100% PE was gasified, the PE conversion amounted to 22%. More C₂H₄ was produced from the mixtures with PE. The surplus of C₂H₄ in the product gas from the mixtures showed that PS, PP and PET also generated ethylene as a decomposition product.

$$X_{PE} = \frac{\dot{m}_{C_2H_4, \text{product gas}}}{\dot{m}_{PE, \text{feedstock}}} \cdot 100\% \quad (6)$$

The monomer of PP, C₃H₆, could not be measured explicitly with the equipment that was currently available at the pilot plant. However, CH₄ and the gaseous hydrocarbons C_xH_y were detected and were also suitable to describe the conversion of PP in Fig. 16. The conversions of PP to CH₄ and C_xH_y were calculated in analogy to Eq. (6) and relate the concentrations of CH₄ and C_xH_y in the product gas to the mass flow of PP as feedstock. At 850 °C, the predominating conversion product of PP was CH₄. A total of 28% of PP fed to the gasification reactor formed CH₄ in the product gas. With a decrease in gasification temperature, the conversion of PP to CH₄ decreased steadily, although the CH₄ concentration in the gas was maximal at 750 °C. As the gas production was lower at lower temperatures, the conversion of PP to CH₄ also decreased. The conversion of PP

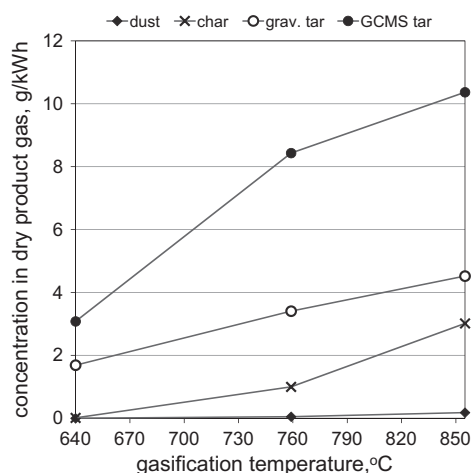


Fig. 13. Influence of gasification temperature on tar formation (PP).

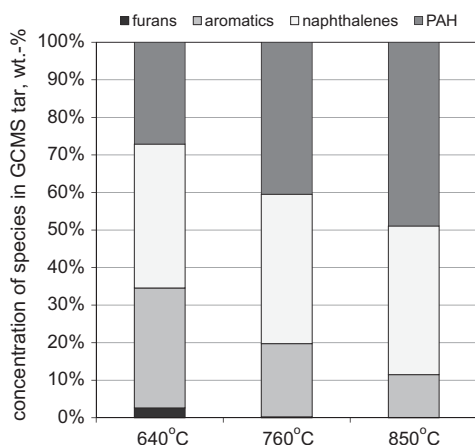


Fig. 14. Influence of gasification temperature on GCMS tar composition (PP).

Table 9
Specific reaction parameters.

		640 °C	750 °C	850 °C
Specific gas production	N m ³ /kg	0.6	0.8	1.0
Specific gas production	N m ³ /kW	0.05	0.06	0.21
Lower calorific value (LCV)	MJ/N m ³	41.2	32.5	27.2
Water conversion	%	1.7	4.3	8.0
Specific power of gasification	kW/kW	0.01	0.04	0.06
Char for combustion	kW/kW	0.06	0.09	0.09
Specific power of combustion	kW/kW	0.19	0.20	0.25

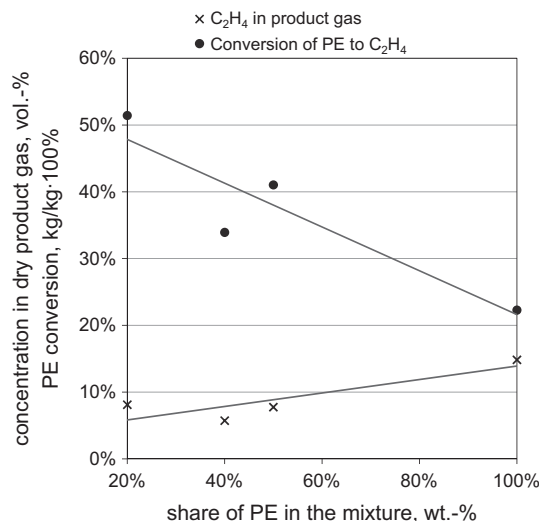


Fig. 15. Conversion of PE to C₂H₄.

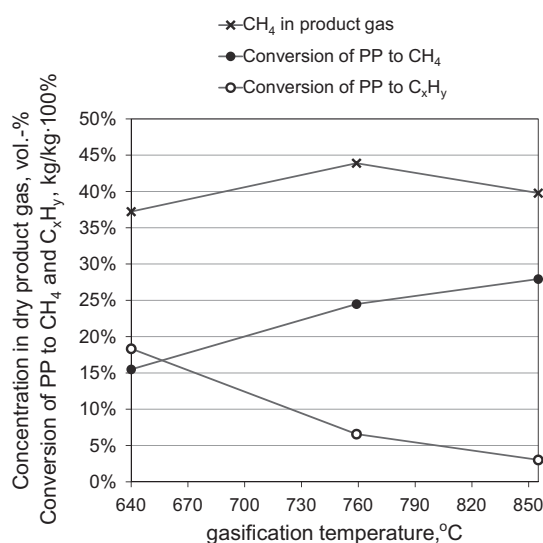


Fig. 16. Conversion of PP to CH₄ and C_xH_y.

to C_xH_y increased steadily, when the gasification temperature was lowered. At 640 °C, C_xH_y was the predominating conversion product yielded from 18% of PP.

6. Conclusion

Steam gasification of plastic waste materials was carried out successfully in the DFB pilot plant. In order to investigate the important reaction parameters of gasification, pure PE and PP, as well as mixtures of PE with PP, PS and PET were tested. It was found that the product gas from PE was rich in CH₄ and C₂H₄ and had a high LCV of 26 MJ/N m³. About 22% of PE was converted to the monomer C₂H₄. Different mixtures of PE with other polymers showed, that CH₄ and C₂H₄ increased with increasing share of PE and were the main decomposition products. The mixtures yielded higher conversion of PE to C₂H₄, which showed, that the other polymers also generated C₂H₄ as a decomposition product. Product gas from pure PP contained more CH₄ and less C₂H₄ compared to the product gas from PE. The formation of CH₄ seems to be attributable to the methyl group in the repeating unit of PP.

The polymer mixtures behaved differently from the pure substances. Significantly more H₂ and CO were generated from PE + PP and PE + PS. It was assumed that the decomposition products of the two polymers in the mixture interacted strongly and influenced alternately the gasification process. As CO was generated from reactions with steam, H₂ was also released and increased similarly. More steam was converted to product gas, therefore, the gas production increased. The reforming reactions were enhanced and yielded H₂ and CO at the expense of CH₄ and C₂H₄. Also more power for gasification and combustion was necessary for gasification of the mixtures. The mixture of PE + PET differed from the other polymers because of the high oxygen content of PET. Thus, 28% of CO₂ were measured in the product gas. By contrast, CO₂ was the range of 8%, when oxygen-free polymers were gasified.

Gasification of polymers resulted in significantly high tar loads in the product gas in the range of 100 g/N m³ or 13 g/kW h fuel. GCMS analysis of tars showed that the tars from polymers mainly consisted of PAH and aromatics. Naphthalene was the most important compound. Despite of the originally linear structure of the polymers, the tars generated were aromatic molecules, similar to tertiary tars from the gasification of biomass. Gasification of PP at different temperatures showed that PP also formed secondary tars, such as furans, and smaller aromatics at lower temperatures.

The furans disappeared with an increase in temperature and the smaller aromatic compounds recombined to tertiary tars at 850 °C. Interestingly, the compositions of the GCMS tar from the pure substances PE and PP and the mixture of PE + PS were similar. The PE + PP mixture yielded considerably less tar, which had a different composition than the tars from the two pure substances, PE and PP. This also indicates interactions between the polymers in the mixtures.

This experimental work demonstrates that the tested polymers are suitable feedstock for the DFB gasifier. In contrast to incineration, steam gasification can also be applied for chemical recycling of polymer wastes. In addition to heat and power production, the selective separation of valuable compounds, such as CH₄ and C₂H₄, could also be an interesting application for the product gas from plastic gasification. Therefore, further investigations how to control and reduce tar formation from plastic materials are necessary. Both primary and secondary measures should be considered, such as enhanced contact to catalytic bed material or adaption of the downstream equipment of the gasifier (heat exchangers and gas cleaning equipment).

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