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Olivine as a Tar Removal Catalyst During Fluidized Bed Gasification of Plastic Waste

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Natural olivine was used as bed material during the gasification of plastic waste in a pilot-scale bubbling fluidized bed reactor. The results indicate that it works as an excellent in-situ tar reduction agent, considerably improving the quality of the gas produced, in terms of low tar content, high hydrogen volume fraction and large syngas yield. The phenomena concurring to the activation of the catalyst are described together with those that can contribute to deactivate it. A phenomenological description of the different stages occurring during gasification of plastic waste in a fluidized bed of olivine particles is also reported. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 1656–1667, 2008
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Introduction

Waste management techniques should always become more sustainable and provide greater recovery value from waste. Despite its many drawbacks, landfill is still the preferred option even in many industrialized countries although there are several countries in Europe and Asia that are currently experiencing huge difficulties in finding landfill sites. Incineration, the traditional waste-to-energy process, is a proven alternative with about 130 million tonnes of municipal solid waste that are combusted annually in over 600 facilities.[1,2] However, it still has some drawbacks, such as low energy efficiency, high capital and maintenance costs (nearly three times as high as that for a coal-fired power plant generating the same amount of electricity), and harmful final process residues. In the last decade, a number of novel technologies utilizing gasification processes have emerged to address the issue of greater environmental sustainability and to improve the value of energy or materials output.[3,4] These technologies are expected to play a key role in the future of solid waste management since the conversion of municipal and industrial solid wastes to a gaseous fuel (producer gas or synthesis gas) significantly increases its value. Gasification has several advantages over traditional combustion of solid wastes: a limited formation of dioxins and of large quantities of nitrous and sulphur oxides; considerable reduction in the process gas volume; a wide range of products immediately obtainable from syngas (from electricity and heat generation in conversion devices to gaseous or liquid clean fuels, or bulk chemicals like ammonia and methanol); a reduced amount of secondary wastes; the possibility of applying the process at a smaller scale.[5,6]

Of all waste gasification technologies, fluidization is one of the most promising[7,3] due to several further advantages that can be obtained with one of the available different kinds of fluidized bed reactors[4,8]: the almost uniform isothermal conditions throughout the reactor, which allows a reliable process control; the very high heat and mass transfer between gas and particles, which provides for uniform products (that are not constrained in their application) and allows short residence times at lower operating temperatures; the absence of moving parts in the hot regions and the lower operating temperatures, which reduce maintenance times and costs; the great operating flexibility that makes it possible to utilize

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different fluidizing agents, reactor temperatures and gas residence times, to add reagents along the reactor freeboard or riser and to operate with or without a specific catalyst.

On the other hand, during gasification, tars, heavy metals, halogens, and alkaline compounds are released within the gas and can cause environmental and operational problems. Since the markets for gasifiers without gas cleaning are rather limited,[7,9,10] the key to achieving economically and environmentally efficient energy recovery from solid waste gasification is to overcome problems associated with the formation and release of these contaminants. Most research efforts address the main problem of gas cleanings that of proper control of the tar content. Tar is a complex mixture of a broad spectrum of condensable hydrocarbons, which includes single ring to multiple ring aromatic compounds along with other oxygen-containing hydrocarbons. It has been operationally defined in gasification as the material in the product stream that is condensable in the gasifier or in downstream processing steps or conversion devices[11] or as all organic compounds with a molecular weight larger than benzene (excluding soot and char).[12] Its control (i.e., its destruction or removal or cracking or conversion, etc.) aims to avoid various problems associated with condensation, formation of tar aerosols and polymerization of more complex structures, which may damage process equipment as well as the devices for end-use application of the syngas or may create difficulties in handling tar-water mixtures or contamination of waste streams.[13]

Basically, there are two options for controlling the tar content in gasifier product gas[12,14,15]: secondary measures, that is, downstream cleaning processes, or primary measures, that is, proper selection of gasifier design and operating conditions. Secondary methods include physical removal, thermal conversion and catalytic destruction of tars. Physical processes (wet or wet-dry scrubbing, cyclones, baffle separators, cooling towers, demisters, fabric or electrostatic filters, ceramic or metallic fabrics) play an important role for the commercial implementation of gasification: their main problem is that condensed tars are merely transferred into another (water or solid) phase which has to be disposed of in an environmentally acceptable manner.[11] Thermal tar cracking to acceptable levels requires temperatures higher than 1100°C (thus about 200°C higher than those typical of fluidized bed gasifiers) and produces soot.[16,17] The catalytic, hot-gas cleanup involves the treatment of gasifier raw gas in a second bed containing non-metallic catalysts such as dolomite, or metallic catalysts such as Ni: their main problem is to obtain a favorable combination between catalyst lifetime and catalyst cost, particularly in large scale tar cracking.[11,18,19] In conclusion, most of these secondary measures are reported to be very effective in several cases, even though they are not always economically viable and are particularly complex when a considerably low tar content is required. On the other hand, primary methods include appropriate selection of the main operating parameters (gasification temperature, equivalence ratio, residence time, etc.), the use of a proper bed additive or catalyst as well as specific gasifier design modifications. These tar control treatments inside the gasifier are gaining much attention for solid waste gasification since they may eliminate or strongly reduce the need for downstream cleanup.[15] A distinction should be made between firing the product gas in a stand-alone boiler and more advanced applications. When the product gas is kept at high temperature and then fired in a stand-alone boiler, proper selection of gasifier design, or operating conditions seems to offer good possibilities of avoiding severe tar-induced fouling problems.[12] When the product gas must be fired in a gas engine or a gas turbine, and so a much cleaner gas is required, a suitable combination of different primary and secondary treatments is likely to improve gasifier performance and produce a syngas with minimum tar concentration.

It has been recently reported[12,14,15,20] that fluidized bed biomass gasifiers operated with a bed of natural olivine, $(Mg,Fe_2)SiO_4$, showed very good control of tar content in the product gas even though additional constraints to downstream equipment and new input and by-product streams have to be taken into consideration.[21] These promising results suggest that an interesting primary method to avoid or reduce tar formation, in particular during fluidized bed gasification of wastes, is the "in situ" catalytic removal of tar precursors and intermediates by means of a metal-based catalyst on a silicate or aluminosilicate support. The tar precursors, such as cycloparaffins, naphthenes, and aromatics, forming during ternary reactions of the wax-like intermediates produced by primary cracking,[8] can be decomposed to carbon and hydrogen by means of metal-based catalysts. These contain transition metals such as Fe, Co, Ni, Cr, V, Mo, Pt, Y, Mg, Si, or their alloys, that is, those typically used for the reforming of hydrocarbons.[22] The decomposition mechanism is based on a combination of two actions: the isomerization reactions due to acidic sites like SiO_2 or Al_2O_3 and the catalysis of hydrogenation/dehydrogenation reactions due to metallic sites. This combination activates the isomerization of straight-chain paraffins to branched-chain molecules, the dehydrocyclization of paraffins to cycloparaffins, the dehydrogenation of naphthenes to aromatics and the further decomposition of aromatics to pure carbon and hydrogen.[23,24]

This study aims to investigate how a natural olivine may act as an in-situ tar reduction agent during the fluidized bed gasification of a plastic waste in a pilot-scale bubbling fluidized bed reactor.

The Reactor, Materials, and Experimental Procedures

The pilot-scale bubbling fluidized bed gasifier (BFBG) consists of three main sections: the feeding system, the fluidized bed gasifier, and the syngas treatment unit (Figure 1). The feeding system can be divided into blast feeding (measuring, mixing and injection of gasification agents, heated up to 600°C before entering the reactor) and fuel feeding (measuring and injection of solid feedstock, fed over-bed into the reactor and assisted by a small flow rate of nitrogen). The fuel and the blast flow rates are mutually adjusted so that, at a fixed fluidizing velocity, the desired equivalence ratio ER (defined as the oxygen content of air supply divided by the oxygen required for complete combustion) is obtained. The gasification section comprises a cylindrical BFB reactor, with an internal diameter of 0.381 m and a maximum feeding capacity of 60 kg/h, equipped with several control and protection devices.[25] It is heated up to the reaction temperature thanks to the sensible heat of preheated blast gases and a set

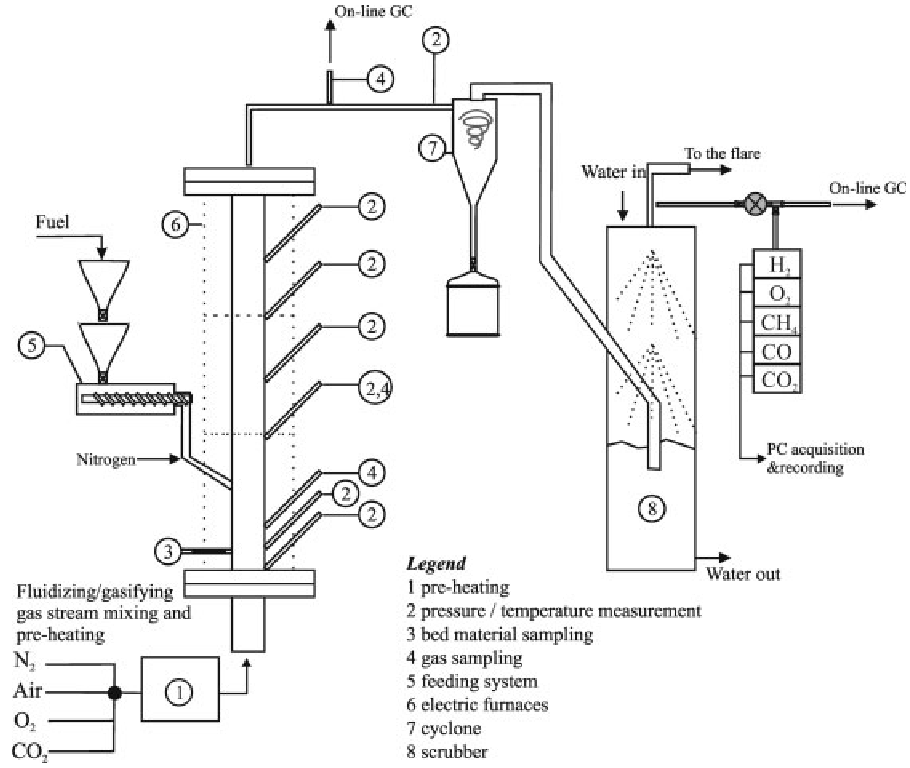

Figure 1. Schematic of the pilot-scale gasification plant.

of three pairs of external electric furnaces. The gas generated in the reactor is sent to the syngas treatment section consisting of a high-efficiency cyclone, a wet scrubber (for removal of tars, residual fly ashes and acid gases) and a flare. A more detailed description of the plant can be found elsewhere.[25]

The air-gasification experiments were carried out with pellets (5 mm in diameter and 2 mm in thickness, with a particle density of 940 kg/m^3 and a bulk density of 570 kg/m^3) of recycled polyethylene (PE) from the separate collection of municipal solid wastes. Two types of bed materials were used during the experimental runs: a quartz sand, with a size range of 0.2–0.4 mm and a particle density of 2600 kg/m^3, and an olivine (a magnesium-iron silicate mineral), $(Mg,Fe_2)SiO_4$, with the same size range and a particle density of 2900 kg/m^3. The olivine used comes from Austria and consists of different oxides: $MgO = 48–50\%$; $SiO_2 = 39–42\%$; $Fe_2O_3 = 8–10.5\%$; $(Al_2O_3+Cr_2O_3+Mg_3O_4) = 0.8$; $CaO < 0.4\%$.

The reactor was electrically heated up to a temperature of 850°C. At this point, a feed rate of PE was injected into the reactor so that the air flow-rate provided the selected fluidizing velocity and the desired value of equivalence ratio. When the gas composition remained constant for a certain time, the gas and solid sampling procedures were activated, and measurements were taken of pressure, temperature, syngas composition, carbon loading in the bed, fines collected at the cyclone. In all the runs, the gas composition downstream of the syngas treatment section was measured on-line by means of two systems: the first utilizes IR analyzers (Horiba VA-3115 for CO, CO_2, and O_2, Horiba VA-3001 for CH_4 and Teledyne Analytical Instr.-2000 for H_2), the other uses a micro-gas-chromatograph (Agilent 3000 for O_2, N_2, CO, H_2, and C_nH_m with $n < 6$). Gas was also sampled at two other points by means of Tedlar bags: at a level of 2 m along the reactor and just after the gasifier exit.

Because the tar content is one of the major concerns, two different methods of tar evaluation were used. The first conservatively imputes to the tar amount (assumed to be composed of all organic compounds with a molecular weight larger than benzene, excluding soot and char) the whole carbon loading which, as a result of a mass balance on atomic species with an overall error <5%, cannot be attributed either to the produced gas or to the solids collected at the cyclone or inside the bed. The second method evaluates the amount of C_nH_m with $n > 6$ on the basis of quantitative determinations obtained by sampling the syngas stream for a fixed time of 30 s by means of Supelco Tenax TA cartridges. These are then analyzed in a Perkin Elmer Clarus 500 GC-MS coupled with a Perkin Elmer Turbomatrix ATD thermal desorber. Data reported below are those obtained with the first method, which are always slightly larger that those from the second method.

On-line and off-line measurements and data from chemical analyses were processed to develop complete balances on atomic species for each run. The flow rate of produced syngas was determined by the tie component method[26] applied to the value of nitrogen content in the dry syngas, as obtained by GC measurements. The carbon balance allows determination of tar content on the basis of the above-recalled assumption while the hydrogen balance allows that of water content in the syngas.[27] For experiments carried out with olivine, a certain amount of carbon was found as a layer

Table 1. Operating Conditions of Experimental Runs with Recycled Polyethylene Together with the Main Results, as Measured Downstream of the Scrubber

Runs #	Bed material	W_{bed} (kg)	U (m/s)	Q_{fuel} (kg/h)	ER	Q_{syngas} (m^3_N/h)	CO (%)	H_2 (%)	CH_4 (%)	C_2H_m (%)	Q_{tar} (kg/h)	CGE
7	Sand	131	0.7	31.0	0.20	93	2.8	9.1	10.4	4.8	14.6	0.51
5	Sand	131	0.7	27.9	0.22	92	2.4	9.6	9.1	4.6	12.1	0.52
6	Sand	131	0.7	20.0	0.31	86	2.3	8.3	7.1	2.9	7.0	0.51
10	Olivine	145	0.7	31.4	0.20	132	18.4	30.1	3.4	1.4	0	0.69
9	Olivine	145	0.7	22.6	0.27	122	20.0	26.9	2.2	0.5	0	0.76
12	Olivine	145	0.7	21.8	0.28	123	20.1	27.1	2.1	0.5	0	0.79
13	Olivine	145	0.7	19.8	0.31	119	19.5	24.0	2.0	0.9	0	0.82
11	Olivine	145	0.6	21.4	0.25	112	19.3	29.2	2.1	0.6	0	0.76
16	Olivine	215	0.7	29.1	0.21	140	19.0	30.8	3.2	1.1	0	0.78
14	Olivine	215	0.5	18.1	0.24	96	18.2	29.3	2.5	0.5	0	0.77
15	Olivine	215	0.5	16.2	0.27	91	21.3	25.4	1.8	0.3	0	0.76

covering bed particles or fines elutriated from the reactor and separated by the cyclone. The latter were periodically collected, weighed, and analyzed, so that their production was easily determined. That of carbon present in the bed was instead determined by means of two methods: carbon loading at a specific time of the run was evaluated by taking solid samples from the bed at that time, analyzing them and determining the carbon percentage in the sample, and then in the bed; the overall amount of carbon deposited on bed particles during the whole run was estimated by establishing oxidizing conditions in the reactor at the end of the run, that is, after the stop of plastic waste feeding, and calculating the related amounts of correspondingly produced CO and CO_2.

Experimental Results

The effect of olivine on tar control

The pilot scale bubbling fluidized bed gasifier was first operated with air and PE pellets injected in a bed of quartz sand particles. The results of these experiments[28] indicated that the average tar concentration in the exit gas, as measured downstream of the scrubber unit, was of the order of 100 g/(m^3_N). These tar contents do not allow gas utilization in internal combustion systems (which require loads lower than 100 mg/m^3_N), in industrial gas turbines (which require tar contents of about 1 mg/(m^3_N) and less than ever in catalytic conversion processes (which require tar loads further lower).[11] The same experiments indicated that it is not possible to obtain sufficient tar abatement from proper selection of the variation range of the main operating parameters (gasification temperature, gas residence time, equivalence ratio). These results are in agreement with several experimental studies on air gasification of biomass.[12,15,29–31] In particular, an increase in gasification temperature or residence time in the reactor, in the range of interest of fluidized bed gasifiers, leads to a certain reduction in the total tar content and to a contemporaneous increase of 2–3 ring and 4–7 ring PolyAromatic Hydrocarbons (PAHs) with a substantial increase in tar dewpoint.[21] On the other hand, an increase in equivalence ratio is obviously limited by the need to obtain a sufficiently large heating value of the gas: the possible strong decrease in total tar content (see runs 5, 6, and 7 in Table 1) is, however, accompanied by an increase in tar dewpoint, related to the increase in heavy PAH compounds.[12,28]

The use of olivine as an active bed additive inside the gasifier was suggested by the promising results obtained in fluidized bed biomass gasifiers operated with a bed of natural olivine.[12,14,15,20,32] The measurements made in air-gasification runs with recycled PE injected in a bed of olivine particles indicated a high quality of the produced gas, in terms of low tar content, large syngas yield and high hydrogen volume fraction (Table 1). Tar yields decreased to 0 kg/h downstream of the scrubber, that is, tar was not detected in the gas sampled after the syngas treatment unit. The specific production of syngas correspondingly increased by about 40%, leading to values as high as 6 m^3_N/kg_{fuel}. Mass balances on atomic species, such as those reported in Table 2 for two pairs of runs with and without olivine, also indicate that olivine allows a larger quantity of fuel carbon to be converted in syngas (65% vs. 59% and 81% vs. 65%, respectively) together with all the fuel hydrogen, with a considerable increase in CO and H_2 concentrations. Interestingly, only in the runs with olivine was part of the fuel carbon found in the bed or collected in the cyclone as elutriated fines.

Figure 2 shows, for a typical run with a bed of olivine, the composition of syngas downstream of the scrubber unit, as a function of run time. Three regions in the gas concentration profiles have been identified. Following the standard experimental procedure, before the start of plastic waste feeding, the reactor is kept at 850°C and fluidized with an air stream. Under these conditions, Devi et al.[33] found that the iron contained in the olivine particles progressively segregates at the external surface and is then oxidized. It appears mostly as flakes, which progressively build up over the particle surface, as confirmed by a series of scanning electronic microscope observations and EDAX analyses like those reported in Figure 3 for two levels of magnification. Just after the injection of plastics, their fast cracking establishes a reducing environment in the reactor (region I in Figure 2) that in turn allows the beginning of olivine activation: when hydrogen is able to reach iron sites and reduce them, these react with the products of primary cracking of plastics. The very good mixing of solids in the fluidized bed makes the catalytic effect start substantially at the same time for all particles. This is clearly identified in all the experiments: a huge, sharp increase in hydrogen content in the produced syngas separates regions I and II and indicates that the endothermic decomposition of polymer chain fragments is now catalyzed by the active iron sites on the olivine particle surface (Figure 2). The cracking

Table 2. Balances on Atomic Species for Two Experimental Runs of Air Gasification with Quartz Sand or Olivine as Bed Material, Carried Out at Different Equivalence Ratios

	In (kmol/h)					Out (kmol/h)			
	C	H	O	N		C	H	O	N
Run #7, Quartz Sand, ER = 0.20									
PE	2.2	4.3	0	0	Syngas	1.3	3.3	0.9	5.3
Air + N_2		0	1.3	5.3	Water		0.3	0.1	
					Tar	0.9	0.8	0.2	0
					Elutriated fines	0	0		
					C in the bed	0	0		
Total	2.2	4.3	1.3	5.3	Total	2.2	4.4	1.2	5.3
Run #6, Quartz Sand, ER = 0.31									
PE	1.4	2.8	0	0	Syngas	1.0	2.2	0.9	5.3
Air + N_2		0	1.3	5.3	Water		0.3	0.1	
					Tar	0.4	0.4	0.1	0
					Elutriated fines	0	0		
					C in the bed	0	0		
Total	1.4	2.8	1.3	5.3	Total	1.4	2.9	1.1	5.3
Run #10, Olivine, ER = 0.20									
PE	2.3	4.4	0	0	Syngas	1.5	4.7	1.3	5.3
Air + N_2		0	1.3	5.3	Water		0	0	
					Tar	0	0	0	0
					Elutriated fines	0.05	0.01		
					C in the bed	0.77	0		
Total	2.3	4.4	1.3	5.3	Total	2.3	4.7	1.3	5.3
Run #9, Olivine, ER = 0.27									
PE	1.6	3.2	0	0	Syngas	1.3	3.5	1.3	5.3
Air + N_2		0	1.3	5.3	Water		0	0	
					Tar	0	0	0	0
					Elutriated fines	0.01	0		
					C in the bed	0.3	0		
Total	1.6	3.2	1.3	5.3	Total	1.6	3.5	1.3	5.3

Note that a small flow rate of nitrogen is used to facilitate the fuel feeding and that the molecular weight for tar was assumed to be that of naphthalene.

of hydrocarbon fragments ($pC_xH_y \rightarrow qC_nH_m + rH_2$) is enhanced and accompanied by a parallel carbon formation ($C_nH_m \rightarrow nC + {}^{m}/_{2}H_2$). Accordingly, region II, that is, that of the steady-state regime, shows a very low concentration of methane (hence C_nH_m), a strong in-situ reduction in tar formation and considerable carbon deposition over the bed particles. This is supported by SEM pictures and EDAX analyses: the transition from regions I and II is accompanied by a different morphology (and activity) of the olivine particles that interact with the primary products of the decomposition, becoming covered by a progressively wider layer of carbon. Figure 3 reports images of an SEM-EDAX analysis of an oli-

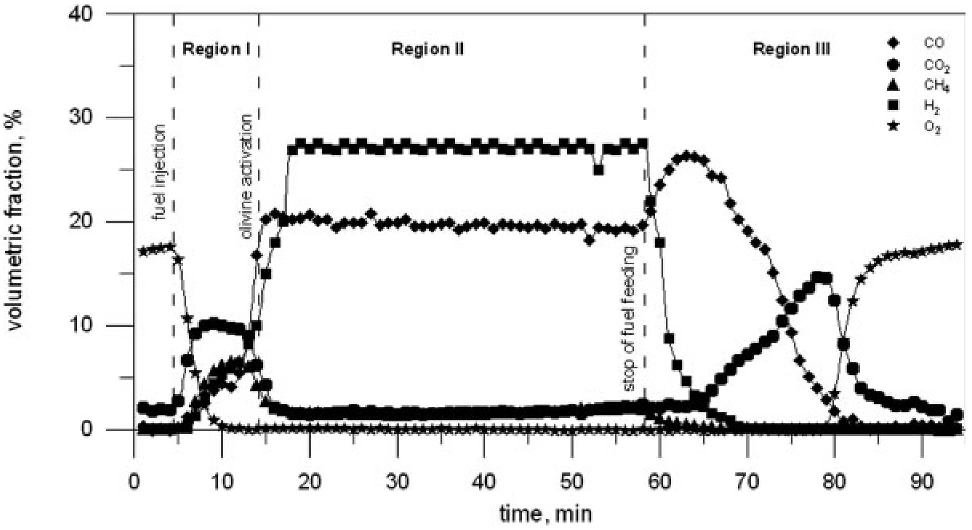

Figure 2. Gas concentration profiles measured downstream of the scrubber and reported as a function of time during the gasification test #9, with a bed of 145 kg of olivine, at 850°C, 0.7 m/s of superficial velocity, ER = 0.27.

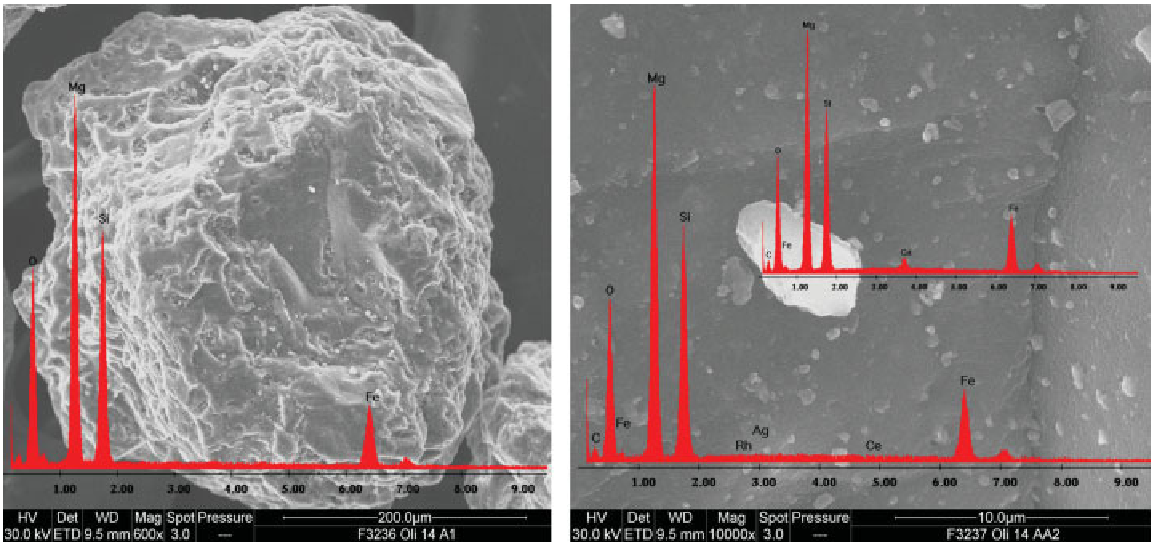

Figure 3. Scanning electronic microscope pictures and EDAX analyses of the external surface of an olivine particle as sampled from the bed during region I of the gasification test #9 and at two levels of magnification.

In the picture on the right the EDAX analyses refer to the white flake and to the background, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

vine particle sampled during region I, showing a large presence of iron, while Figure 4 reports those of another particle sampled during region II, demonstrating the presence of carbon on its surface.

When the plastic waste feeding is stopped, a rapid decrease in hydrogen and hydrocarbon concentrations and a progressive increase in those of carbon monoxide and then of carbon dioxide are observed (region III). The gasifier again has an oxidizing environment that progressively burns the carbon which covers the olivine particles.

If fuel feeding is not stopped for a longer time, and there is no make-up of olivine, the amount of carbon deposited on bed particles progressively increases. Figure 5 reports for another experimental run the syngas composition profiles together with the values of carbon loading in the bed evaluated in region I and in two different zones of region II. It is possible to detect an initial zone of this region where gas concentrations remain almost constant and a final zone where H_2 and CO contents gradually decrease, those of CH_4, (hence of C_nH_m) and CO_2 increase, all indicating the corresponding reduction in the catalytic effect. Chemical and thermogravimetric analysis of the three solid samples indicates (see the values reported on Figure 5 and SEM pictures and EDAX analyses of Figures 6–8) that the first, taken at the beginning of region

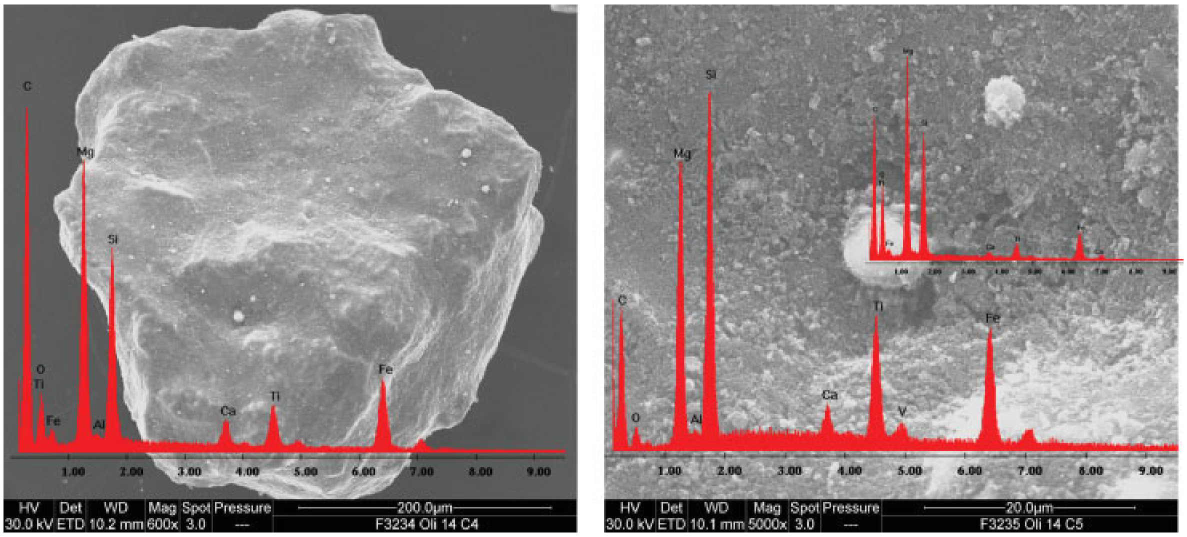

Figure 4. Scanning electronic microscope pictures of the external surface of an olivine particle as sampled from the bed during region II of the gasification test #9 and at two levels of magnification.

In the picture on the right the EDAX analyses refer to the white flake and to the background, respectively. The surface is covered by carbon deposits. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

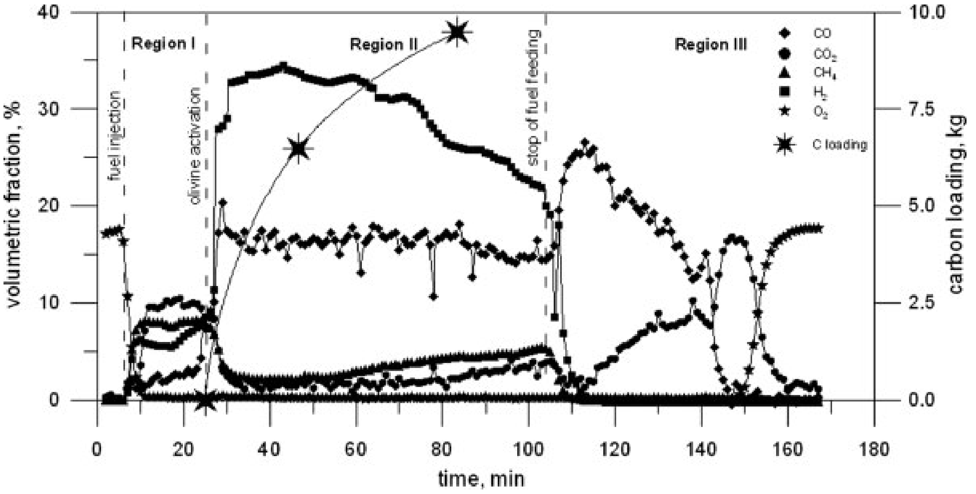

Figure 5. Gas concentration profiles measured downstream of the scrubber and solid carbon loading in the bed, both reported as a function of time during the gasification test #16, with a bed of 215 kg of olivine, at 850°C, *U* = 0.7 m/s, ER = 0.21.

II, has no carbon on the olivine particle surface while the second and the last present an increasing average carbon content (3.2% and 4.8%, respectively). This suggests that the onset of inhibition of active sites could be related to a carbon mass fraction in the bed greater than about 3.5%, which is likely to be able to cause the beginning of a substantial masking effect of catalytic sites. The result has immediate practical application, since it can be used to evaluate the mass flow rate of exhausted olivine which must be removed and that of fresh olivine which must be fed into the reactor.[34]

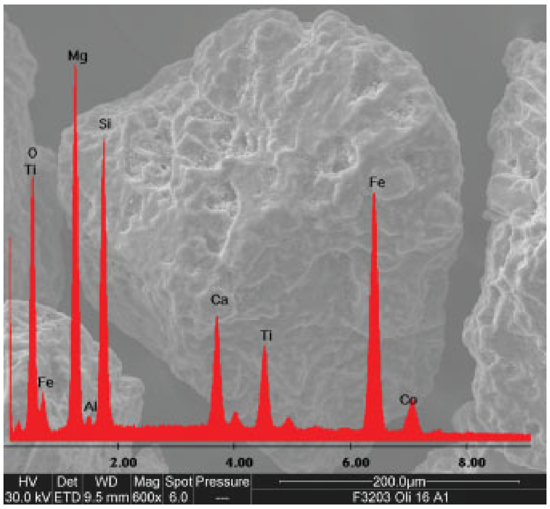

Figure 6. Scanning electronic microscope pictures of the external surface of an olivine particle as sampled from the bed during region I of the gasification test #16 reported in Figure 5.

There is no carbon on particle surface, as confirmed by EDAX analysis. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Activation and deactivation of olivine particles

The catalytic action of iron can be explained on the basis of the general behavior of transition metals. These elements (and their oxides) act as heterogeneous poly-addition catalysts so that the molecules containing vinyl groups can react on the active sites by forming carbonaceous deposits (Figure 9A).[35] When these deposits generate a relatively thick uniform layer, diffusive resistance is no longer negligible (Figure 9B). The carbon formation rate gradually decreases as a consequence of the progressive inhibition of catalytic reactions and parallel starting of a series of radicalic reactions (Figure 9C). An example of a radicalic reaction is the addition of unsaturated molecules on structures formed by the catalytic step, commonly known as the Diels-Alder reaction.[24] The gas profiles shown in Figures 2 and 5 support the proposed mechanism. The sharp increase in hydrogen and carbon monoxide concentrations, which is shown in Figures 2 and 5 for the transition between regions I and II, is in agreement with an almost immediate development of the catalytic reactions. Similarly, the gradual decrease in hydrogen and carbon monoxide concentrations with the corresponding increase in those of methane and carbon dioxide, which is shown in Figure 5 for the second part of region II, is in agreement with the gradual decrease in carbon formation rate related to the progressive substitution of catalytic reactions by those of free radicals.

The same behavior was observed in all the experiments carried out under different fluidizing velocities (from 0.5 to 0.7 m/s), bed amounts (from 135 to 215 kg) and equivalence ratios (from 0.2 to 0.3). Differences were instead observed under operating conditions with larger amounts of oxygen, that is, at higher equivalence ratios. For ER > 0.35 the length of region I appeared much greater, that is, the particles of olivine had more difficulty in being activated and, under further oxidizing conditions, might never be activated. A possible explanation is that the large amount of oxygen in the blast agent may prevent iron reduction or may react with the produced solid carbon to

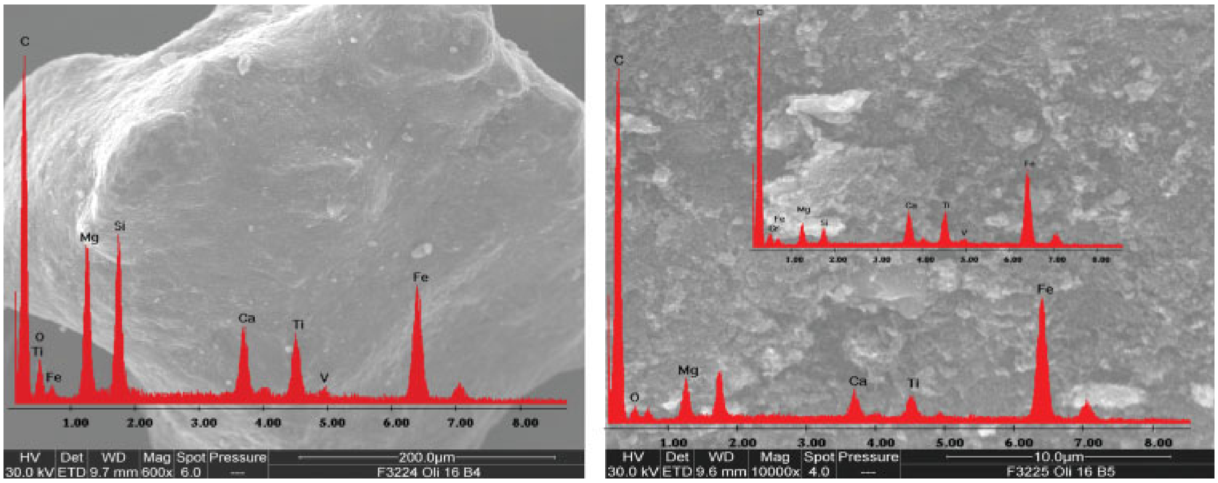

Figure 7. Scanning electronic microscope pictures of the external surface of an olivine particle as sampled from the bed during steady state part of region II of the gasification test #16 reported in Figure 5.

In the picture on the right, taken at a higher level of magnification, the EDAX analyses refer to the white flake and to the background, respectively. The surface is covered by carbon deposits. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

generate CO which, in turn, binds the iron to different kinds of carbonyls (such as $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, and their hydrides): in both cases, iron catalytic activity is inhibited.[24] The formation of iron carbonyls at high temperatures and under a reducing environment is possible since carbon monoxide is an important π orbital acceptor and is particularly reactive with transition metals (group d) like iron. The high electronic density of the latter elements can be delocalized into the free π orbital of carbon monoxide, thus allowing bonding between the neutral molecule of CO and iron atoms. The experimental evidence of an interaction between CO and iron and of its effect on degradation products (solids, gases and liquids) has already been highlighted by the authors in parallel studies related to carbon nanostructure formation in a BFB pyrolyser fed with the same PE pellets used in this study.[36]

This inhibiting effect of high equivalence ratios is confirmed by data reported in Figure 10 where the specific carbon deposition rates, averaged on the whole time length of region II, are reported as a function of equivalence ratio for some experimental runs. These values were obtained as the ratio between the overall carbon loading of the run and the time length of region II and by dividing the result by the total amount of plastics fed into the reactor in the same time period. The extrapolation of experimental data suggests the existence of a threshold value of oxygen content after which there is no carbon deposition on olivine particles, due to the absence of any catalytic effect of olivine on heavy hydrocarbon cracking.

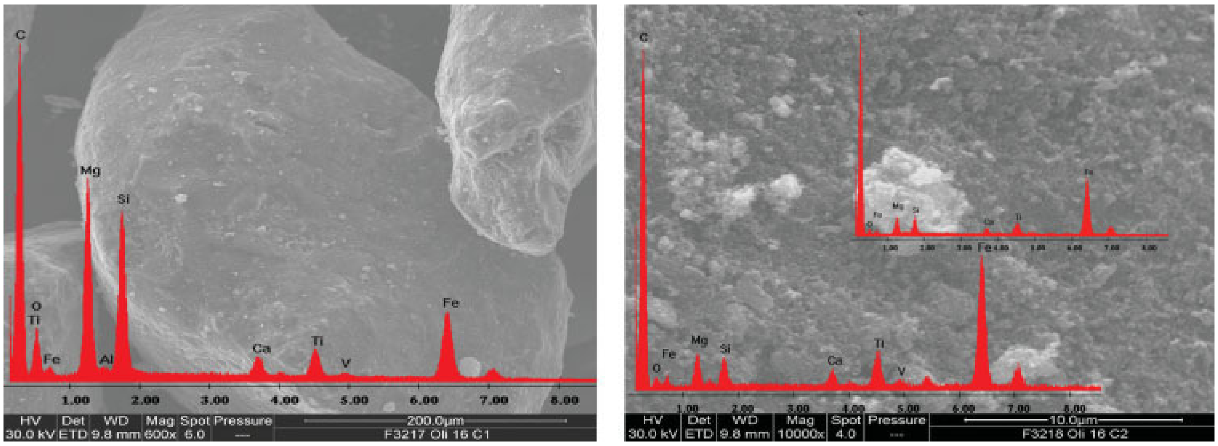

Figure 8. Scanning electronic microscope pictures of the external surface of an olivine particle as sampled from the bed during final part of region II of the gasification test #16 reported in Figure 5.

In the picture on the right, taken at a higher level of magnification, the EDAX analyses refer to the white flake and to the background, respectively. The surface is covered by carbon deposits. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

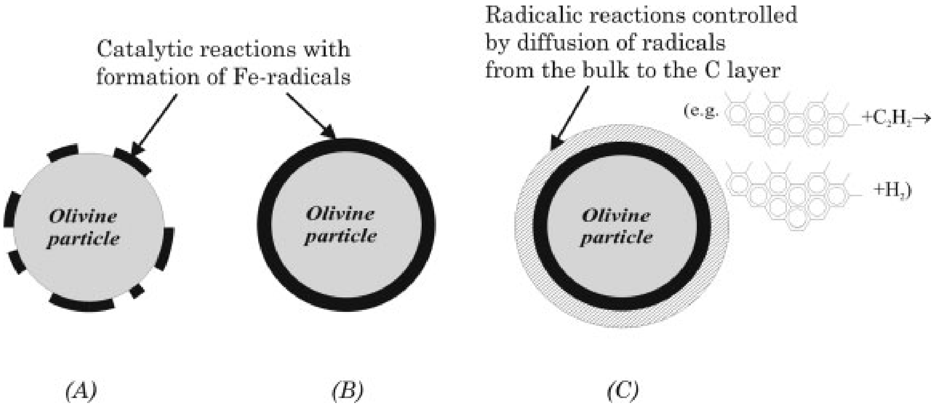

Figure 9. Carbon formation kinetics scheme.

A: The catalytic reactions between different radicals (aliphatic, R, or aryl, Ar) begin to produce carbonaceous deposits. B: The deposits generate a uniform layer with a progressively larger thickness and a no longer negligible diffusive resistance. C: The diffusive resistance is so high that catalytic reactions are inhibited and a series of radicalic reactions occurs.

A phenomenological description of the different stages of the process

A series of measurements were made at different levels along the reactor's height to investigate how olivine acts during gasification of polyethylene pellets. Specific interest lay in understanding why the large production of carbon monoxide during gasification (with volumetric percentages of about 20%) has no effect on the catalytic activity of olivine while the CO produced by oxidation of carbon deposits on olivine particles contributes to rapid deactivation.

The axial profiles of volumetric fractions of the main gaseous species present in the reactor are reported in Figure 11 for two runs carried out with a bed of olivine and different equivalence ratios. The profiles show no substantial changes between the compositions at 2 m (i.e., less than 1 m above the bed splashing zone) and that at 4.3 m (i.e., at the reactor exit), with minor variations in the composition measured downstream of the scrubber. This indicates that at a reactor height of 2 m the cracking and gasifying reactions were almost completed, that is, they mainly occurred inside the bed, the splashing zone and a small part of the freeboard immediately adjacent to this zone.

This finding together with the main results of a series of studies on fluidized bed pyrolysis and gasification of polyethylene and other plastic wastes[8,36–39] helps develop a phenomenological description of the different stages occurring during air gasification of polyethylene pellets in a fluidized bed of olivine particles. Figure 12 schematically represents the sequence of these physical and chemical stages. The heating and softening of the polymer occur in the splashing zones during the falling of plastic pellets from the over-bed feeding point towards the bed surface (point 1 in Figure 12). In the dense bed the following stages occur, strongly enhanced by the high rates of mass and energy transfer typical of a BFB reactor: physical interaction between olivine particles and the molten plastic pellet that immediately activates a layering process between them[8,37–39] (point 2 in Figure 12); heating and primary thermal cracking, which cracks polymer chain into hydrocarbon fragments[36] and catalytic reactions between active sites of olivine and hydrocarbon fragments with the consequent dehydrogenation and carbonization (point 3 in Figure 12). Interestingly, the primary cracking is not related to the whole plastic pellet but to a thin layer of polymer, which coats and adheres to the external surface of single bed particles. In determining the heating and devolatilization time

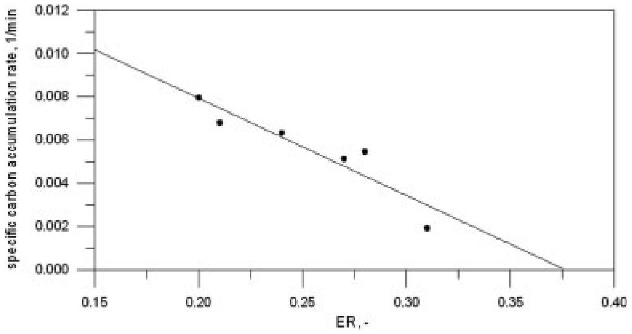

Figure 10. Specific carbon deposition rate over olivine bed particles during region II of gas concentration profiles as a function of equivalence ratio for the experimental runs carried out at 0.7 m/s.

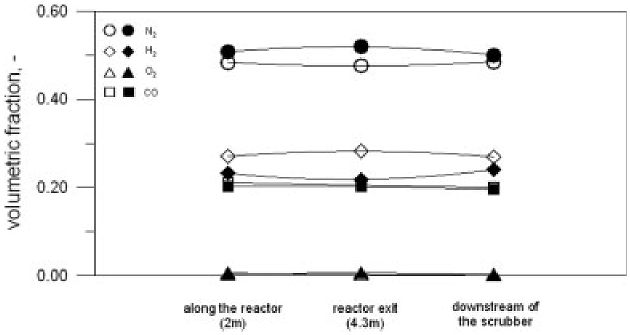

Figure 11. Gas composition at different sampling points for two runs with a bed of 135 kg of olivine, U = 0.7 m/s; ER = 0.27 (shaded symbols), 0.31 (open symbols).

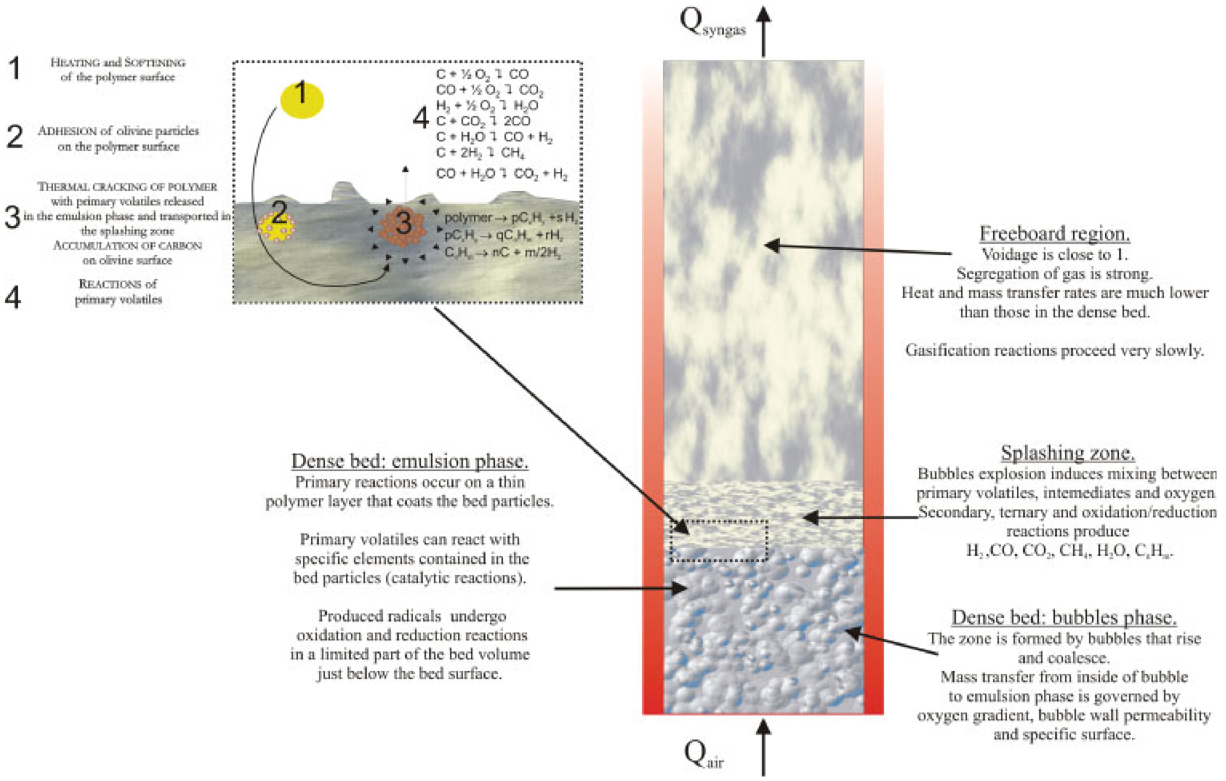

Figure 12. Sequence of physical and chemical phenomena occurring during fluidized bed gasification of plastics in a bed of olivine particles.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of the plastic pellet, this means that the internal resistance becomes negligible and the intrinsic kinetics become the controlling stage of the primary cracking process. The latter is then completed in a time that has been estimated to be shorter than 1 ms.[38] As a consequence, the bed region mainly affected by all these phenomena is that just below the top of the bed (points 2 and 3 in Figure 12).

The resulting gaseous compounds that enter the splashing zone mainly consist of light hydrocarbons (in particular methane) since aromatics (and their precursors as acetylene) have already undergone cyclization and polycondensation reactions. Here (point 4 in Figure 12), the hydrocarbons mix and react with oxygen segregated in the bubbles that erupts at the bed surface, thus forming a large quantity of carbon monoxide. The oxidation of hydrogen to water is instead limited as found in parallel experiments.[36] The role of the freeboard region is generally negligible with reference to the main components of syngas since the cracking of hydrocarbon fragments requires the presence of catalytic sites.

According to this phenomenological description, carbon monoxide produced during gasification reactions (point 4) is mainly generated in the splashing zone and the first part of the freeboard; from here it is rapidly entrained out of the reactor and is not in contact with olivine (and cannot affect its catalytic action). The carbon monoxide generated by the oxidation of carbon deposits covering olivine particles is instead produced inside the bed. Therefore, when the amount of available oxygen is high (i.e., ER $\gg$ 0.30) the related production of CO inside the bed could inhibit the process of olivine particle activation.

Conclusions

The experimental results show that the use of a natural olivine as an in-situ tar reduction agent greatly catalyzes the reactions of heavy hydrocarbon cracking and carbon formation. The quality of the syngas obtained during the bubbling fluidized bed air-gasification of a plastic waste is considerably improved, in terms of low tar content, high hydrogen volume fractions, large thermal efficiency and syngas yield.

The different physical and chemical phenomena that concur in the activation or deactivation of the olivine particles were described with the support of on-line and off-line gas measurements as well as chemical analyses and scanning electronic microscope observations on solid samples. The rate of carbon deposition on the external surface of olivine bed particles was experimentally evaluated and used as an index of the existence, or otherwise, of in-situ catalytic reduction in tar formation. In particular, under the operating conditions of the tests reported, the experimental results allowed the identification of an equivalence ratio above which the olivine particles have more difficulty being activated or might never be so. The amount of carbon in the bed that can induce deactivation was also estimated: it can be used to evaluate the mass flow rate of exhausted olivine which must be removed and that of fresh olivine which must be fed into the fluidized reactor.

A phenomenological description of the different stages occurring during gasification of the tested plastic waste in a fluidized bed of olivine particles is also reported.

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Notation

CGE, cold gas efficiency (also known as *apparent thermal efficiency*) = ratio between the chemical energy of obtained syngas and that of fuel [syngas flow rate × LHV_{syngas}/fuel flow rate × LHV_{fuel}]
ER, equivalence ratio = ratio between the oxygen content of air supply and that required for the stoichiometric complete combustion of the fuel effectively fed to the reactor
LHV = lower heating value
$m^3{}_N$ = cubic meters under normal conditions (0°C and 1 atm)
Q_{air} = mass flow rate of fluidizing air
Q_{fuel} = mass flow rate of fuel fed into the gasifier
Q_{syngas} = volumetric flow rate of obtained syngas, under normal conditions
Q_{tar} = mass flow rate of tar as measured downstream of the scrubber unit
U = superficial fluidizing velocity
W_{bed} = amount of bed material (sand or olivine particles)

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