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Article

Development of Oxygen Transport Properties by Olivine and Feldspar in Industrial-Scale Dual Fluidized Bed Gasification of Woody Biomass

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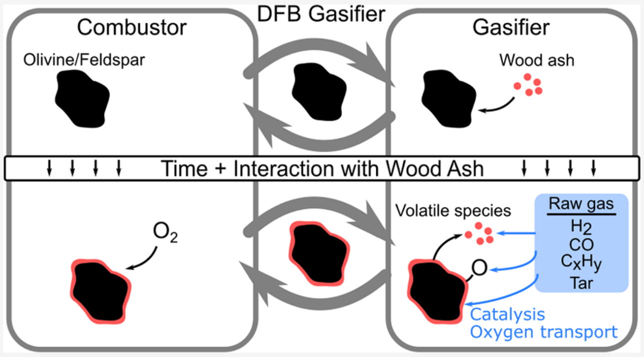
ABSTRACT: In dual fluidized bed (DFB) gasification, the interaction of the bed material with the fuel ash leads to the development of a bed catalytic activity toward tar-abating reactions. However, the formation of ash layers may also be detrimental to the process, especially in terms of the uncontrolled transport of oxygen from the combustor to the gasifier. A few previous studies investigating the development of catalytic activity in bed materials have also reported the development of oxygen transport, although the latter was not the focus of these studies. This work verifies that olivine and feldspar, which are bed materials with limited and no intrinsic oxygen transport capacities, respectively, develop the capacity to transport oxygen by interacting with the fuel ash. We correlate this development in oxygen transport to the development of bed catalytic activity. Our results imply that the volatile species that are released by the bed material to the gas phase in the gasifier contribute to the developed oxygen transport. Sulfur is proposed as one of the components of these volatile species, and its potential contribution is investigated. For feldspar, the results support the notion that sulfur is involved in the transport of oxygen, both as a volatile species and as a species remaining within the ash layer. The results also suggest that other species, including volatile ones, are involved. These aspects are investigated based on experimental results obtained from the Chalmers gasifier—a semi-industrial-scale DFB gasifier—and are isolated in laboratory-scale experiments.



1. INTRODUCTION

Dual fluidized bed (DFB) gasification is a promising technology for the production of synthetic gas, which is a precursor to a wide range of chemicals and fuels. In DFB gasification, solid fuels, such as biomass and waste, are converted into a gaseous mixture at a high temperature using steam. The heat required for the gasification and reforming reactions is produced in a separate reactor, the combustor, connected to the gasification reactor. In a DFB system, the fuel decomposition reactions in the gasification reactor lead to the production of char. Part of the char exits the reactor and is transported to the combustor, where it is combusted. The heat released during the combustion is transported from the combustor to the gasifier by means of a bed material that circulates between the two fluidized bed reactors. In the gasifier, the bed material interacts with the released gas species. Among these gas species are heavy hydrocarbons, referred to as "tar," the presence of which in the gas can lead to operational problems. The interaction of the bed material with the gas species often results in a decrease in the tar content of the gas, a capability of the bed material that is referred to as "catalytic activity." The use of an in-bed catalyst has been extensively investigated as a primary measure for tar abatement.[1,2] The bed material, therefore, plays a central role in DFB gasification, not only affecting the energy balance of the process but also its product output.

In addition to heat, the bed material transports chemical species between the reactors. Some bed materials, referred to as oxygen carriers, can bind oxygen in the combustor, thereby releasing heat, and then transport that oxygen to the gasifier, where it reacts with the reducing gas. This phenomenon is the basis for the chemical looping combustion (CLC) technology, which, in opposition to traditional combustion processes, relies on the oxidation of an oxygen carrier rather than a fuel to

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produce heat, which results in a flue gas free of CO_2. The oxygen carrier is reduced in an interconnected reactor, using a fuel and steam, thereby producing a gas containing CO_2 and H_2O only, which greatly facilitates the sequestration of CO_2.[3−5] The ability of some bed materials to bind oxygen is also the basis for the oxygen carrier-aided combustion (OCAC) technology, whereby the use of an oxygen carrier improves the fuel burnout in fluidized bed combustors.[6] The development of the CLC concept has led to investigations of various chemical looping technologies that take advantage of the possibility to transport species between two reactors with different thermodynamic conditions by means of a bed material. One offshoot of the CLC concept is the chemical looping gasification (CLG) technology, which also uses oxygen carrier bed materials to transport oxygen but limits the transport of oxygen to produce a high-energy-content gas in the fuel reactor.[7] The CLG concept can be regarded as an iteration of the DFB gasification technology, whereby all carbon can, ideally, be concentrated into a single stream, thus avoiding the costly separation of CO_2 from the flue gas if CO_2 emissions to the atmosphere are to be avoided. However, for traditional DFB gasification, oxygen transport is not considered beneficial, since it leads to oxidation of part of the raw gas, which in turn leads to an increased energy demand for the separation of CO_2 from the synthesis gas.

Among the bed materials with potential for use in DFB gasification, olivine and feldspar have attracted considerable interest, due to their availability, mechanical stability, and higher catalytic performance, compared to silica sand. Olivine is the bed material that has been used in all of the large-scale DFB gasifiers, such as the GoBiGas facility in Gothenburg, Sweden;[8] the Senden gasifier in Senden, Germany;[9] and the Güssing gasifier in Güssing, Austria.[10] Feldspar has been investigated as an alternative to olivine as it is cheaper, more widely available, and free of hazardous components.[11,12] For these reasons, olivine and feldspar are the bed materials investigated in the present work. Under laboratory conditions, olivine has been shown to have both catalytic[13−20] and oxygen-carrying[17,20,21] properties. These properties have been linked to its iron content and have been shown to be enhanced by an activation process that occurs during repeated oxidation−reduction cycles at a high temperature and that leads to the migration of iron to the surface and the formation of iron oxides. Feldspar, owing to its lack of transition metals, has no intrinsic oxygen-carrying capability.[22] It has been shown to have some catalytic activities, which have been linked to its alkali content, based on the fact that alkalis are known catalysts in gasification processes.[22]

However, during DFB gasification, the composition of the bed material is not static but changes as a consequence of interactions with the fuel ash. With the change of bed material composition, the properties of the bed material also evolve. The interaction of bed materials with fuel ash during DFB gasification leads to the formation of ash layers on the particles, and these have been linked to the development of a catalytic activity of the bed material.[23,24] These ash layers can be formed through: condensation or chemical reaction with volatile ash species such as alkali, through sticking of molten ash particles; or attachment of particles through van der Waals forces.[25−27] With time and continued interaction with the fuel ash, the ash layer evolves, forming several sublayers as a consequence of the diffusion of ash and bed material species and the subsequent formation of new structures. This ash-bed material interaction that leads to the formation of ash layers and their sublayers has been investigated in a number of publications in which different bed materials have been in focus, including silica sand,[28−30] olivine,[30−33] feldspar,[11,30,34−37] and bauxite.[38] Due to these changes in the structure and composition of the bed material, the properties apparent in an environment that does not promote the formation of ash layer may not be manifested during DFB gasification, which means that the underlying phenomena may no longer be relevant. For instance, for olivine, the roles of iron and its migration in the transport of oxygen may differ when interactions occur with the fuel ash and, if oxygen transport develops, it may do so following a mechanism different from that identified under laboratory conditions.

Indeed, the change in surface composition of the bed material particles can also result in the development of an oxygen-carrying capability by the bed material, even in materials that do not exhibit this capability intrinsically, which can contribute to the development of bed material activity along with its catalytic activity. Berdugo Vilches et al. measured oxygen transport in the case of quartz sand, which does not contain oxygen-carrying species in its virgin composition, after the material had spent a week in the Chalmers DFB gasifier.[39] The observed oxygen transport was attributed to the bed material ash content.[39] These authors also reported that an olivine bed to which potassium carbonate and sulfur had been added had, after only 1 day of exposure in a DFB system, an oxygen transport capacity that was comparable to that of an untreated olivine bed that had resided for a week in the system. Similarly, Marinkovic et al. reported an association between an increase in the oxygen transport capacity of bauxite and time spent in the bed of the Chalmers DFB gasifier.[38] These authors attributed the observed oxygen transport with the migration of iron to the surface linked to the oxidation−reduction cycles and the accumulation of ash components. Notably, the authors reported that calcium formed thick shells around the particles, in which sulfur could also be found. They suggested that CaS−$CaSO_4$ cycles, as proposed by Pecho et al.,[40] could be responsible for part of the measured oxygen transport. Similarly, Berguerand et al. have suggested that species in the ash layer could contribute to oxygen transport.[11] For example, calcium present in high concentrations, could, *via* sulfate−sulfide cycles, explain the strong increase in oxygen transport that the authors measured for feldspar after 4 days of exposure in the DFB gasifier.[11] Studying the samples obtained from that experimental campaign, Faust et al. have reported the presence of iron and manganese in the ash layers of the feldspar particles, which might explain the measured level of oxygen transport.[36]

The chemical species transported by the bed material influence the reactions that are taking place in the gasifier due to the interactions of the ash layer with the raw gas derived from the fuel conversion. In addition, chemical species can be released from the ash layer to the gas phase, where they may also interact with the raw gas. In the Chalmers gasifier, the release of chemical species by the bed material has been demonstrated for sulfur.[33] The concentrations of H_2S exceeded the levels that could be explained by the sulfur input of the fuel to both the combustor and the gasifier. This indicates that the bed material accumulates sulfur and only releases a portion of the sulfur to the gas phase in the gasifier thanks to the overall reducing gas environment.[33] It should be noted that in the

Chalmers gasifier the raw gas is combusted in the boiler, which enhances the retention of volatile fuel ash species within the system. Based on the observed high H_2S concentrations, Marinkovic et al. have proposed that the transport of potassium from the combustor to the gasifier in a DFB system occurs *via* the interaction of K_2SO_4 with the bed material in the combustor and the subsequent release of potassium and sulfur in the gas phase in the gasifier.[33] Following this, a hypothesis can be made that the release of sulfur to the gas phase would be accompanied by the release of up to four oxygen atoms, thereby contributing to the transport of oxygen from the combustor to the gasifier. Sulfur could, therefore, be involved in the development of an oxygen transport capacity of a bed material due to its presence in the ash layer, possibly *via* CaS–$CaSO_4$ cycles, as mentioned above, or by virtue of its release from the ash layer.

As oxygen transport is a crucial parameter in the heat balance and the composition of the gas produced by the gasifier, its potential development in a bed with limited or no intrinsic oxygen-carrying capability is an important factor in the operation of the DFB process. Given that the formation of ash layers is unavoidable, and even desirable to establish a high catalytic activity toward tar abatement, it is important to know whether oxygen transport can also develop. While, as mentioned above, a few studies have reported the development of oxygen transport in bed materials with limited or no initial oxygen-carrying capability, investigating this phenomenon and its connection to the development of catalytic activity was not the focus of those studies. The aims of this work are, therefore, to verify that oxygen transport develops in beds that contain olivine and alkali-feldspar, which are two materials with limited and no initial oxygen-carrying capability, respectively, and to show that this evolution correlates with the development of catalytic activity. The tar yield in the product gas and the water-gas shift (WGS) reaction are used as measures of the catalytic activity of the bed.

The contributions of volatile ash species to the oxygen transport are investigated, mainly *via* experiments conducted in a laboratory-scale fluidized bed reactor. In this work, the hypothesis is presented that sulfur, present in the ash layers of olivine and feldspar, contributes to the developed oxygen transport, including as a volatile species released in the gasifier. Under this hypothesis, the contribution of sulfur to the oxygen transport is investigated. Results suggesting distinct contributions of sulfur as a persistent species in the ash layer and as a volatile species released to the gas phase are presented.

2. METHODS AND EXPERIMENTAL SETUP

In this work, experiments at the laboratory and semi-industrial scale were combined to explore the development of oxygen transport in olivine and feldspar, and the role of sulfur in this oxygen transport. The Chalmers gasifier and its corresponding gas analysis system, and the laboratory reactor are described. For the large-scale experiments, the method for determining the oxygen transport is also detailed. The experiments in the Chalmers gasifier are used to establish the correlation between oxygen transport and bed catalytic activity. Perturbations, in the form of virgin bed material and elemental sulfur, were introduced to the system to explore the contribution of volatile species, including sulfur, to the oxygen transport. Laboratory-scale experiments were applied to bed samples taken from the Chalmers gasifier, to measure their oxygen-carrying capacity, and to subject them to oxidation–reduction cycles to evidence a possible activation process or loss of species. Finally, Section 2.4.2 describes the bed material analysis conducted to determine the potential release of sulfur from samples exposed to the aforementioned cycles in the laboratory reactor.

2.1. Measuring the Catalytic Activity of the Bed.

The development of bed catalytic activity consequent to the formation of ash layers is manifested as an intensification of a number of reactions, including cracking and reforming reactions of tar and their precursors,[41−44] reforming of light hydrocarbons,[42] and the WGS reaction.[39,42,45,46] Since the extents of these reactions tend to increase concurrently along with the bed catalytic activity (although not necessarily having the same magnitudes), the overall catalytic activity of the bed can be represented indirectly and qualitatively using a limited number of variables. In this work, two measures of the bed catalytic activity are chosen: (1) the tar yield, expressed in g/kg daf (*i.e.*, relative to the dry, ash-free fuel), which decreases with increasing bed catalytic activity in the range of temperature selected in this work; and (2) the difference in the extent of the WGS reaction relative to its equilibrium, expressed as the ratio of the quotient of reaction of the WGS reaction to its equilibrium value K_{WGS}/K_{eq}, which is expected to increase with catalytic activity and have a value of 1 at its maximum. The WGS reaction is described in reaction 1 (R1), and the expressions of the quotient of reaction K_{WGS} are given in equation 1 (eq 1), with p referring to the partial pressure of the gas components. The value of the quotient of reaction at equilibrium, K_{eq}, as a function of temperature, is given in eq 2, taken from ref 47.

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \tag{R1}$$

$$K_{WGS} = \frac{p_{H_2O} \cdot p_{CO}}{p_{H_2} \cdot p_{CO_2}} \tag{1}$$

$$\log(K_{eq}) = -2.4198 + 0.0003855 \cdot T + \frac{2180.6}{T} \tag{2}$$

One of the main goals of this paper is to show the correlation between the development of oxygen transport and the development of bed catalytic activity. However, establishing this correlation relies on an important assumption, that is, the changes in the tar yield and the K_{WGS}/K_{eq} ratio must be attributable primarily to the development of bed catalytic activity rather than to the oxygen transport itself. Otherwise, the tar yield and K_{WGS}/K_{eq} ratio cannot be used as measures of bed catalytic activity. To verify these assumptions, the tar yield and K_{WGS}/K_{eq} obtained from experiments carried out in the Chalmers gasifier with ilmenite and a manganese ore, which are two commonly used oxygen carriers, are reported in this work. These oxygen carriers are used to represent the behaviors of the two measures of bed catalytic activity when oxygen transport dominates over catalytic activity.

2.2. Chalmers DFB Gasifier.

2.2.1. Description of the Unit.

The Chalmers gasifier consists of a 12 MW_{th} circulating fluidized bed (CFB) boiler and a 2–4 MW_{th} bubbling fluidized bed gasifier connected *via* two loop seals. The CFB boiler is fed primarily with wood chips and the feeding can be complemented by wood pellets, whereas the gasifier was fed with wood pellets only for the experiments presented in this work. The raw gas from the gasifier is combusted in the boiler. The CFB boiler provides heat to the university campus where it sits and is, therefore, always operating during wintertime. Conversely, the gasifier is only operated during planned experimental campaigns. The CFB boiler is, therefore, over-dimensioned with respect to the heat demand of the gasifier. The rate of fuel feeding to the CFB boiler is about an order of magnitude higher (on a mass basis) than the fuel feeding rate to the gasifier. A detailed description of the Chalmers gasifier can be found in ref 48.

2.2.2. Gas Measurement Setup.

Raw gas is sampled from the raw gas line of the gasifier and is filtered to remove particulate matter. Two streams are then collected for analysis. The first stream is quenched with isopropanol, to condense the tar and water, and is analyzed in a micro-gas chromatography (micro-GC) Varian CP4900 gas chromatograph equipped with a PoraPLOT Q and a molecular sieve (MS) 5 Å column, using helium and argon as carrier gases, respectively. The gas species analyzed are: H_2, He, N_2, CO, O_2, CO_2,

Table 1. Variations in the Bed Temperature, Fuel Feeding Rate, and Steam−Fuel Ratio for the Six Experimental Sets[a]

set	number of experimental points	bed temperature, range (°C)	fuel feeding rate, range (kg daf/h)	steam−fuel ratio, range (kg/kg daf)
olivine set 1	9	808−819	264−273	0.83−0.94
olivine set 2	6	808−829	265−271	0.83−0.86
feldspar set 1	10	809−828	268−271	0.85−0.88
feldspar set 2	15	816−824	270−279	0.82−0.86
ilmenite	6	811−828	244−267	0.74−0.86
manganese ore	1	809	276	0.79
complete set	47	808−829	244−273	0.74−0.94

[a] The number of experimental points refers to the number of measurement points in each set, with a "point" corresponding to averaged gas and tar yields over a period of more than 20 min.

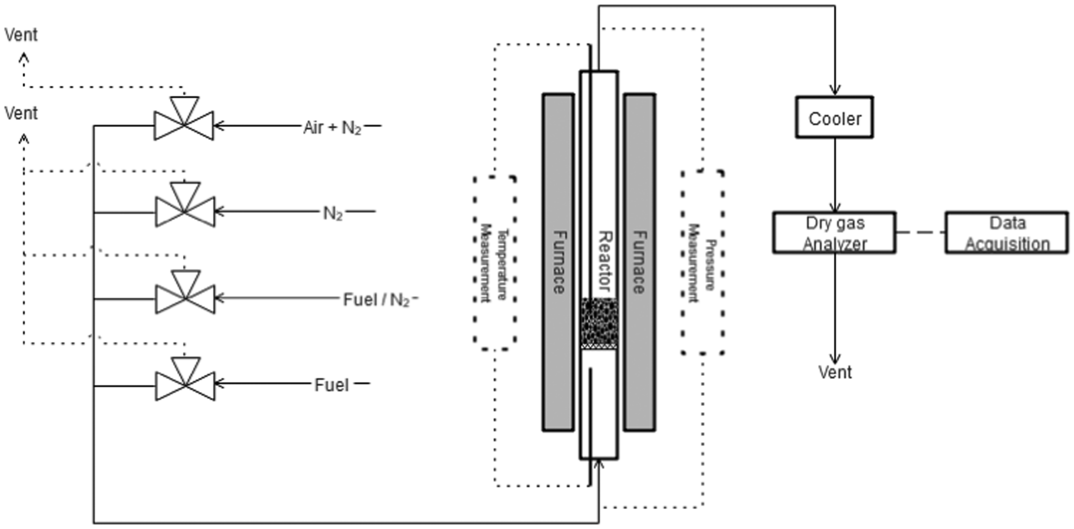

Figure 1. Schematic representation of the laboratory-scale fluidized bed reactor used for analyses of oxygen-carrying capacities in batch reactor laboratory tests in this work. Adapted with permission from ref 52. Copyright 2018, the authors.

CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, and H_2S. To obtain molar yields, in moles per kilogram of dry, ash-free (daf) fuel fed, helium is injected as a tracer in the gasifier. A sampling port prior to the quenching point allows for the sampling of tar using the solid-phase adsorption (SPA) method, as described by Israelsson et al.[49] The SPA columns used in this work consisted of an activated carbon layer followed by an aminopropyl-bonded silica layer. The adsorbed hydrocarbons are thereafter eluted and analyzed in a Bruker-430 GC equipped with a flame ionization detector. The hydrocarbons detected range from benzene to chrysene, and this range is referred to as tar in the remainder of this work.

The second raw gas sample stream is further reacted in a high-temperature reactor (HTR), wherein it is cracked down to H_2, CO, CO_2, and H_2O, at 1700 °C, as described by Israelsson et al.[50] It is then analyzed in a micro-GC similar to that used for the first sample stream, equipped with PoraPLOT U and MS 5 Å columns, with helium and argon, respectively, as carrier gases. In this work, the elemental (C, H, and O) composition of the cracked gas is compared to those of the raw gas, the fuel, and the unconverted fuel, to determine the level of oxygen transport between the boiler and the gasifier. The amount of unconverted fuel (or char) leaving the gasifier is derived by comparison of the carbon content of the raw gas given by the HTR and the carbon content of the fuel.

2.2.3. Determination of the Oxygen Transport. The oxygen transport is determined based on the elemental balance provided by the HTR, as described by Israelsson et al.,[51] and as represented in eq 3. In this equation, n_i refers to the yield of C, H, and O, the subscript fuel refers to the elemental composition of the fuel, HTR refers to the elemental composition of the gas downstream of the HTR, unc is the unconverted fuel leaving the gasifier, and tr is the transported oxygen. The first term represents the difference between the oxygen measured from the HTR and that coming from the fuel. From this term is subtracted the oxygen leaving the gasifier in the char, corresponding to the second term of the equation. The third term represents the oxygen added in the gasifier and in the HTR by reaction of water with the gas. This term is determined from the hydrogen balance, since one oxygen atom is introduced for every two hydrogen atoms reacted from the water.

$$n_{\mathrm{O,tr}} = (n_{\mathrm{O,HTR}} - n_{\mathrm{O,fuel}}) - (n_{\mathrm{C,HTR}} - n_{\mathrm{C,fuel}})\cdot\left[\frac{\mathrm{O}}{\mathrm{C}}\right]_{\mathrm{unc}} - \left(n_{\mathrm{H,HTR}} - n_{\mathrm{H,fuel}} - (n_{\mathrm{C,HTR}} - n_{\mathrm{C,fuel}})\cdot\left[\frac{\mathrm{H}}{\mathrm{C}}\right]_{\mathrm{unc}}\right)\cdot\left[\frac{\mathrm{O}}{\mathrm{H}}\right]_{\mathrm{H_2O}} \quad (3)$$

The oxygen transport defined in this way is relative to the fuel input and to the rate of solids circulation. Instead, oxygen transport relative to the bed mass is defined in moles of O_2 per kilograms of bed. This does not represent the absolute oxygen-carrying capacity of the bed, but rather the actual amount of oxygen transported and reacted by the bed, per unit mass of bed. To calculate this value, the circulation rate of the bed material must be assessed. This is done in the Chalmers gasifier by momentarily interrupting the fluidization of the second loop seal, which returns the bed material to the combustor. Thus, the pressure-drop across the combustor decreases, which can be related to the mass flow of solids in the system. This approach has been described by Larsson et al.[48] Note that, even when defined in this manner, the oxygen transport remains indirectly dependent upon the fuel flow and the rate of solids circulation, as they both affect how much oxygen is extracted from the bed material in the gasifier. Nevertheless, this represents how much oxygen is transported per unit mass of bed material for comparable conditions regarding the fuel flow and circulation rates.

2.2.4. Experimental Matrix for the Chalmers Gasifier Experiments. The development of oxygen transport in gasifier beds of olivine and feldspar is investigated based on two sets of experimental data for olivine and feldspar. In addition, as described in Section 2.1, the results for olivine and feldspar are compared with experimental data from batch reactor laboratory runs with ilmenite and manganese ore. To limit the effects seen to the development of bed catalytic activity and oxygen transport of the particles themselves rather than to varying operational conditions, the experimental points were selected within narrow ranges of temperature, fuel feeding rate and steam−fuel ratio. At a constant fuel feeding rate, the latter constrains both the ratio of steam to fuel in the gasifier and the mixing behavior of the bed. Note that the steam−fuel ratio is defined based on the total amount of steam input to the gasifier, including the part of the steam fed to the loop seals that slips to the gasifier and the steam formed from the moisture in the fuel. These two contributions do not vary between experimental points. The variations of the three aforementioned parameters are listed in Table 1. It is important to note that there are no fundamental differences between the operating ranges to which the two different sets of experiments for olivine and feldspar were subjected. Nonetheless, they are separated in this work because, as shown in Figure 2, they led to slightly different results. The differences between the experimental sets for olivine and feldspar are not reflective of different operational conditions, and explaining these differences is outside the scope of this work.

2.3. Laboratory-Scale Fluidized Bed Reactor. The laboratory fluidized bed reactor, depicted in Figure 1, is a quartz glass, tubular reactor, with an inner diameter of 22 mm. Within the reactor, there is a porous plate on which the bed material is placed. The reactor is installed in an electrically heated oven and is equipped with pressure transducers to measure pressure variations across the bed, thereby checking that the bed is well fluidized. Thermocouples are inserted in the bed and before the porous plate, to monitor the temperature. The flue gases are condensed in a cooler, prior to the gas analyzer, which is a Rosemount NGA 2000 instrument that measures the concentrations of CO, CO_2, CH_4, H_2, and O_2. A variety of gas mixtures can be fed into the reactor: air and gaseous fuels, diluted or not diluted with nitrogen. For all experiments, the reactor was heated up to 850 °C with a gas flow rate of 900 mL/min (under normal conditions of temperature and pressure). This corresponds to fluidization velocities that are 9−12 times the minimum fluidization velocity, depending on the bed material used. During heating, the bed material is fluidized with air.

In this work, feldspar samples from the Chalmers gasifier, corresponding to set 1 in Table 1, were exposed to cycling oxidation and reduction conditions, with flows of nitrogen gas flushing in between to inertize the reactor. Each cycle consisted of, in order of occurrence: (1) an inert phase with a flow of nitrogen with a duration of 300 s; (2) an oxidation phase with 5% O_2 in N_2 for 600 s; (3) a second inert phase for 300 s; and (4) a reduction phase with either 50% CO in N_2 for 40 s or syngas (50% H_2 and 50% CO) for 20 s. Hereinafter, these four phases are simply referred to as a "cycle." The level of oxygen transport was calculated by comparing the outlet and inlet concentrations of O_2 during the oxidative phase. The amount of oxygen that reacted with CO to form CO_2 was also determined. The experiments were carried out twice for a given bed material, using either CO or syngas as the reductant. This was to determine whether the presence of hydrogen during the reductive phase affected the release of volatiles species, measured by leaching of the bed samples pre- and post-exposure, as described in Section 2.4.2.

Comparisons of the levels of oxygen transport measured from the first cycle for inert and active bed materials were carried out to assess the development of oxygen transport capacity. Furthermore, the evolution of the oxygen transport with progressive cycles was followed to elucidate whether an activation process was occurring or whether species contributing to the oxygen transport were lost, which would be evidenced by an early and relatively rapid decrease in oxygen transport.

2.4. Materials. *2.4.1. Bed Materials and Fuel Compositions.* Table 2 shows the elemental compositions of the bed materials used in this work. The given compositions are those of the virgin materials, prior to their introduction into the gasifier. As the particles interact with fuel ash components their compositions diverge from that of the virgin material. Concerning olivine and feldspar, the bed material state referred to as "inert" corresponds, in this work, to bed materials that have spent a limited amount of time, typically less than 1 day, in the Chalmers gasifier. They have compositions resembling those of the corresponding virgin materials. Table 3 shows the proximate and ultimate analyses of the fuels used in the Chalmers gasifier during the experiments reported in Table 1. For wood chips, the moisture content can vary widely depending on the weather conditions, so a typical value is given. The typical ash compositions of the wood chips and wood pellets are given in Table 4.

Table 2. Elemental Compositions of the Four Bed Materials Used in This Work, in Their Virgin States (As-Received), Given in wt %

element	olivine	feldspar	ilmenite	manganese ore
Al	0.24	9.95	0.19	3.40
Si	19.49	31.55	0.19	3.72
Fe	5.18	0.08	24.48	5.15
Ti		0.01	30.57	0.23
Mn			0.82	37.73
Mg	29.91	0.02	0.60	0.25
Ca		0.86	0.01	1.88
Na		3.19		
K		6.97		0.99
Cr	0.21			
Ni	0.25			
O (balance)	44.72	47.37	43.14	46.65

Table 3. Typical Proximate and Ultimate Analyses of the Fuels Used in This Work

	wood chips	wood pellets
moisture (wt % as-received)	typically 40%	8
ash (wt % dry basis)	0.5	0.4
Cl (wt % dry basis)	<0.01	<0.01
S (wt % dry basis)	<0.02	<0.02
C (wt % dry basis)	50.2	50.5
H (wt % dry basis)	6.0	6.1
N (wt % dry basis)	0.12	0.07
O (wt % dry basis, approximate by difference)	43.0	43.0
LHV (MJ/kg, dry basis)	18.4	18.8

2.4.2. Bed Material Analysis. Bed material samples were taken from the loop seal connecting the particle distributor, which collects the bed material from the return leg of the cyclone, to the gasifier. They were analyzed both before and after their exposure to the cycles in the laboratory-scale fluidized bed reactor, as described in Section 2.3. The samples were leached with deionized water, followed by an analysis of the leachate with ion chromatography (IC) using the Dionex ICS90 system, to detect SO_4^{2-} ions. The leaching was performed with 10 mL of deionized water for 72 h for 1 g of bed material sample. The levels of leachability of species are used to study their volatile behaviors in the gasifier environment, *i.e.*, their propensities to be released from the ash layer to the gas phase. Bed material samples that contain lower levels of leachable species would likely release smaller amounts of these species in the gasifier. The aim of the analysis in this work was to investigate whether volatile sulfur

Table 4. Typical Ash Compositions of the Fuels Used in This Work

	concentration (mg/kg, dry basis)	
element	wood chips	wood pellets
Al	20	50
Si	80	150
Fe	20	30
Ti	<10	<10
Mn	70	13
Mg	230	210
Ca	1200	950
Ba	20	10
Na	40	30
K	670	460
P	80	70

species contribute to part of the oxygen transport that is potentially developed. The release of sulfur is identified based on the concentrations of SO_4^{2-} ions in the leachates. Decreases in both leachable sulfur and oxygen transport (as measured in the laboratory-scale reactor) after several cycles would support the hypothesis that the released sulfur contributed to the oxygen transport. In addition to the leaching tests, the total sulfur content of the bed particles was determined for three samples from the olivine set 1 (see Table 1), using inductively coupled plasma optical emission spectrometry following the total dissolution of the bed material, as described previously.[53] This gives an estimate of the maximum contribution of sulfur to the oxygen transport, including the sulfur that is not released to the gas phase and the sulfur that is released but not measured.

3. RESULTS AND DISCUSSION

3.1. Concomitant Development of Oxygen Transport and Bed Catalytic Activity in Olivine and Feldspar Beds.

The oxygen transport levels as a function of the two measures of bed catalytic activity (tar yield and K_{WGS}/K_{eq}), as defined in Section 2.1, are shown in Figure 2 for the four sets of olivine and feldspar (a and b), compared with the oxygen transport measured in the case of ilmenite and manganese oxygen

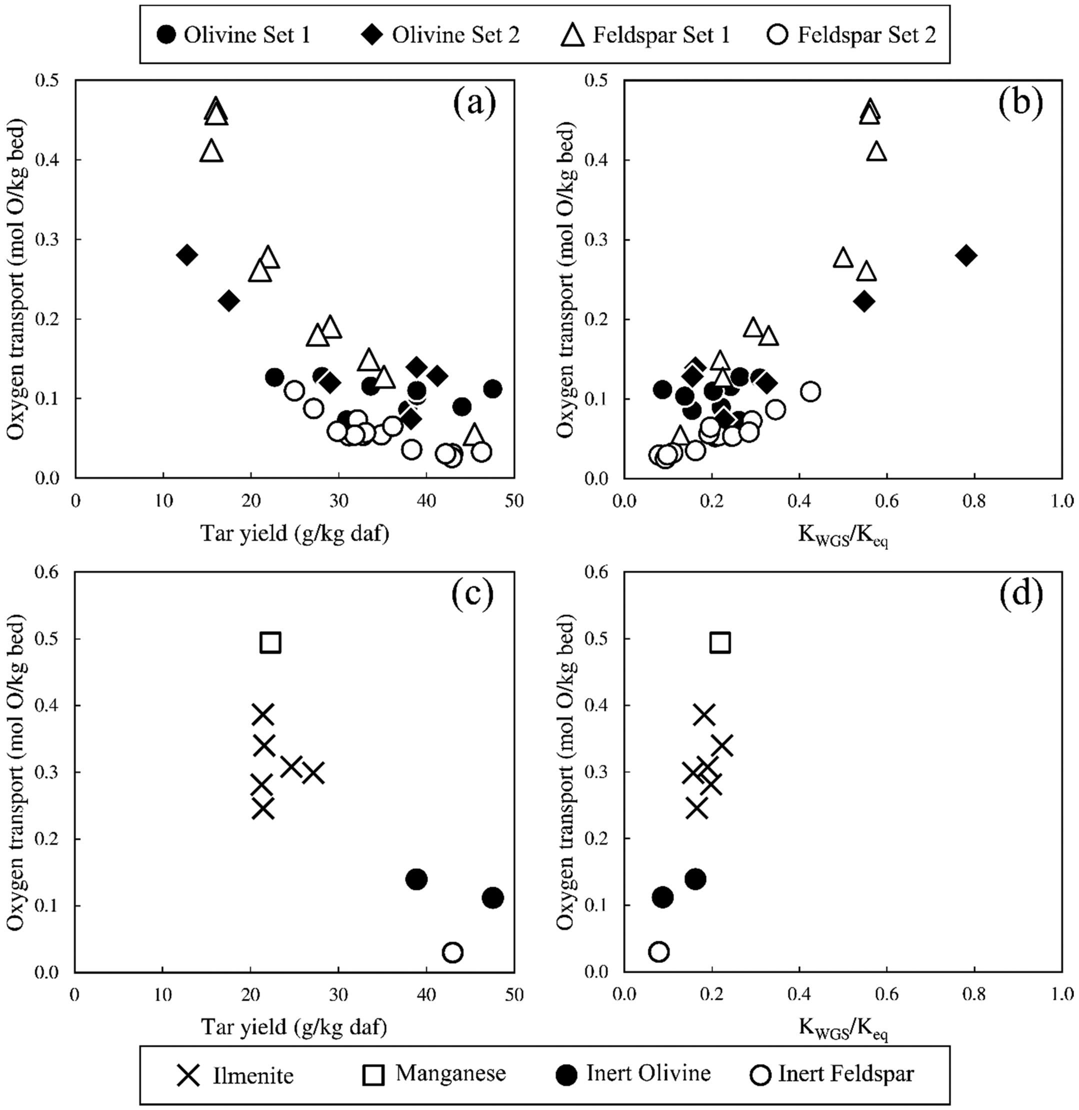

Figure 2. Oxygen transport levels deduced from the elemental balance over the Chalmers gasifier, as a function of the total tar yield (a, c) and the ratio of the reaction quotient of the WGS to its equilibrium value (b, d). Shown are the levels of oxygen transport in relation to these two measures of activity for: the olivine and feldspar sets (a, b) and for the ilmenite and manganese sets (c, d). In panels (c) and (d), the values for the inert olivine and feldspar are shown for reference.

carriers (c and d). Figure 3 shows the tar yield in relation to the K_{WGS}/K_{eq} ratio. From Figure 2d, it is apparent that the oxygen transport has no significant impact on the value of the K_{WGS}/K_{eq} ratio. Although the K_{WGS}/K_{eq} ratio is slightly increased compared with the values for inert olivine and feldspar, it remains low compared with the values obtained with active olivine and feldspar, as shown in Figure 2b.

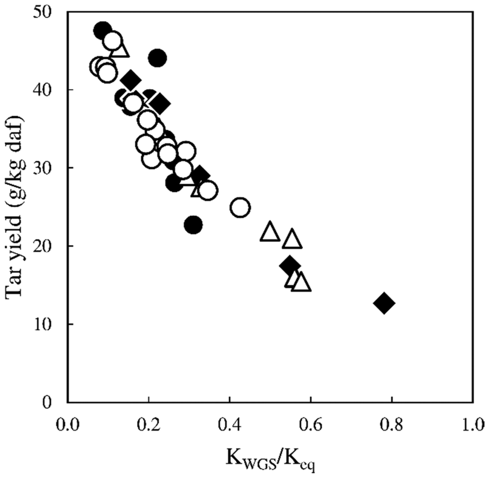

Figure 3. Correlation between the ratio of the quotient of reaction of the WGS to its equilibrium value, *i.e.*, K_{WGS}/K_{eq}, and the tar yield, expressed in g/kg daf, for the different bed material sets.

Regarding the decrease in tar yield, it is not possible to attribute it predominantly to the increase in bed material catalytic activity based solely on the data in Figure 2a,c. Indeed, beyond a certain level of oxygen transport, the oxidation of tar may be limited by contacts between the oxygen carrier and volatile hydrocarbons. This would explain the observed lack of correlation between oxygen transport and tar yield for ilmenite and manganese, and makes it impossible to exclude a significant contribution of oxygen transport to the decreased tar yield seen with olivine and feldspar in Figure 2a,c. However, the contribution of the oxygen transport can be shown to be negligible, based on the results in Figure 3, which show a near-perfect correlation between the tar yield and the K_{WGS}/K_{eq} ratio. Given the lack of impact that the oxygen transport has on the K_{WGS}/K_{eq} ratio, if the oxygen transport had a marked effect on the decrease in tar yield, no correlations would be observed for the two measures of bed catalytic activity. Therefore, it can be concluded from the results in Figures 2 and 3 that it is the development of the bed catalytic activity rather than the development of oxygen transport that is primarily responsible for the observed changes in the two measures (tar yield and K_{WGS}/K_{eq}) used to evaluate the bed material catalytic activity. From this, the development of oxygen transport capacities by the olivine and feldspar beds concomitant with the development of their catalytic activities is demonstrated.

The development of oxygen transport by active olivine and feldspar was confirmed by subjecting the inert and active materials to a reducing atmosphere in the laboratory-scale fluidized bed reactor. In this case, CO was used as the reductant. The results are shown in Figure 4 for olivine set 2 and feldspar set 1. A significant increase in oxygen-carrying capacity is noted for both materials. It is worth noting that olivine has some oxygen-carrying capacity even in its inert state, which is likely related to its iron content.

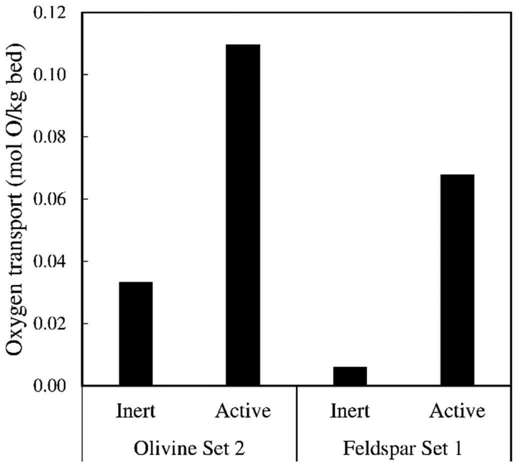

Figure 4. Oxygen-carrying capacities of inert and active olivine and feldspar, as measured in samples from the laboratory-scale fluidized bed reactor, using CO as reductant.

3.2. Contribution of Volatiles Ash Species to the Oxygen Transport.

The ash-induced oxygen transport can be linked to both ash species that are permanently incorporated in the ash layer and ash species that are released from the layer upon changing their oxidation state. In this section, the contributions to the oxygen transport of ash species present in the ash layer of bed particles and released to the gas phase in the gasifier, simply referred to as "volatile species", are investigated. The investigation was carried out in the Chalmers gasifier and consisted of replacing part of the aged bed with fresh bed material. This was done for the feldspar set 2 experiments, as depicted in Figure 5, which shows the levels of oxygen transport measured in the Chalmers gasifier in relation to the measured tar yield. The aging of feldspar from day 2 to day 7 was followed by the replacement of 20−33% of the bed inventory with virgin feldspar. Comparing the "day 7" and "day

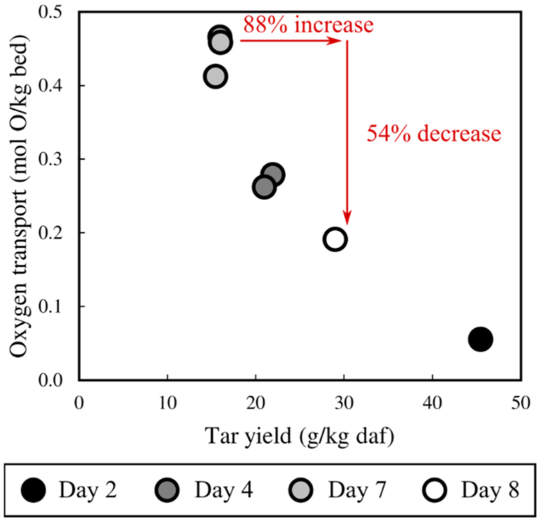

Figure 5. Oxygen transport of feldspar measured from the elemental balance over the Chalmers gasifier plotted as a function of the total tar yield as a measure of catalytic activity. Between the series day 7 and day 8, an estimated 20−33% of the bed inventory was replaced with virgin feldspar.

8" series, it appears that both the oxygen transport and tar yield varied by more than 50%, even though less than half of the bed was replaced with virgin particles. This disproportional effect indicates that the simple dilution of the bed with fresh particles, which are considered to be inactive with respect to catalytic and oxygen-carrying properties, is not sufficient to explain the measured effect. A possible explanation is, therefore, that the aged feldspar particles release volatile species within the gasifier, and these contribute to the measured oxygen transport, with the introduction of virgin feldspar creating a sink for these species. This type of effect has been proposed for the disproportional loss of catalytic activity by olivine when an inert bed (silica sand) replaces part of the aged olivine. Potassium is one of the suggested volatile species captured by the inert particles.[33]

The contribution of volatile species to the development of the oxygen transport was also investigated by subjecting feldspar particles sampled from the Chalmers gasifier to cycles of oxidation and reduction, as described in Section 2.3. Figure 6 shows the evolution of the oxygen transport, determined from the difference in O_2 concentration between the inlet and outlet gas flows of the reactor, for inert and active feldspar, with the latter being cycled with either CO or syngas. The results for the active feldspar reduced with CO do not show the pattern that would be expected if volatiles species were progressively released. Instead, an activation process is observed, whereby the oxygen transport increases from 0.09 to 0.27 mol O/kg bed. Conversely, when reduced with syngas, the active feldspar shows a decrease in oxygen transport along the cycles, which is consistent with the expected loss of volatiles species with increasing number of cycles. The oxygen transport level in the syngas-reduced case starts at a much higher value than for the CO-reduced feldspar, at 0.37 mol O/kg bed, and drops to 0.30 mol O/kg bed after 11 cycles. The fact that the oxygen transport level is higher from the first cycle with syngas and the lack of decrease in the CO-reduced case indicate that hydrogen atoms are required for those species to be released. This is in line with the hypothesis that sulfur is involved, as sulfur in the gasifier is measured as H_2S. It should be noted that the activation seen in the CO-reduced feldspar case may also occur in the syngas-reduced case such that the release of volatiles may be greater than is suggested by Figure 6. If the activation is of the same magnitude, then the decrease in oxygen transport due to the release of volatile species would be 0.25 mol O/kg bed.

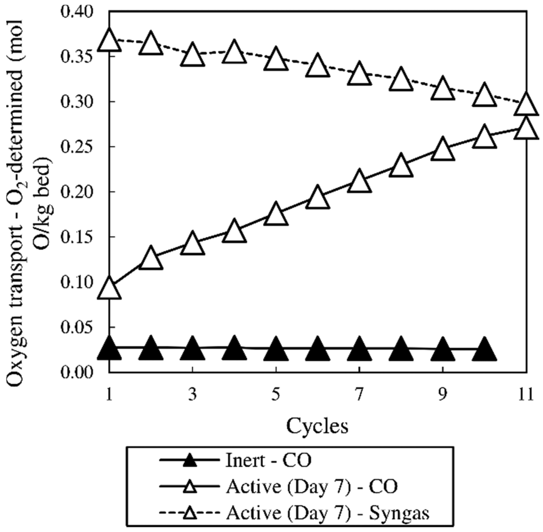

Figure 6. Evolution of the oxygen transport (mol O/kg bed), as determined from the O_2 concentration, with increasing number of cycles. Two samples of the active (day 7) feldspar set 1 were cycled, with changes to the reducing gas: one with CO, and the other with syngas.

3.3. Contribution of Sulfur to the Oxygen Transport.

The oxygen transport associated with the release of sulfur to the gas phase in the Chalmers gasifier, assuming four oxygen atoms per sulfur atom, is shown in Figure 7 against the total oxygen transport for olivine and feldspar. Figure 7a shows these values in absolute terms (in mol O/kg bed), whereas Figure 7b shows the values relative to the total oxygen transport. From Figure 7a, there is a correlation between the oxygen transport associated with volatile sulfur (measured as H_2S) and the total oxygen transport developed by the feldspar particles, although no such correlation can be established for the olivine particles. Moreover, there is no correlation between the fraction of the measured oxygen transport that originates from sulfur and the oxygen transport itself, as shown in Figure 7b. Note that, since the total sulfur content of the feldspar particles was not measured, a correlation between the potential contribution of the total sulfur (volatile and bound to particles) and the total oxygen transport cannot be excluded.

The correlation seen between the oxygen transport by volatile sulfur and the total oxygen transport (Figure 7a) on the one hand, and the correlation between oxygen transport and bed catalytic activity (established in Figure 2) on the other hand, together support the notion that the mechanism underlying the development of the catalytic activity toward tar reactions and the mechanism behind the development of oxygen transport *via* volatile species are similar. This suggests that potassium, an active volatile species in the reaction of tar and its precursors, is released by the bed along with sulfur and oxygen, as has been proposed by Marinkovic et al.[33] The lack of a correlation for olivine is, nonetheless, surprising, given that it was also found to accumulate sulfur. However, part of the sulfur might remain on the bed particles and still be involved in oxygen transport, for instance through $CaS-CaSO_4$ cycles,[40] which would result in the transport of four oxygen atoms per atom of sulfur bound to calcium.

To account for this, the total sulfur content of three olivine samples was determined and the corresponding oxygen transport is shown in Figure 7, as the series Olivine Set 2 - Potential transport total S. Note that the values for that series are divided by 10 in Figure 7a. When one accounts for all of the sulfur the potential for oxygen transport is about an order of magnitude greater than the level of oxygen transport based on the sulfur found in the form of H_2S in the gas phase. The latter corresponds to only a small fraction (up to 16%) of the total oxygen transport measured, as shown in Figure 7b. It is apparent that another mechanism is involved in the development of oxygen transport by olivine, which most likely relates to the migration of iron to the surface, which has been shown by Faust et al. to occur even in ash-layered olivine.[30,54]

The role of volatile sulfur in the development of oxygen transport by feldspar is confirmed by looking at the effect of the addition of elemental sulfur to the DFB system. Results from the addition of about 2.3 kg of elemental sulfur to the combustor of the Chalmers gasifier with feldspar as the bed material were reported by Berdugo Vilches[55] and are shown in

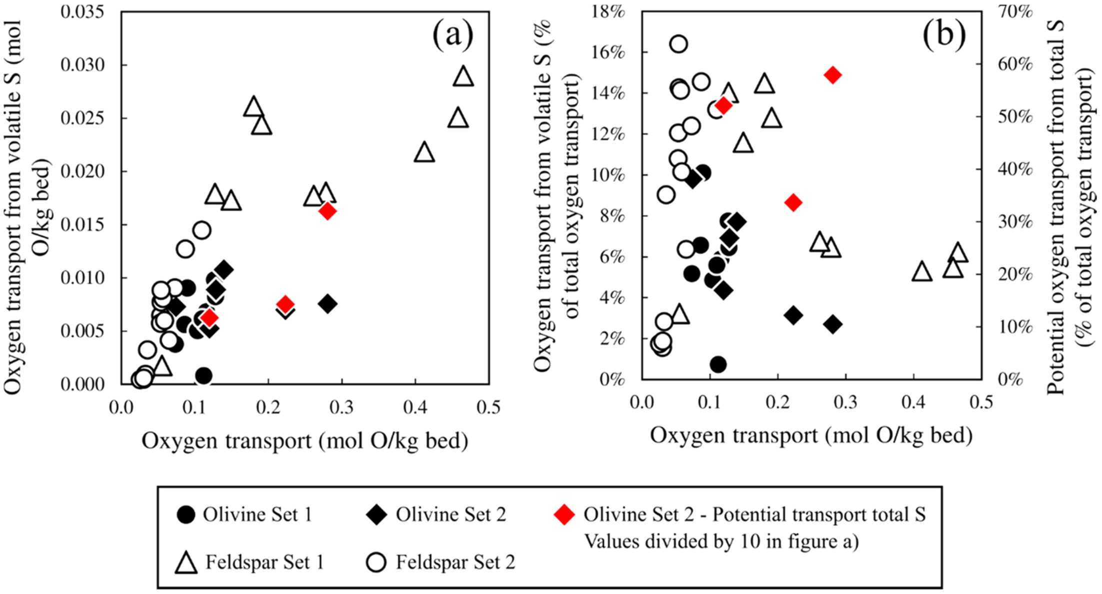

Figure 7. Oxygen transport from sulfur (assuming sulfate SO_4^{2-} involvement, for which four atoms of oxygen are bound per atom of sulfur), as determined from the H_2S yield in the raw gas, *versus* the total oxygen transport, for feldspar and olivine. (a) Absolute oxygen transport by sulfur, in mol O/kg bed; (b) this value relative to the total oxygen transport measured. The series "Olivine Set 2 - Potential transport total S" represents the oxygen transport based on the sulfur measured by elemental analysis of the olivine particles. The values for that series are divided by 10 in (a). Note that the first value for oxygen transport from sulfur for that series (corresponding to the lowest total oxygen transport) corresponds to the detection limit of the analysis method.

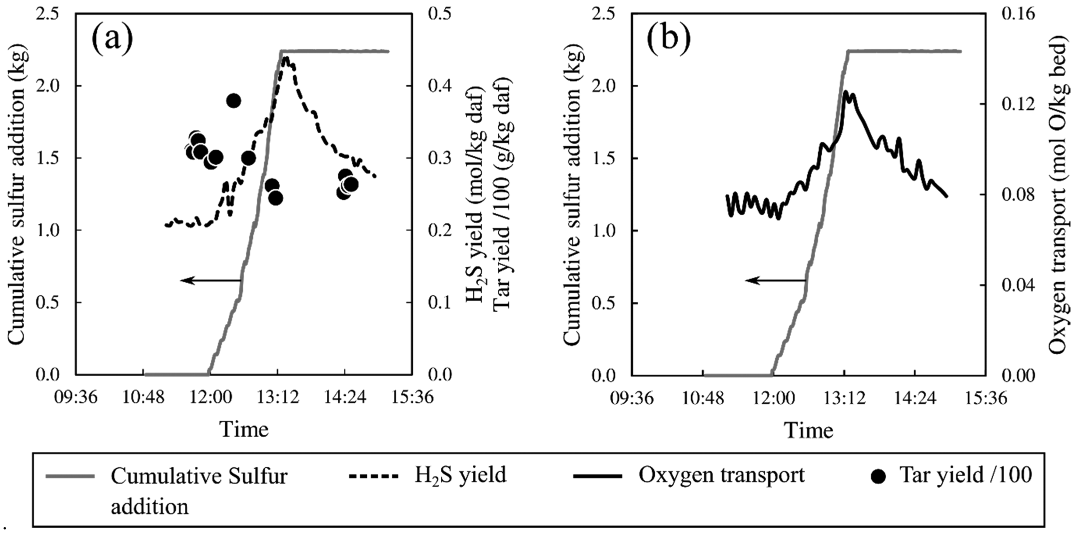

Figure 8. Effects of the addition of elemental sulfur to the Chalmers gasifier on the H_2S yield, tar yield, and oxygen transport. The H_2S and tar yields are shown in (a), with the values for the latter being divided by 100 to fit on the same axis. The oxygen transport is shown in (b). The values for the "cumulative sulfur addition" series are shown on the left *y*-axis, and the values for the other series are shown on the right *y*-axis. Adapted with permission from ref 55. Copyright 2018, the author.

adapted form in Figure 8. As shown in Figure 8a, as sulfur is added to the combustor, the H_2S yield in the gasifier increases, indicating the net transport of sulfur by the bed material. Along with the increase in H_2S yield, the oxygen transport from the combustor to the gasifier increases, as shown in Figure 8b. When the sulfur addition is complete, the H_2S yield decreases and so does the oxygen transport, reverting to a level close to its value prior to sulfur addition. This shows that the species that led to the increase in oxygen transport have been lost, confirming the contribution of volatile sulfur species. As is evident in Figure 8a, the tar yield also slightly decreases with the addition of elemental sulfur, which further strengthens the hypothesis that the release of H_2S in the gasifier is accompanied by the release of catalytic, potassium-rich compounds.

In laboratory-scale experiments, the contributions of sulfur species to the development of oxygen transport by olivine and feldspar were further investigated by subjecting the two active feldspar samples that were exposed to cycles in the laboratory reactor (see Figure 6) to leaching tests, whereby the SO_4^{2-} concentration in the leachate was measured. The results are shown in Figure 9. The active feldspar sample prior to cycling was also analyzed. The results show that there is no difference in the SO_4^{2-} concentration in the leachate between the

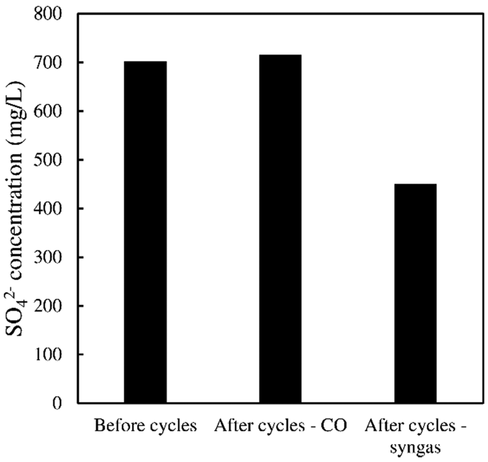

Figure 9. Concentrations of SO_4^{2-} ions (in mg/L) measured in the leachate, and potential oxygen transport associated with the sulfur, in mol O/kg bed, assuming four atoms of oxygen are transported by an atom of sulfur. The values shown are for the leachate from feldspar set 1, corresponding to day 7, prior to oxidation−reduction cycles in the laboratory-scale reactor, and after these cycles, carried out with either CO or syngas as the reductant.

material prior to cycling and after cycling with CO as the sole reductant. This confirms that the release of sulfur to the gas phase and its potential oxygen transport do not occur with CO as the sole reductant, which is consistent with the lack of decrease in oxygen transport with increasing number of cycles, as seen in Figure 6. Additional tests and spectroscopic analyses of the material after leaching could further support the contribution of sulfur to the oxygen transport, but would not provide new information, as an inhibition of the oxygen transport cannot be attributed solely to the release of sulfur, since other volatile species may have been lost.

Based on the leaching test, the oxygen transport associated with the sulfur released over the 11 cycles for the syngas-reduced feldspar corresponds to an estimated 0.11 mol O/kg bed. This value can be compared to the decrease in oxygen transport determined for the same case from the gas measurement, which is estimated to be 0.07 mol O/kg bed. The magnitudes of these two values are comparable, as expected if the decomposition of sulfur compounds into volatile species is responsible for a share of the oxygen transport observed with feldspar.

Nonetheless, the oxygen transport associated with volatile sulfur is greater than the decrease measured in the syngas-reduced feldspar case (0.07 mol O/kg bed), although it is lower than the decrease would be if the activation seen with the CO-reduced feldspar is occurring (0.25 mol O/kg bed). Furthermore, the difference in oxygen transport between the syngas-reduced and CO-reduced cases is 0.14 mol O/kg bed in the first cycle, which is much greater than what could originate from the sulfur contribution, which is occurring over 11 cycles. A number of reasons can be put forward to explain this phenomenon. First, the hydrogen in the syngas may be able to reduce nonvolatile oxygen-carrying structures that CO cannot reduce. Second, it might be that the activation seen in the CO-reduced case is not occurring with the same magnitude or at all in the syngas case. This is supported by the fact that the amount of oxygen from the bed that reacted with CO to form CO_2 decreased with each cycle in the case of the syngas-reduced feldspar. Third, the leaching is carried out over several hours with complete wetting of the particle surface, whereas in the laboratory reactor, exposure is in the order of seconds and the surface is not entirely in contact with water molecules, which may result in an overestimation of the amount of releasable sulfur. On the other hand, the high temperatures in the laboratory reactor greatly increase the rate of reactions and mass transfer phenomena. Furthermore, hydrogen (in H_2 or radical form) may be more efficient than H_2O at releasing sulfur from the bed in the form of H_2S, which would lead to an underestimation of the amount of releasable sulfur.

Besides H_2S, sulfur may be released as part of other volatile species that are not measured but that can contribute to the measured oxygen transport. This is suggested by the results shown in Figure 8. The change in oxygen transport cannot be explained solely by the change in measured H_2S yield, which would only explain about 20% of the change. This indicates that other sulfur-containing volatile species are released in the gasifier. This hypothesis is supported by the results obtained from the partial regeneration of the feldspar bed (see Figure 5). Figure 10 shows the H_2S yield for the feldspar set 1 experiment, corresponding to the same points as shown in Figure 5. The H_2S yield does not show the same disproportional—higher—decrease than is seen for either the tar yield or the oxygen transport. Instead, the decrease in H_2S yield is consistent with or even lower than what would be expected from dilution. Nevertheless, the disproportional decrease in oxygen transport seen in Figure 5 strongly suggests that volatile species are captured by the introduced virgin material and, thus, cannot contribute to the oxygen transport. Consequently, it is likely that other volatile species are involved, which may or may not contain sulfur. The results of this work do not shed light on the nature of those species.

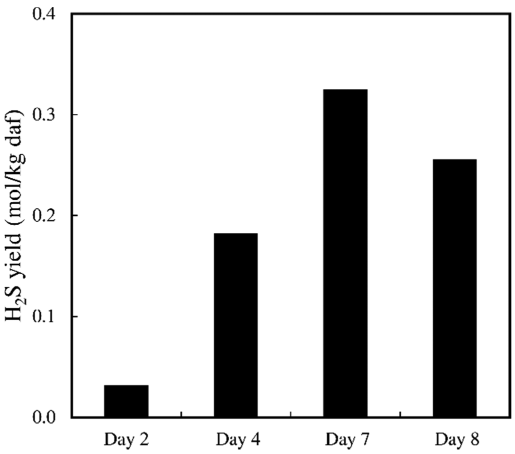

Figure 10. H_2S yield obtained with feldspar set 1, corresponding to the same experimental points as in Figure 5. Between day 7 and day 8, an estimated 20−33% of the bed inventory was replaced with virgin feldspar.

4. GENERAL DISCUSSION

The results of this work support the hypothesis that sulfur is implicated in the development of oxygen transport in feldspar. However, the results are inconclusive in the case of olivine. For feldspar, the results show that sulfur is released when hydrogen is present in the gas phase, and, concomitant with the release of this sulfur, the oxygen transport capacity of the feldspar decreases. Furthermore, the release of H_2S by feldspar to the gas phase is correlated with the development of oxygen transport (see Figure 7) and, consequently, with the development of catalytic activity, as demonstrated in this work. As described in the introduction, sulfur likely binds to the bed particles in the form of K_2SO_4 in the boiler. As sulfur is released to the gas phase in the gasifier, it seems likely that potassium is also released, given its propensity to form volatile compounds. The presence of potassium in the gas phase may contribute to catalytic activity toward a number of reactions. Therefore, the uptake and release of potassium and sulfur may contribute to both the bed catalytic activity and oxygen transport in the gasifier, with important consequences for the raw gas composition and quality. The hypothesis that sulfur and potassium are bound and released together is supported by the correlated response of the oxygen transport and catalytic activity to a replacement of part of the bed with a fresh one and to the addition of sulfur to the bed, as shown in Figures 5 and 8, respectively. The results also suggest the involvement of other volatile species, which may or may not contain sulfur, in the transport of oxygen. This warrants further research on the contributions of the bed material to gas-phase phenomena.

Although additional work is needed to confirm the role of sulfur and, more generally, the roles of volatile species in the development of oxygen transport, the present study clearly shows that oxygen transport does develop along with catalytic activity in the cases of both olivine and feldspar. This has important consequences for the raw gas composition and DFB process operation. As shown in Figure 2, the oxygen transport levels attained using olivine or feldspar are comparable to the levels measured with the use of pure ilmenite and manganese in the Chalmers gasifier. Although mixing most likely limited the level of oxygen transport in the cases of the pure oxygen carriers, this nonetheless shows that high levels of oxygen transport can be reached with bed materials that have zero or limited intrinsic oxygen transport capabilities, even with relatively ash-poor fuels such as wood chips and wood pellets. These high levels of oxygen transport lead to high CO_2 yields, thereby decreasing the energy content of the gas. The process effectively shifts toward a CLG process, since oxidation of the bed material in the combustor will contribute to covering the heat demand. This means that as oxygen transport develops less char needs to be combusted, so more is available for gasification. Furthermore, oxygen carriers are known to increase the gasification rate by removing its inhibitors around char particles.[56−58] This further contributes to increasing the gasification rate. In contrast, intensification of the gasification reactions, as well as of the reforming and cracking reactions, due to the development of the catalytic activity entails an increase in the heat demand.

Overall, the development of oxygen transport along with catalytic activity can alter the balance of the DFB process. Control of the process can become challenging due to the competition between char combustion and bed oxidation for oxygen in the combustor. Finally, these changes affect the process beyond the DFB unit, in that as the gas composition changes, the downstream separation and synthesis steps are affected. Moreover, the transfer of CO_2 from the combustor to the gasifier, due to the contribution of the bed material itself to the heat production, may lead to a flue gas from which it is more challenging to capture CO_2, while the opposite is true for the raw gas. In a future context in which the recovery and valorization of as many carbon atoms as possible will be essential, these issues will be critical. For all of these reasons, the interaction of the bed material with the fuel ash should be carefully considered, not only with respect to the development of catalytic activity, but also to the development of oxygen transport. Forced activations of the bed using additives, or even recirculation of streams that are rich in ash components, such as the flue gas and raw gas fly ash, should be undertaken with care, so as to avoid dramatically altering the behavior of the bed material.

As mentioned in Section 2.2.1, the design of the Chalmers DFB gasifier has some features that would not be seen in a commercial unit. The CFB combustor is over-dimensioned with respect to the heat demand of the gasifier and the raw gas is burnt in the combustor, which means that recirculation of raw gas fly ash is occurring continuously and is unavoidable. These peculiarities have two main consequences. First, the ash input is dominated by the CFB side. Given that the compositions of the ashes from wood chips and wood pellets are similar, this aspect has no major consequences. Second, the ash input to the circulating bed is greater than it would be in a standalone DFB gasifier, relative to the thermal power input of the gasifier. This means that the interactions between the ash components and the bed material are likely intensified in the Chalmers gasifier. It follows that the bed will reach a given level of interaction with ash components more rapidly in the Chalmers gasifier than it would in a commercial DFB system. Still, after it has spent sufficient time in the system, the bed will have a comparably high level of interaction with the ash. In conclusion, the peculiarities of the Chalmers gasifier do not impact the relevance for a commercial DFB gasifier of the results presented in this work.

5. CONCLUSIONS

The present work verifies that, along with the known development of a catalytic activity by interaction with the fuel ash during DFB gasification of woody biomass, bed materials can also develop an oxygen transport capability, a phenomenon previously reported in a few studies but which had not been investigated. This development of an oxygen transport capacity is verified for olivine and feldspar, *i.e.*, two bed materials with a limited and no initial oxygen transport capacity, respectively. This is shown to correlate clearly with the evolution of the catalytic activity of the bed toward a number of reactions, notably those that reduce the amount of tar. Experiments conducted at the semi-industrial scale and laboratory scale reveal the contributions to oxygen transport to the gasifier of species released by the bed material to the gas phase.

Our results support the hypothesis that sulfur is involved in the development of oxygen transport. Based on leaching tests and on the H_2S yields measured in the Chalmers gasifier, the release of volatile sulfur from the bed is a plausible contributor to the development of oxygen transport. The results suggest that the interactions of the bed with the fuel ash should be carefully considered, beyond the overall positive aspect of development of catalytic activity. As oxygen transport emerges, the carbon and energy balance of the DFB gasifier and that of the entire plant are changed, and this requires careful consideration. With this in mind, the application of additives to the bed, especially with the aim of enhancing its activation, may lead to significant oxygen transport and, thereby, a substantial shift in the operation of the whole plant.

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Notes

The authors declare no competing financial interest.

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