RECIRCULATION OF REACTIVE FINES – AN OPTIMIZATION STRATEGY FOR EXISTING DUAL FLUIDIZED BED GASIFICATION SYSTEMS

Sébastien Pissot, Teresa Berdugo Vilches, Henrik Thunman, Martin Seemann
Division of Energy Technology, Chalmers University of Technology
SE-412 96 Göteborg, Sweden

ABSTRACT: In industrial dual fluidized bed gasifiers, flue gas and producer gas ashes are generally re-injected in the system with the aim of recovering bed material and unconverted carbon. The impact of such recirculation on the gas quality has however not been investigated before. Some of the ash components found in these fly ashes are known to positively affect the gas composition, char gasification and tar content of the producer gas and as a consequence, their recirculation is expected to impact these parameters. In order to investigate these effects, recirculation of coarse fly ashes was carried out in the Chalmers 2-4MWth gasifier, by first artificially creating a substantial amount of fly ashes by injection of fine particles of untreated olivine. The fly ashes collected were recirculated at several occasion and the gas quality assessed. It was found that recirculation of reactive fly ashes enhances the gas quality, in particular in term of tar concentration. This improvement was also observed to be lasting, suggesting change in the bed material composition. Very high bed activity was reached after two days during which only the combustor was functioning, and this despite an extensive regeneration of the bed.
Keywords: gasification, ashes, dual fluidized bed, tar, syngas

1 INTRODUCTION

As a potentially carbon neutral and renewable energy source, biomass gasification is an attractive fuel conversion process. The producer gas resulting from the gasification reactions can be used for power production or synthesis of fuel.

Dual fluidized bed (DFB) gasification is a technology which presents a number of advantages compared with direct gasification. In the latter, the heat required for the gasification reactions is produced by partial combustion of the fuel, which results in dilution of the produced gas with flue gases, and reduce the gasification efficiency. To avoid this issue, in a DFB gasification plant, the required heat is provided by a bed material which gains its heat from combustion of the unconverted char from the gasifier in a combustor, and circulates between these two units. The GoBiGas gasification plant in Göteborg [1], Sweden is such a DFB gasifier, based on the design of the Güssing plant in Austria.

The applicability and sustained operation of a gasifier is mainly limited by the amount of tar produced and the cost of cleaning the gas from them. In order to improve the gas quality and reduced the tar concentration, catalytic active bed material has been found as an effective solution [2], [3].

Olivine is a catalytic bed material which is used in existing pilot and demonstration DFB gasification plant and whose catalytic activity has been extensively investigated [4]–[6].

In the DFB system, ash component released by the fuel have been found to interact with the bed material and lead to increased gas quality [4], [7]. It was shown that an activation process occurs, during which the gas quality increase could be linked to ash layer formation on the olivine surface.

As the ash layers greatly impact the gas quality, the mechanisms by which they are formed and evolve with time spent in the system is of extreme interest. Not surprisingly, this has sparked a lot of research in the recent years [7]–[9].

The ash components aforementioned include mainly Ca, K, Si, Mg, P and Mn. Of particular interest in these ash species are alkali compounds, which are known to catalyze char gasification [10] and gas phase reactions such as the water gas shift (WGS), but also are active towards tar conversion reactions [2].

The ash components in the fuel are released during the breakdown of the char matrix and part of them are entrained as particles by the gasification medium, in this case steam in the gasifier and air in the combustor. Some of these ash components, in particular alkali, can be vaporized and condense in the convection path downstream of the combustor. In a DFB plant such as GoBiGas, the flue gas ashes, meaning the ashes from the combustor side, are then collected from the bottom of the reversing chambers of the convection path, or trapped in the following bag house filter. The raw gas ashes from the gasifier are collected in a filter as well.

In addition to species from the fuel, the fly ashes (both raw gas and flue gas sides) also contain a substantial amount of entrained and attrited bed material. As a consequence, both raw and flue gas fly ashes contain valuable components [11].

In GoBiGas, recirculation of raw gas fly ashes to the boiler and coarse flue gas ashes to the gasifier is performed with the aim of recovering unconverted carbon and entrained bed material, thus increasing the efficiency of the process. However, the impact of these recirculation on gas quality, in particular tar content, has not been explored. As these fly ashes are rich in ash components, it can be expected that the redistribution of these species will impact the system. Recirculation of ashes has been studied in the Güssing DFB plant [11] with the aim of studying the effect on slagging, fouling and agglomeration. Although the associated accumulation of catalytic substances in the system was mentioned, the effect on the gas quality was not the focus.

In order to investigate these aspects, an experimental reproduction of the ash recirculation loop of the GoBiGas gasifier was conducted in the Chalmers 2-4 MW_{th} gasifier, starting with the artificial production of fly ashes by injecting untreated olivine particles in a fine fraction, hereinafter referred to as “olivine fines”.

2 EXPERIMENTAL

The experimental campaign was conducted in the Chalmers DFB gasifier, which consists of a 12 MW_{th} circulating fluidized bed boiler and a 2-4 MW_{th} bubbling bed gasifier, as shown in Figure 1. The bed material circulates between these two units without allowing bypass of the gas between the reactors thanks to two loop seals. Extensive details on the unit can be found elsewhere [12]. As the cyclone (4) is designed for small particle sizes, the Chalmers' gasifier does not have an ash recirculation under usual operation. However, coarser fly ashes can be collected from the secondary cyclone (6) while the finest fraction is collected in the baghouse filter (7).

The Chalmers' gasifier presents at least two notable differences compared with an industrial DFB plant. The raw gas and ashes it carries are directly returned to the combustor side where they are combusted. This imitates the recirculation of raw gas ash in the GoBiGas plant, with the distinction that the ash cannot be collected. Furthermore, given that the plant is used to provide heat to the campus, an additional feeding of fuel is needed to the boiler side. Woodchips are fed to the boiler whereas wood pellets are fed to the gasifier.

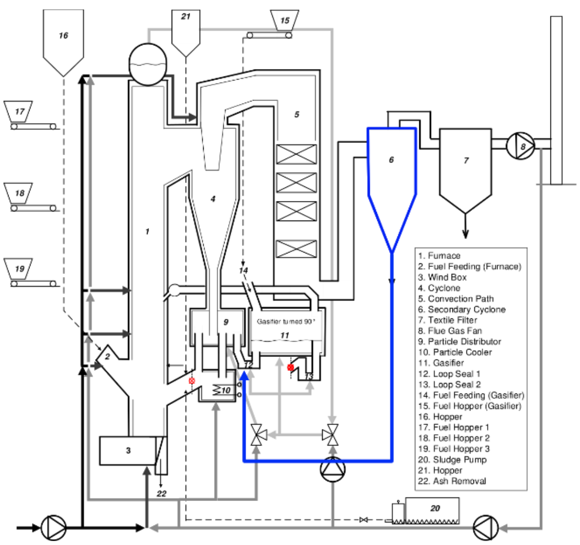

Figure 1: Layout of the Chalmers gasifier.

A fine fraction of untreated olivine was injected through loop seal 1 into the gasifier in order to "artificially" produce fly ashes which were then separated by the secondary cyclone (6), collected in the ash container and recirculated through the same line as the fines. This is indicated by the blue arrow in Figure 1, with the secondary cyclone contoured in blue as well. Moreover, fly ashes deposited on the heat exchange surfaces of the convection path (5) were partially blown out by steam and collected in the secondary cyclone tank as well. Both type of ashes, namely those collected before and after this steam blowing operation, were sampled separately. The finer fraction of fly ashes trapped by the bag house filter were neither collected nor circulated.

The olivine fines injected have a Sauter mean diameter of 94µm based on the supplier specifications and the bed material has an as-received Sauter mean diameter of 266µm.

The raw gas composition is measured by mean of a slip-stream of raw gas which is filtered, cooled and cleaned of its tar using isopropanol as a scrubbing liquid. The cold gas is analyzed in a micro-Gas chromatograph Varian model CP4900 and gas compositions are determined by averaging the value over a stable window of operation of at least 30 minutes. The tar fraction is sampled with SPA (Solid Phase Adsorption) columns fitted with an amine adsorbent and active carbon. The tar sampling point is located before the isopropanol scrubber. The columns content is then eluated and the resulting solution is analyzed in a Bruker GC-430 gas chromatograph. Details of the solid phase adsorption method are found in [13].

Injection of olivine fines and recirculation of the ashes collected thereafter, were carried out during the first day of the experimental campaign. Then a second recirculation was performed on the next day with the fly ashes collected from the first recirculation. Additionally, a measurement was carried out 3 days later, with a 2 days period during which only the boiler was fed with fuel while the gasifier was fluidized with combustion flue gases. It should be noted that this is also done during the nights between experimental days.

Between cases I and II, 610 kg of fresh olivine fines have been added to the system, then approximately 216 kg of coarse fly ashes were collected over a period of 4 hours, ending with a steam blowing of the convection path. The collection of coarse fly ashes begins when the injection stats. 200 kg of these fly ashes were then recirculated and the resulting coarse fly ashes collected during 2 hours until steam blowing. From this recirculation, 160 kg were obtained and 130 kg were recirculated on the second day. The amount of material injected and collected from the secondary cyclone and the duration of these operations is summarized in Table 1. The collection during the second circulation was interrupted directly when the injection stopped, and no steam blowing was performed. As such, the amount collected and the duration of this collection are not comparable with the two preceding operations.

Table 1: Amount and duration of injection and collection of olivine fines and coarse fly ashes.

Operation	Fines injection	1st recirculation	2nd recirculation
Material injected (kg)	610	200	130
Material collected (kg)	216	160	?
Injection duration (min)	194	68	64
Collection duration (min)	240	133	-

In Table 2, each case refers to a stable measurement, however it should be noted that case IV here represents a measurement in the morning whereas the second recirculation was performed on the evening. The gasification temperature is also indicated in Table 2 to show that comparable temperatures were used. Fuel feeding rate and fluidization levels were also comparable for these five gas measurement cases.

Table 2: Description of the measurement cases

	Operation	Gasifier bed temperature (°C)
I	Reference	809
II	After olivine fines injection	822
III	After fly ashes recirculation	819
IV	Next day (before recirculation)	817
V	After the weekend	829

3 RESULTS

The effects of olivine fines injection and fly ashes recirculation on the gas yields were measured. They are here expressed with the unit mol/kg$_{daf}$ for the gas and g/kg$_{daf}$ for the tar. Expressing the yield per unit of dry ash-free fuel (subscript *daf*) allows to relate the yield to the conversion of the fuel and avoid hiding potential dilution effects as can be the case when expressing them per cubic meter of producer gas.

The yields of the main gas species found in the cold gas produced by the gasifier are found in Figure 2.

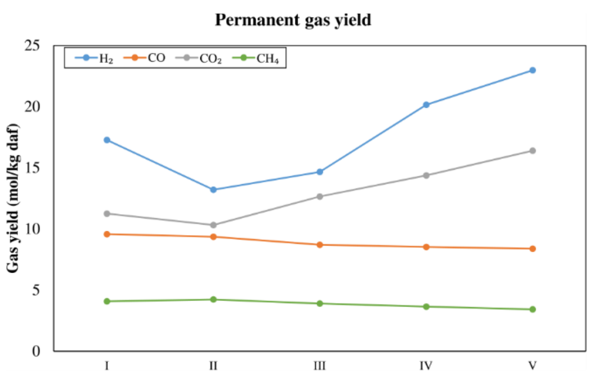

Figure 2: Yield of permanent gas species for the experimental cases

The total tar yield for the five experimental cases is shown in Figure 3. This total yield refers to the sum of yields of all tar species which could be measured by the SPA method as applied here. This includes species with a boiling point between those of benzene and coronene.

The activity, both in terms of gas composition and tar yield, decreases after the addition of fresh olivine fines. This is expected since the material injected is not active due to the absence of an ash layer. In particular, it was estimated that 430 kg of material injected during the four hours from the beginning of fines injection to end of fly ashes sampling, remained in the bed. This includes the fresh olivine fines but also the ash components fed from the two fuel inlet. During this period, 40 kg of fuel ashes were introduced, hence at least 390 kg of olivine fines have become part of the bed material and at most 430 kg, which would represent a dilution of the original bed inventory by inactive olivine to approximately 15%. The amount of retained material was estimated by difference between the mass injected and the mass of fly ashes collected in the secondary cyclone ash container, the mass trapped by the filter and the mass of fuel ash fed.

The recirculation of 200 kg of coarse fly ashes can be seen to lead to an increase in gas quality (case III) as compared with the previous measurement (case II).

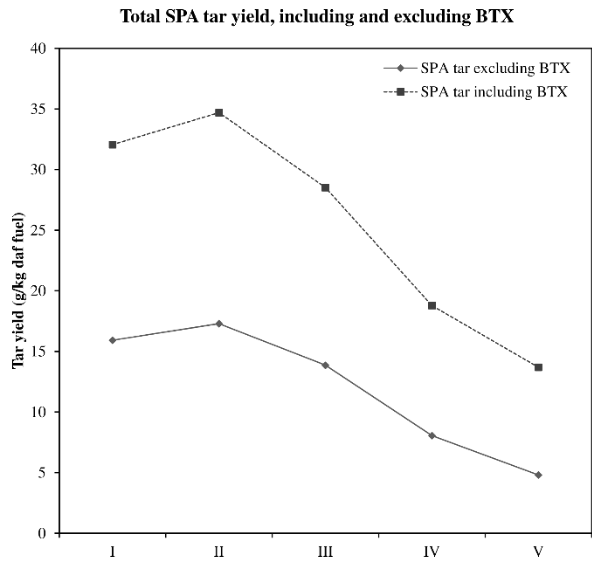

Figure 3: Yield of total SPA-detectable tar including (dashed line) and excluding (plain line) BTX

Although the tar yield in case III decreases even compared with the reference measured at the beginning of the day (case I), the gas composition indicates that the overall catalytic activity is not necessarily higher than this reference. Indeed the level of H_2 is still below that found in the morning, whereas the CO_2 yield has raised significantly. This could be linked to an increase in oxygen transport rather than catalytic activity, which would lead to consumption of part of the hydrogen, carbon monoxide and tar, thus counterbalancing the increased activity towards the WGS reaction and char gasification.

The increased overall catalytic activity of the bed material in cases III-V, at least compared with case II can be linked to several factors. First, the bed material can be expected to still be undergoing its activation process, and this can be extended to the 430 kg of material, mostly olivine fines, retained in the internal circulating system. These olivine fines, by their smaller size than the older bed material can be expected to be transported more easily in the CFB and be more in contact with condensing alkali in the "colder" region of the bed material loop. The potential catalytic activity of the fines which are getting activated is made even greater by their large specific surface area, when compared with the larger, older bed material.

A second factor is the fact that ash components present in the fly ashes recirculated, in particular alkali, can undergo further chemical and physical transformations when they are exposed once again to the gas atmospheres of the furnace and gasifier, leading them to be redistributed. Some of these alkali might indeed be re-introduced as salts which can vaporize in the gasifier and furnace environment and thus be available for gas reactions or interaction with the bed material.

Despite both these factors not being precisely known or possible to distinguish, it is however clear from the measurement in case IV that the gain in activity is not just temporary. Beyond simply conserving the activity level from the previous day, it appears that the gas quality has strongly increased, both in term of tar and hydrogen content.

This trend persists after the weekend (case V), as very low level of tar is reached, 13.69 g/kg_{daf}, which represents a 57% decrease compared with the reference. The total gas yield was found to reach 52.5 mol/kg_{daf} which represents a 19.7% increase compared with the 43.8 mol/kg_{daf} measured on the reference. In particular, a H_2/CO ratio of 2.75 is reached with the hydrogen accounting for almost 45% of the volume of the dry gas.

The substantial activity gain is particularly impressive given that during the week-end between cases IV and V, an extensive regeneration of the bed material occurred with 1.7 tons of fresh olivine being introduced to the system.

This could be of particular interest for the start-up of a DFB plant. At the start of an operation, the bed material is not active and thus the gas produced is of too low quality. In order to reach the operational window imposed by the downstream gas requirement, active species in the form of potassium solution has been used during GoBiGas start-up. However, it led to clogging of gas cooling equipment.

As a diluted source of alkali, coarse fly ashes stored from previous operations could be an efficient means to reach the operational window faster, while pontentially avoiding operational issues. Finally, this semi-continuous source of alkali in the system can soften fluctuations.

4 CONCLUSION

Recirculation of coarse, reactive fly ashes was shown in this work to be of interest not only for bed material and carbon recovery, but also for its gas upgrading potential. By carrying out this recirculation, low levels of tar have been reached and activity has been enhanced within a short time frame. As such, recirculation of coarse fly ashes could be an efficient mean to control the overall activity of the bed material in large scale dual fluidized bed gasifiers.

5 REFERENCES

[1] H. Thunman, A. Larsson, and M. Hedenskog, “Commissioning of the GoBiGas 20 MW biomethane plant.” tcbiomass 2015, Chicago, 2015.

[2] D. Sutton, B. Kelleher, and J. R. H. Ross, “Review of literature on catalysts for biomass gasification,” *Fuel Process. Technol.*, vol. 73, no. 3, pp. 155–173, 2001.

[3] Z. Abu El-Rub, E. A. Bramer, and G. Brem, “Review of Catalysts for Tar Elimination in Biomass Gasification Processes,” *Ind. Eng. Chem. Res.*, vol. 43, no. 22, pp. 6911–6919, Oct. 2004.

[4] J. Marinkovic, H. Thunman, P. Knutsson, and M. Seemann, “Characteristics of olivine as a bed material in an indirect biomass gasifier,” *Chem. Eng. J.*, vol. 279, pp. 555–566, 2015.

[5] S. Koppatz, C. Pfeifer, and H. Hofbauer, “Comparison of the performance behaviour of silica sand and olivine in a dual fluidised bed reactor system for steam gasification of biomass at pilot plant scale,” *Chem. Eng. J.*, vol. 175, pp. 468–483, 2011.

[6] T. B. Vilches, J. Marinkovic, M. Seemann, and H. Thunman, “Comparing Active Bed Materials in a Dual Fluidized Bed Biomass Gasifier: Olivine, Bauxite, Quartz-Sand, and Ilmenite,” May 2016.

[7] F. Kirnbauer and H. Hofbauer, “The mechanism of bed material coating in dual fluidized bed biomass steam gasification plants and its impact on plant optimization,” *Powder Technol.*, vol. 245, pp. 94–104, 2013.

[8] M. Kuba *et al.*, “Mechanism of Layer Formation on Olivine Bed Particles in Industrial-Scale Dual Fluid Bed Gasification of Wood,” *Energy & Fuels*, vol. 30, no. 9, pp. 7410–7418, Sep. 2016.

[9] H. He, X. Ji, D. Boström, R. Backman, and M. Öhman, “Mechanism of Quartz Bed Particle Layer Formation in Fluidized Bed Combustion of Wood-Derived Fuels,” *Energy & Fuels*, vol. 30, no. 3, pp. 2227–2232, Mar. 2016.

[10] D. W. McKee, “Mechanisms of the alkali metal catalysed gasification of carbon,” *Fuel*, vol. 62, no. 2, pp. 170–175, Feb. 1983.

[11] F. Kirnbauer, M. Koch, R. Koch, C. Aichernig, and H. Hofbauer, “Behavior of inorganic matter in a dual fluidized steam gasification plant,” *Energy and Fuels*, vol. 27, no. 6, pp. 3316–3331, 2013.

[12] A. Larsson, M. Seemann, D. Neves, and H. Thunman, “Evaluation of Performance of Industrial-Scale Dual Fluidized Bed Gasifiers Using the Chalmers 2–4-MWth Gasifier,” *Energy & Fuels*, vol. 27, no. 11, pp. 6665–6680, Nov. 2013.

[13] M. Israelsson, A. Larsson, and H. Thunman, “Online Measurement of Elemental Yields, Oxygen Transport, Condensable Compounds, and Heating Values in Gasification Systems,” *Energy & Fuels*, vol. 28, no. 9, pp. 5892–5901, Sep. 2014.

6 ACKNOWLEDGMENTS

This work was supported by Göteborg Energi AB, Valmet AB, Akademiska Hus, the Swedish Energy Agency, and the Swedish Gasification Center.

BioProGReSs has received funding from the European Union’s Seventh programme for research, technological development and demonstration under grant agreement 321477.