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Fluidized bed combustion of petroleum coke coagglomerated with sulphur sorbents†

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The relatively high sulphur content of coke produced during the upgrading of Athabasca bitumen, makes it environmentally unsuitable as a fuel. Using heavy oil or bitumen as a binder, attempts have been made to coagglomerate these cokes with sulphur dioxide capture agents, such as lime, hydrated lime and limestone, to reduce emissions during combustion. By providing an environment in which there is intimate contact between fuel and sorbent, it was hoped that greater utilization of the sorbent could be achieved, compared with the systems in which the sorbent is added separately to the combustion bed. Cokes from both Suncor and Syncrude operations were used in this investigation. The combustion tests on coke-sorbent agglomerates were carried out in a bench scale fluidized bed apparatus at 850°C. Test results indicated sulphur capture of over 60 wt % for Syncrude coke and over 50 wt % for Suncor coke at a calcium to sulphur molar ratio of 1:1. The presence of moisture did not appear to have any significant effect on sulphur capture. Other variables investigated included: the role of binder, the effect of coke size and calcium to sulphur mole ratio. A comparison was made of the efficiency of the various sulphur sorbents in the reduction of sulphur dioxide emissions.

(Keywords: combustion; fluidized beds; sulphur)

Upgrading of Athabasca oil sands bitumen to form a synthetic crude oil produces approximately 4000 t of coke per day. This coke is rather intractable as a fuel, being high in sulphur, very low in volatiles, difficult to grind and containing some carbon forms which are relatively unreactive[1]. Because of serious environmental and potential corrosion problems associated with the combustion of this coke, its use as a boiler fuel is limited and a significant portion of the coke is being stockpiled as a waste product. However, oil sands coke with a calorific value of about 33 MJ kg^{-1} would be an attractive boiler fuel if it could be desulphurized economically.

Of the various methods for the desulphurization of coke, fluidized bed combustion in the presence of limestone, with ash recycle, is emerging as a promising technology that can achieve high combustion efficiency with significantly reduced sulphur dioxide emissions[1,3]. Recently, considerable improvements in sorbent utilization have been made with circulating fluidized bed (CFB) technology. Sulphur capture of over 90 wt % was achieved in the CFB combustion of Syncrude fluid coke in the presence of limestone using an overall calcium to sulphur molar ratio in the range 1.7–2.3 (Ref. 4).

In earlier work, cokes from both Syncrude fluid coking and Suncor delayed coking operations were successfully coagglomerated with various sorbents such as lime, hydrated lime and limestone[5,6]. These agglomerates were ashed at 460–1000°C in a muffle furnace to assess the sulphur retention efficiency of the sorbent. These results demonstrated a greater utilization of sorbent in the agglomerates compared with the case where the sorbent was added separately.

Fluidized bed technology is well suited to the combustion of coke–oil–sorbent agglomerates and the objective of this investigation was to assess the sulphur retention efficiency of coagglomerated sorbent when burnt in this type of equipment. This paper describes results of combustion tests carried out in a micro-scale fluidized bed reactor.

EXPERIMENTAL

Materials

Suncor delayed coking coke and Syncrude fluid coke samples were obtained from the Alberta Research Council sample bank. The Suncor coke was ground to 150 μm size using a centrifugal grinding mill. Syncrude fluid coke was obtained in the 200–600 μm size range and could be agglomerated without further grinding. However, satisfactory agglomeration required longer mixing times for the coarser coke than for the finer material. The composition and calorific value of coke samples are listed in *Table 1*. The bridging or binding liquid used for agglomeration was a sample of coker feed bitumen from Suncor, also obtained from the sample bank.

The sorbents tested in this investigation included a sample of pulverized agricultural limestone from Domtar[5,6] and a pulverized limestone sample from Fort McMurray[7]. Samples of lime obtained from the calcination of Domtar limestone at 850°C, and various samples of laboratory prepared hydrated lime[5] were also used.

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Table 1 Composition and physical data for cokes

	Suncor delayed coke	Syncrude fluid coke
Proximate analysis[a] (wt% d.b.)		
Ash	6.0	8.7
Volatile matter	11.6	7.3
Fixed carbon	82.4	84.0
Ultimate analysis (wt% d.b.)		
Carbon	83.0	76.8
Hydrogen	3.4	1.6
Nitrogen	1.5	1.5
Sulphur	5.9	6.9
Oxygen	2.9	4.4
Ash	3.4	8.0
Calorific value[a] MJ kg^{-1}	33.4	32.6

[a] Alberta Research Council (Fuel Sciences Division)

Procedure

One gram of bitumen was added to the selected sorbent dispersed in 100 ml of tap water contained in a Waring blender. The suspension was agitated at 200 rps for 30 s. Twenty grams of coke, 0.1 g of NaOH, if desired, and an appropriate amount of bitumen were added to this mixture. The contents were agitated at 250 rps for 2 to 5 min. At this stage 2–3 drops of 9-octadecenoic acid were added, if needed, and the blending speed lowered to 120 rps. Blending was continued until discrete agglomerates formed (3–15 min). Coke oil agglomerates were then separated from the aqueous phase by screening. A portion of the agglomerates was used for analysis of bitumen, coke and ash content using a procedure described elsewhere[8]. A second portion of the agglomerates was dried at 100°C to a constant weight.

Combustion of coke–oil–sorbent agglomerates

Before combustion, wet agglomerates were dried to constant weight in an oven at 80°C in order to facilitate analytical calculations. However, because of the potential economic benefits of burning wet agglomerates, this type of material was also tested in the fluid bed unit.

In the combustion procedure a sample of agglomerates (1 g) was gravity fed from a hopper to a bench scale fluidized bed reactor[7], containing coarse sand heated to 850°C. The SO_2 concentrations in the combustion gas were measured with an infrared analyser. Tests were also carried out with blank samples containing no sorbent. The percentage retention of SO_2 by the sorbent was calculated by comparison of the results from the two tests. Corrections were made for the different sulphur contents of the agglomerates used as a blank and those containing sorbent.

RESULTS AND DISCUSSION

Recently, it was demonstrated that the coagglomeration of a sulphur dioxide sorbent with coke results in its greater utilization during combustion, compared with the systems where the sorbent was added separately[5,6]. There appear to be two main reasons for this observation. Firstly, coagglomeration of sorbent allows much finer sorbent particles to be used in the fluid bed system. It is well known[9] that finer particles will give increased SO_2 adsorption. Secondly, agglomeration provides intimate contact between the sorbent and fuel particles. Also, during burning, sulphur dioxide formed within the agglomerates is not subject to the flushing action of the fluidizing gas and consequently has a longer period of contact with the sorbent compared with the case for physical mixtures. If or when the agglomerates break down, this advantage is lost.

The earlier results were based on combustion tests carried out in a muffle furnace. As fluidized bed technology is the most likely option for the utilization of petroleum cokes[1], the present study was based on combustion tests in a micro-scale fluidized bed apparatus Although the absolute values for the retention of SO_2 by the various sorbents were different in the two investigations, the trends were essentially the same, as shown in *Table 2*.

It is evident from these results that the combustion of coke–oil agglomerates containing limestone produced substantially lower sulphur dioxide emissions than the agglomerates without sorbent. The tests without addition of limestone indicate that 5 and 2 wt % of the sulphur was captured by the ash constituents of Syncrude and Suncor coke respectively. Sulphur capture from the combustion of coke–oil–limestone agglomerates, with a calcium to sulphur molar ratio of 1:1, was 61 wt % for Syncrude coke and 53 wt % for Suncor coke corresponding to a calcium utilization of 56 and 51 wt% respectively. The considerably lower reduction in the sulphur dioxide emissions from the combustion of coke-sorbent agglomerates in a fluidized-bed reactor compared with the combustion in a muffle furnace is noteworthy. This can be explained by a more rapid breakdown of agglomerates owing to attrition in the fluidized-bed reactor. The flushing of the system by the fluidizing gas would then give a shorter SO_2 residence time.

The results in *Table 2* also indicate a greater utilization of the limestone for Syncrude coke compared with Suncor coke. This is consistent with previous results[5,6], and can be explained on the basis of the differences in the reactivities of the two cokes[10]. As a result of its greater reactivity Suncor coke burns faster than Syncrude coke thereby releasing SO_2 at a greater rate. Consequently, the contact time between SO_2 and sorbent will be less for Suncor than Syncrude, resulting in lower utilization of sorbent in the former case.

The role of NaOH on sulphur dioxide capture by sorbents

Coke-sorbent agglomerates were prepared in the presence of NaOH, because of its beneficial effect on the coagglomeration of the components, resulting in the use

Table 2 SO_2 capture by limestone[a]

		Per cent SO_2 capture			
		Syncrude coke		Suncor coke	
Run No.	Description	Muffle furnace	FB-reactor	Muffle furnace	FB-reactor
1	Coke–oil agglomerates prepared without sorbent	5	–	2	–
2	Coke–oil agglomerates prepared in the presence of limestone	94	61	77	53

[a] Combustion conditions in the fluidized-bed reactor: temperature = 850°C; velocity of air = 680 cm per min; combustion temperature in the muffle furnace = 1000°C; agglomerates prepared using 15 wt % Athabasca bitumen; Ca:S = 1; agglomerates dried at 80°C

of smaller quantities of bitumen[5]. Improved coagglomeration of the components arises from the improved wettability of the agglomerate constituents towards the bridging oil because of *in situ* formation of surfactants by reaction between the alkali and certain bitumen components[5]. Sodium is also a well known agent for the enhancement of the sulphation process in fluidized-bed combustion systems[11]. It is said to result in the activation of the CaO surface for SO_2 adsorption as a result of formation of Na–O–Ca species. Sodium also increases sintering of the lime, producing pores of an optimum size (around 0.3 μm) so that the sulphation reaction is not inhibited by pore plugging[9,12,13].

The effect of moisture on the sulphur capture by limestone

Coke–oil agglomerates were prepared from aqueous slurries and contained 20–40 wt% water. These agglomerates were normally dried in an oven before combustion. However, the combustion of wet agglomerates is economically more attractive and consequently some experiments were carried out to test the combustion of this type of material. The results are given in *Table 3*.

The difference in the sulphur capture from the dry and wet agglomerates falls within the range of error of the measuring system. Thus, it can be assumed that comparable levels of sulphur dioxide sorption are obtained from both wet and dry agglomerates. However, these results must be treated with caution as the presence of moisture may have interfered with the analysis of SO_2 by the infrared analyser.

The role of oil in the coagglomeration of coke with limestone

The type of oil plays an important role in the coagglomeration of cokes with limestone. Although most oils will bind the coke particles together, only a few are suitable for conditioning the surface of the limestone particles to make them hydrophobic and allow coagglomeration with cokes. In the present investigation, three different oils: Athabasca oil sands bitumen, fuel oil No. 1 and No. 4 (50/50 vol% mixture of fuel oils No. 2 and No. 6) were tested for their ability to act as a binder for both coke and limestone. Although all three oils agglomerated the coke particles alone, only Athabasca oil sands bitumen was found to be suitable for coagglomeration of the cokes with limestone. Because of its heteroatom content and the presence of polar groups Athabasca bitumen is an excellent conditioner for limestone. Whereas over 60 wt% limestone (based on the weight of the coke) can be coagglomerated with cokes using Athabasca oil sands bitumen, the amount of limestone agglomerated with fuel oils No. 2 and No. 4 ranged between 5 and 10 wt% only.

The amount of oil used determines the agglomerate size, with larger quantities producing larger agglomerates. Depending upon the application, both small and large agglomerate sizes have their advantages. The use of minimum amounts of oil (smaller agglomerates) would be more economical for applications requiring only the reduction of sulphur dioxide emissions from the combustion of high sulphur cokes/coals. On the other hand certain applications, e.g. the recovery of residual hydrocarbons from oil sand tailings using carbonaceous materials[14], require the collection of the maximum quantity of oil with a minimum amount of the collector solid.

Table 3 The effect of moisture on the capture of SO_2 by limestone[a]

Description	Sulphur capture (as wt% of total sulphur)	
	Syncrude fluid coke	Suncor delayed coke
≈ 1 mm size dry agglomerates	61	53
≈ 1 mm size wet[b] agglomerates	51	59

[a] Conditions as listed in *Table 2*

[b] Water content: Suncor coke agglomerates, 35 wt%; syncrude coke agglomerates, 20 wt%

Table 4 The effect of increasing amounts of limestone[a]

Ca:S molar ratio	Sulphur capture (as wt% of total sulphur)	
	Syncrude coke	Suncor coke
0.85	52	–
0.9	–	39
1.00	61	53
1.50	53	31
2.00	62	39

[a] Conditions as listed in *Table 2*; all agglomerates were ≈ 1 mm size and prepared using 15 wt% Athabasca oil sands bitumen. Agglomerates were dried before combustion

The effect of coke size on coagglomeration

The size of the coke particles did not have any significant effect on the ability of the coke to agglomerate in the presence of limestone. Two different size coke particles, 75–150 μm and 300–500 μm, were tested in this investigation. Although the larger size took a little longer to agglomerate, both sizes responded well. This is an important point because the particle size of unground Syncrude coke lies mostly in the 300–500 μm range and thus there is no need for grinding this coke prior to agglomeration.

The effect of calcium to sulphur mole ratio

The results in *Table 4* demonstrate the effect of calcium to sulphur molar ratio on the retention of sulphur by limestone. Contrary to previous investigations in a muffle furnace[5,6], and to the conventional fluidized bed combustion studies involving physical mixtures[1], increased quantities of limestone were not beneficial. Maximum limestone utilization was achieved for a limestone quantity corresponding to a calcium to sulphur molar ratio of 1. Increasing the load of limestone beyond this amount resulted either in decreased SO_2 sorption or no further improvement. This can only be explained on the basis of the dominance of the calcination reaction with increasing amounts of limestone in the agglomerates. Increased CO_2 pressure from the calcination of limestone could result in breakage of agglomerates, with a concomitant reduction in contact time between SO_2 and the sorbent within the agglomerates. This argument is supported by the effect of the calcium to sulphur molar ratio on the retention of SO_2 by coagglomerated lime as shown in *Figure 1*. Here, the effect of calcium to sulphur molar ratio on the retention of sulphur dioxide is shown to be similar to that observed for combustion tests in a

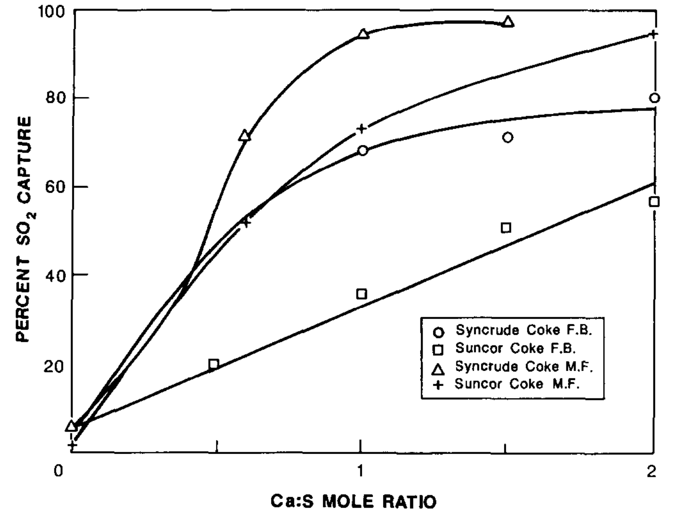

Figure 1 Ca:S ratio effect on the retention of SO_2 by lime: F.B., fluidized-bed; M.F., muffle furnace

Table 5 SO_2 capture by hydrated lime and New Brunswick marl

Sorbent[a]	Sulphur capture (as wt % of total sulphur) Syncrude coke	 Suncor coke
Hydrated lime		
Sample 1	60	38
Sample 2	55	36
Sample 3	58	–
Sample 4	58	31
Sample 5	59	37
NB-marl	49	44

[a] Conditions as in *Table 2*. Hydrated lime samples were prepared under different conditions as described in Ref. 5. Ca:S molar ratios: hydrated lime 1:1; NH-marl 0.9:1

Table 6 Comparative sulphur capture efficiency of various sorbents Syncrude coke vs. Suncor coke[a]

Sorbent	Sulphur capture (as wt % of total sulphur) Syncrude coke	 Suncor coke
Domtar activated limestone	61	53
Lime	68	36
Hydrated lime	58	36
NB-marl	54	49

[a] Conditions as listed in *Table 2*. Ca:S molar ratio 1:1 in each case

muffle furnace where the degree of sulphur dioxide retention increased with increasing amounts of lime in the agglomerates. The effect was again more pronounced for Syncrude coke than for Suncor coke. Also, as with limestone, the sulphur sorption efficiency of lime is greater with Syncrude coke than for Suncor coke.

Other sorbents

Coagglomeration of cokes with various samples of hydrated lime prepared in the laboratory[5] and a sample of New Brunswick marl (NB-marl) was also attempted. Sulphur retention results obtained from the combustion tests on these samples are listed in *Table 5*.

Considering the accuracy of the measuring system, it is evident from the results in *Table 5* that for both types of coke, the sulphur capture efficiency of all the hydrated lime samples is similar. However, the sulphur sorption efficiency of the hydrated lime samples with Syncrude coke is about double that for Suncor coke, which is the greatest difference in sorbent utilization by the two cokes observed in any test. These results differ from static bed combustion results that indicated different sulphur sorption efficiencies for each hydrated lime sample and a relatively small difference in the sorbent utilization for the two cokes[5]. New Brunswick marl appears to be an effective sorbent for both cokes with no significant difference in its capacity to retain sulphur from the two fuels.

The results discussed have demonstrated that coagglomerating cokes with sulphur sorbents such as limestone, lime and hydrated lime could be an effective way for controlling sulphur dioxide emissions from the combustion of these cokes. The procedure is slightly more efficient for Syncrude coke than for Suncor coke, as is evident from the results in *Table 6*. This is consistent with the static combustion test results in a muffle furnace and can be ascribed to the difference in the reactivities of the two cokes[10]. The results in *Table 6* also demonstrate the relative efficiencies of the various sorbents investigated. It is clear from these results that activated limestone is the most efficient in its capacity to retain SO_2 when both types of coke are considered. Activated limestone and lime show similar efficiences with Syncrude coke, but activated limestone is much more effective with Suncor coke than is lime. Again, the efficiencies of hydrated lime and NB-marl appear to be comparable for Syncrude coke, but NB-marl is the most effective of the two for Suncor coke.

The observed high efficiency of activated limestone for SO_2 retention is of considerable economic significance. The cost ratio of lime to limestone on a molar basis may vary from 2 to 4 depending on the transportation distance[15]. Even the costs for transportation and handling of limestone tends to be lower than that for lime as it can be transported in open trucks. However, lime does have an advantage over limestone in that it does not lose its effectiveness at higher calcium to sulphur ratios.

In the present investigation combustion tests were carried out without recycling cyclone fines back to the bed. Consequently, the results overpredict the sorbent requirement for effective sulphur removal. Recycling of cyclone fines has been shown to improve the utilization of limestone and thus reduce the calcium to sulphur molar ratio by about 10%[4]. Hence, it is reasonable to assume that further improvement in sulphur capture will be possible in a circulating fluidized-bed combustor.

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