CARBONYL SULFIDE PRESENCE IN SYNGAS STREAM PRODUCED FROM BIOMASS GASIFICATION PROCESSES: MEASUREMENT AND CALCULATION

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Summary

For a biomass gasification process, the removal of sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) from the dirty producer gas is considered to be relatively easy (e.g. by scrubbing); however, the removal of carbonyl sulfide (COS) is more difficult. To help with the development of a suitable gas clean-up strategy, the presence of COS species was considered in more detail in this study by both experimental measurements and theoretical thermodynamic equilibrium calculations. The results indicated that the theoretical thermodynamic equilibrium calculation showed a good match with experimental data, when equilibrium temperature of over 900°C was assumed. It is interesting to note that the temperature of over 900°C was also the highest temperature observed in the hot zone of gasification experiments.

Key words: *Biomass gasification, thermodynamic equilibrium, on-line gas analysis, quadrupole mass spectrometer (QMS), sulfur, gas clean-up.*

1. Introduction

In a down-draft air biomass gasifier, the fuel to air equivalence ratio is about 0.25 [1]. This means that only 25% of the stoichiometric requirement of air (to achieve complete combustion) is provided. The reactions between hydrogen and sulfur compounds are likely to lead to the formation of H_2S, and the oxidation reactions could lead to the formation of SO_2. However, other reactions can also lead to the formation of lower quantities of COS. The removal of SO_2 and H_2S from the dirty producer gas was considered to be relatively easy (e.g. by scrubbing) while the removal of COS is more difficult.

Depending on the source of biomass (e.g. refuse-derived fuel), its sulfur content will vary. As an example, based on information from one supplier [2], the sulfur levels of refuse-derived fuels can vary from 0.12 to 0.17wt%, yet can even be as low as 0.09wt%, or peak as high as 0.3wt%. These variations have huge implications for the design of the subsequent gas clean-up processes, especially as the final emission limits on the plant must conform to the Waste Incineration Directive (2000/76/EC), otherwise known as WID limits [3].

From an engine maintenance perspective, feeding a heavily contaminated gas into a reciprocating engine is not desirable. Any residual sulfur compounds in the gas: (a) may act as catalyst poisons and affect the performance of the catalysts used to clean up the emissions in the exhaust gas (after the gas engine), or (b) when burnt in the gas engine, are likely converted to oxides of sulfur, which could exceed the WID limits [3] in the exhaust gas emissions from the plant. Also, because of the dilution effect (as air is added), the volumetric flow rate of the exhaust gas is approximately 3x higher than the producer gas fed into the engine. So purely from a volumetric perspective, the size of gas clean-up equipment could increase and so would the associated operating costs.

Therefore, to help with the development of a suitable gas clean-up strategy, the presence of COS species is considered in more detail in this paper, under the following themes: (a) experimental gasification in a quartz tube reactor and a commercial pilot-scale down-draft gasifier: measurements were taken when wood, straw, refuse derived fuel (RDF) and waste-wood pellets were gasified, and the ratio of H_2S and COS species was quantified; (b) theoretical thermodynamic equilibrium calculations.

It is also noted that all experimental works presented in this paper are a brief review of an earlier study [4]. Based on information of gas composition of that previous work [4], a theoretical study was conducted in this paper to see what would be predicted at different values of gas temperature, and to discover what temperature matched the data most closely.

2. Material and methods

2.1. Experiment

2.1.1. Laboratory-scale gasifier

Gasification experiments were performed in a small laboratory-scale quartz tube gasifier, in which earlier work [5] showed that it can produce a gas stream similar in composition to a pilot-scale gasifier. An outline schematic of the gas sampling scheme is shown in Figure 1.

The gas flowed from the bottom of the gasifier, then through a cooler, and any condensate was trapped in the first plastic vessel. The gas then passed through a cooling coil, where more of the liquid condensed. The gas was then passed through a glass wool filter and then discharged into the vent from the fume cupboard. Samples of gas were drawn from the exhaust line and passed through another glass wool filter and a filter coalescer before going to a gas chromatograph (GC) and a QMS for analysis. This system of filters helped to remove the majority of tars and particulates in the gas stream, so as not to damage the analytical equipment. Further details on this experimental set-up are available in earlier work [5, 6].

2.1.2. Measurements on a pilot-scale plant

Gas analysis measurements were also taken on a commercial pilot-scale plant operated by Refgas Ltd. at a test site in Sandycroft (near Chester, UK). A ‘waste-wood’ was used as a fuel. The term "waste-wood" is used to describe a material that has been mainly produced from recycled wood, but may also contain a small amount of other contaminants (e.g. plastic, paper).

In its present configuration, this pilot-scale plant had a nominal capacity of 150 to 250kg/h, depending on the material fed into the gasifier and the choice of operating conditions. The potential electrical output from the gas produced from this plant could vary from 150 to 250kWe.

A simplified schematic of the process flow diagram is shown in Figure 2.

The waste-wood chips were fed from a hopper into the gasifier. The down-draft gasifier operates under a negative pressure, and the gases are drawn from the gasifier by the centrifugal gas blower. The gas leaves the reactor at the bottom of the unit, at a temperature of about 550°C. Char is discharged from the base of the gasifier, and char fines/ash are also trapped in the two cyclones. The dirty gas from the cyclones is quenched with water and then passes through a HESS unit (which is a high-efficiency water scrubber), and a heat exchanger (chiller). The blower draws the gas from the gasifier, and then blows it through the filters, into the storage tank, and then to the gas engine, and/or to the gas flare.

The gas sample to the QMS was drawn from the line, at the point where the gas was sent to flare (Figure 2). At this point, the gas was at positive pressure. The gas sample then flowed through a glass wool filter and a filter coalescer, the same procedure to protect the QMS as shown in Figure 1, before going to the QMS for analysis.

Further details on this experimental set-up are available in earlier work [4].

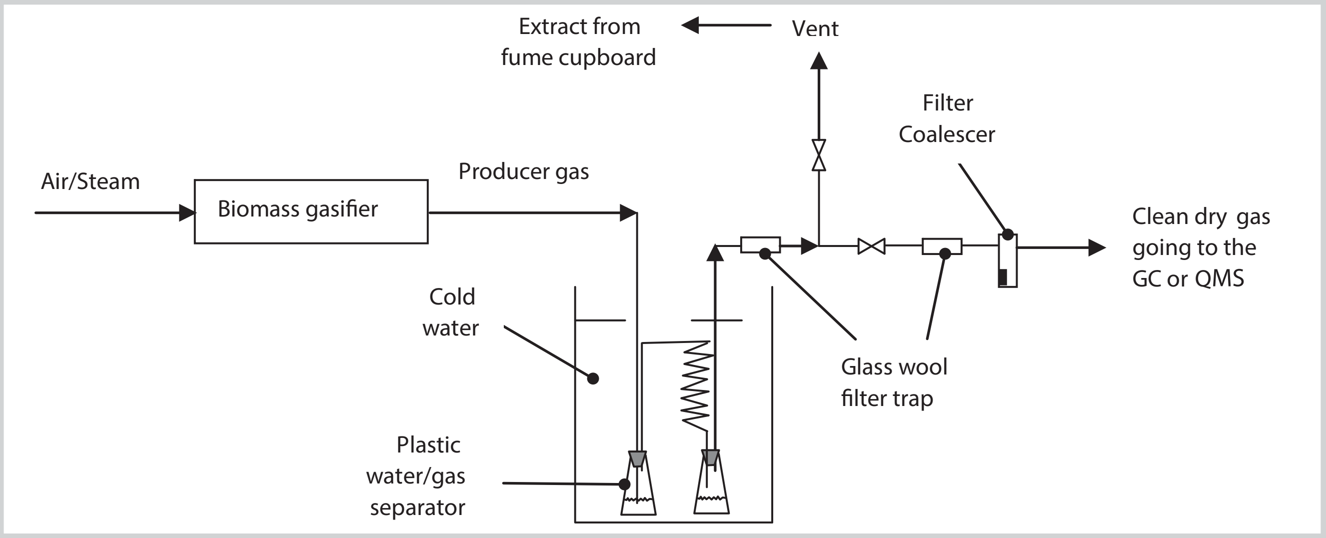


Figure 1. *Outline schematic of the gasification experiment, focusing on gas analysis*

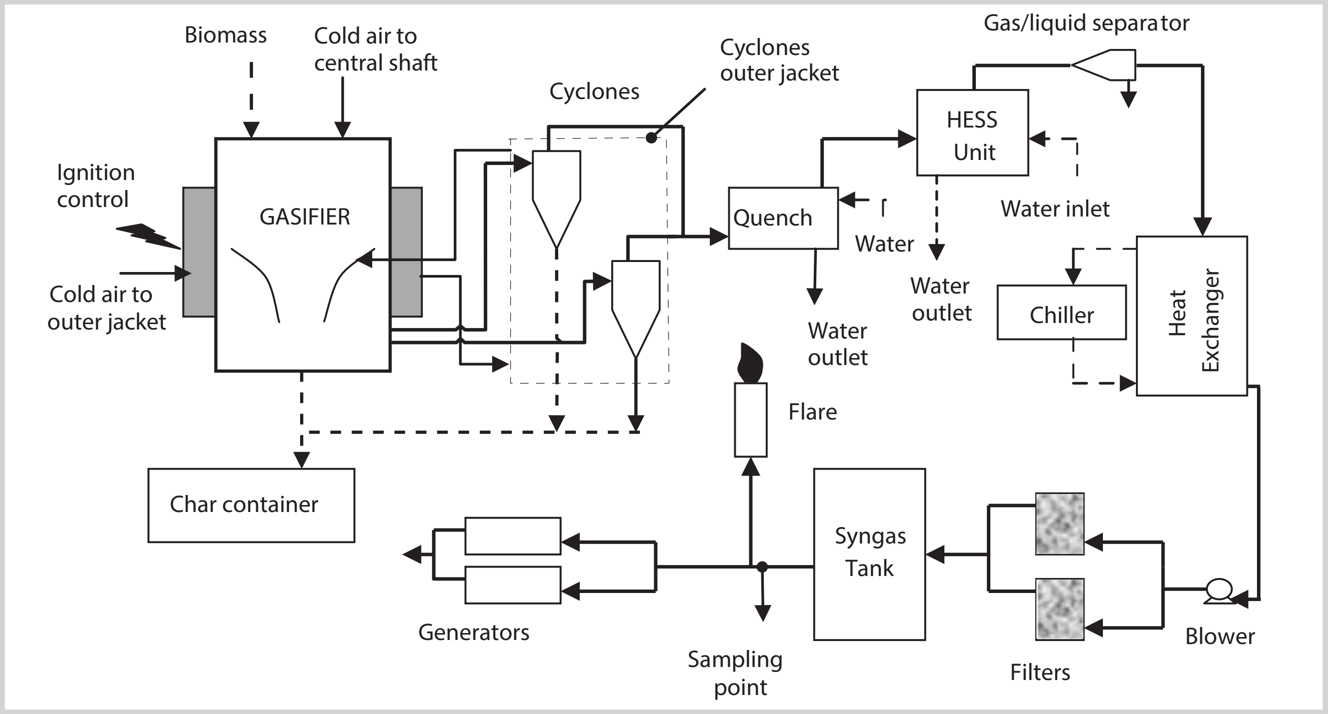


Figure 2. Simplified process flow diagram of the commercial pilot-scale plant

Table 1. Properties of the fuels used with/for proximate analysis

Properties	Waste wood chips(1)	Wood pellets(2)	Straw pellets(3)	RDF pellets(4)
Dimensions:				
- Diameter (mm)	-	5	6	14
- Length (mm)	-	5 - 17	5 - 17	30 - 80
Moisture (wt% in wet basic)	10.0	7.4	10.9	7.2
Volatiles (wt% in wet basic)	70.6	72.6	65.9	39.7
Fixed carbon (wt% in wet basic)	19.1	18.8	21.7	29.2
Ash (wt% in wet basic)	0.3	1.3	1.4	23.9

(1) Obtained from an actual pilot-plant, Refgas Ltd, Sandycroft; (2) Supplied by Treenergy Ltd, Monmouth; (3) Supplied by Agripellets Ltd, Evesham; (4) Supplied by Refgas Ltd, Sandycroft

2.2. Analysis

2.2.1. Gas analysis

In this study, for experimental measurements, a standard Hiden HPR-20 Quadrupole Mass Spectrometer (QMS) was used to analyse the gas produced from gasification processes. A quantitative method of on-line gas analysis was then developed on this QMS to measure the gas composition of up to 8 species (e.g. N_2, CO, CO_2, H_2, CH_4, O_2 and traces of H_2S and COS) when a range of fuels was gasified.

The repeatability of measurements using the QMS was checked, where a bag-sample of gas was taken during one gasification experiment. The gas was then connected to the QMS sampling line for checking over a 10-minute period. It was found that, during the checking time, the average composition of the species was: N_2 = 58.34 (± 0.28) vol%; CO = 15.62 (± 0.16) vol%; H_2 = 9.1 (± 0.16) vol%, CO_2 = 14.31 (± 0.09) vol%, CH_4 = 1.48 (± 0.01) vol%, O_2 = 9987 (± 80) ppmv, H_2S = 83 (± 5) ppmv, COS = 6.55 (± 0.11) ppmv.

Further details on this method are described in earlier work [4].

2.2.2. Proximate analysis of fuels

The proximate analysis of fuels gasified in this study was done in the laboratory in earlier work [4], and is shown here in Table 1.

2.2.3. Thermodynamic calculation

For theoretical thermodynamic equilibrium calculation, a commercial package, known as Aspen Plus® (version 7.1), using Gibbs free energy minimisation, was used. Making use of the software in Aspen Plus®, calculations were performed where the interaction between many species was considered, and this included: H_2, CO, CH_4. CO_2, N_2, O_2, H_2O, SO_2, SO_3, H_2S, COS, and CS_2.

The work on the theoretical equilibrium calculations was previously published [7].

3. Results and discussion

3.1. Laboratory-scale gasification experiment

3.1.1. Composition of the gas produced

These experiments were performed with/on a small scale, 21mm i.d. quartz tube gasifier filled with wood pellets (5mm diameter and 13mm length), to a depth of about 400mm. The air flow was kept constant at 3 litres/min, and temperatures in the hot zone were in the region of 912 to 1,046°C. Further information on that experimental facility is available in [5].

The same experimental procedures were repeated, using straw and RDF pellets, and a brief review of this previous work [4] is presented here as follows:

The average values of gas composition produced from gasification of different biomass sources are shown in Table 2.

It can be seen from Table 2 that there are significant differences in the gas composition generated by gasification of different biomass sources. The straw pellets produce a slightly higher H_2S gas concentration, and the COS concentration is very similar, compared to the wood pellets. This might come from the fact that, according to Little [8], the sulfur content in straw pellets was typically about 0.1wt%, higher than those of wood pellets made from heather (0.07wt%), gorse (0.08wt%), and rhododendron (0.02wt%).

Table 2. *Comparison of gas compositions produced from different biomass sources [4]*

Component	Wood pellets	Straw pellets	RDF pellets
CO (vol%)	16.44	13.91	10.39
H_2 (vol%)	10.11	12.83	4.97
CH_4 (vol%)	2.08	2.11	1.11
CO_2 (vol%)	15.12	17.17	14.57
N_2 (vol%)	56.06	53.77	67.90
O_2 (ppmv)	1,510	1,736	10,063
H_2S (ppmv)	99	123	286
COS (ppmv)	10	11	28

Also, it is not surprising to see that the concentration of H_2S and COS produced from RDF pellets is about three times higher than values from the wood and straw pellets, as the RDF was expected to have a higher sulfur content. Depending on the source of RDF, its sulfur content will vary. For example, sulfur levels, based on information from one RDF pellets supplier [2], generally vary from 0.12 to 0.17wt%, yet can even be as low as 0.09wt%, or peak as high as 0.3wt%.

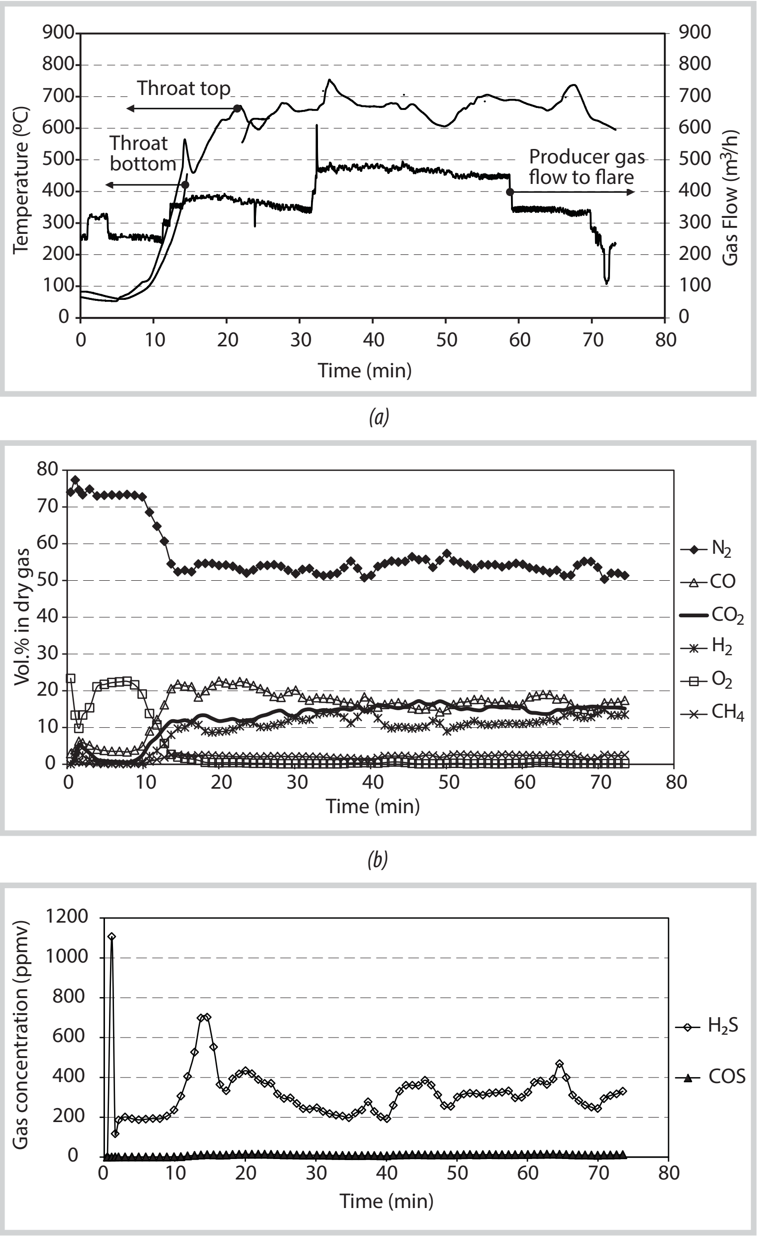
In addition, there is a consistency in the molar ratio of the concentration of H_2S to COS (i.e. around 10:1) in the gas streams produced from gasification of wood, straw and RDF pellets, in which 1,084°C was the highest temperature observed in the hot zone. This will be a very useful information for development of gas clean-up strategies for commercial plants.

3.1.2. Thermodynamic equilibrium calculation

At this point, it was decided to calculate the thermodynamic equilibrium (using Aspen Plus) for the gas produced from experiments to see what would be predicted at different values of gas temperature, and to discover what temperature matched the data most closely. The gas produced from RDF gasification was chosen, and the moisture content in the gas stream was assumed to 16.5vol% (the reason for choosing this number can be seen in [7]). A range of reaction temperatures from 600 to 1,200°C was explored. The adjusted wet gas composition and the calculation results are shown in Table 3.

Table 3. *Variation of species - simulations on a complex system using Aspen Plus®*

Species	Adjusted wet gas composition	Temperature					
		600°C	700°C	900°C	1,000°C	**1,100°C**	1,200°C
H_2 (vol%)	**4.15**	9.655	8.636	6.893	6.257	**5.739**	4.967
CO (vol%)	**8.68**	4.809	6.062	7.814	8.450	**8.969**	9.757
CH_4 (vol%)	**0.93**	0.065	0.002	0.000	0.000	**0.000**	0.000
CO_2 (vol%)	**12.17**	16.710	15.493	13.742	13.105	**12.586**	11.797
N_2 (vol%)	**56.71**	56.214	56.143	56.140	56.140	**56.140**	56.137
O_2 (vol%)	**0.84**	0.000	0.000	0.000	0.000	**0.000**	0.000
H_2O (vol%)	**16.5**	12.521	13.638	15.385	16.022	**16.540**	17.316
H_2S (ppmv)	**239**	253	251	247	244	**239**	224
COS (ppmv)	**23**	7	9	13	15	**17**	18
SO_2 (ppmv)	**-**	0	0	0	1	**4**	18
SO_3 (ppmv)	**-**	0	0	0	0	**0**	0
CS_2 (ppmv)	**-**	0	0	0	0	**0**	0



(a)

(b)

(c)

Figure 3. *The results of a test run performed on the pilot-plant: temperature and gas flow (a), dry gas composition (b) and concentration of H_2S and COS in dry gas (c) [4]*

From Table 3, it is likely that the gas composition estimated matches the experimental data at calculation temperatures higher than 900°C. This may be reasonable because the reaction rate is high at high temperature, and thermodynamic equilibrium could be reached quickly. The temperature of 1,100°C seems to match the data most closely, and it is also nearly the highest temperature observed in the hot zone of gasification experiments [5].

It is interesting to see that the molar ratio of H_2S to COS at calculation temperature of 1,100°C is about 14:1, which is close to the one (10:1) obtained from experiments. Also, the presence of SO_2 becomes significant at high temperature (e.g. 4ppmv at 1,100°C).

For thermodynamic equilibrium calculation, the concentrations of sulfur species also vary with the moisture content of the gas stream. It was found that, for set values of the moisture content between 8 to 20vol%, the temperature of 1,100°C always gave the best match. Therefore, it may be useful to see what moisture content matches the experimental data best at a temperature of 1,100°C. By adjusting the moisture content of the gas stream in the Aspen Plus model, it was found that the value of 10 to 13vol% of moisture gave the best match, where the molar ratio of H_2S to COS was approximately the same as the experimental value (10:1).

3.2. Composition of the gas produced from the pilot-plant

Again, a brief review of the previous work [4] on the measurement of the pilot-scale gasification is presented as follows:

Figure 3 presents the change of gas composition during one run of the pilot-scale gasifier. The changes in H_2S and COS levels are shown in Figure 3c, where the concentration of H_2S varies from about 200 to 700ppmv, while the COS concentrations were in the region of 6 to 17ppmv, which are ~30 times smaller than the concentrations of H_2S. This is not surprising due to the variation of the composition of the waste-wood that is being gasified at a particular moment. Also, the molar ratio of H_2S and COS levels from the pilot-plant is not similar to the findings in the laboratory, where the molar ratio of H_2S:COS was around 10:1 for all three types of biomass (wood, straw and RDF pellets). This difference might arise from the possibility of COS hydrolysis reactions taking place, with the presence of ash particles as a catalyst, in the water quench and absorption units, leading to the conversion of COS into H_2S [9].

Using a similar technique, as described in section 3.1.2, for the gas produced from a pilot-scale gasifier, at a number of snap-shots in time, the thermodynamic equilibrium calculations were performed, using the measure values of gas composition at these points. The results show that there is a good match in the gas composition at a calculation temperature between 800 to 900°C, which was the operating temperature measured in the throat of the pilot-scale gasifier (Figure 3). Also, the measured concentration of COS in the producer gas stream is just slightly lower (e.g. 2ppmv) than the theoretically calculated values (e.g. 12ppmv).

4. Conclusion

From laboratory experiments, there is a consistency in the molar ratio of the concentration of H_2S to COS (i.e. around 10:1) in the gas streams produced from gasification of wood, straw and RDF pellets. This will be a very useful information for development of gas clean-up strategies for commercial plants.

Concentrations of two key sulfur compounds (H_2S and COS) in the gas produced from a commercial pilot-scale gasifier were measured. Concentrations of H_2S varied from 200 to 1,000ppmv, and this is probably connected to the variation in the composition of the waste-wood fed into the gasifier. In addition, the thermodynamic calculated H_2S and COS levels broadly match the experimental measurements for all calculations.

By adjusting the calculation temperature in the thermodynamic equilibrium model, it was found that 1,100°C was the best value that matches the experimental data most closely at every moisture content (from 8 to 20vol%) of the gas phase. It is interesting to note that the temperature of about 1,100°C was also found to be the highest temperature observed in the hot zone of gasification experiments. It was likely that in the gas phase of the gasifier, thermodynamic equilibrium of reactions could be reached at this temperature, as the reaction rate would be high at high temperature.

Also, by adjusting the moisture content of the gas stream in the thermodynamic equilibrium model, the range of 10 to 13vol% of moisture was found to give the best match, where the molar ratio of H_2S to COS was approximately the same as the experimental value (10:1).

Finally, the importance of considering gas clean-up strategy, and how this may in turn affect the ability of the plant to meet the WID limits for SO_2 was explored, and how concentrations in the RDF translate into emissions. Also, the importance of considering the impact of contaminants on catalyst systems was emphasised, rather than just looking at WID limits on their own.

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