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Hydrodesulphurisation of Petroleum Coke

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Abstract

Hydrodesulphurisation in a fluidized bed offers the most attractive process for the desulphurisation of petroleum coke. Results of coke hydrodesulphurisation clearly indicate that the rate of sulphur removal is greatest at about 1100 K. The hydrodesulphurisation process is particularly effective with cokes of high sulphur content and high ash and heavy metals content, as at temperatures less than 1100 K the adverse effects of high ash and heavy metals content on desulphurisation is largely avoided. The process leads in general to increased porosity, density and surface area and improved reactivity. These properties are dependent on the sulphur concentration. The greater the amount of sulphur removed, the greater the structural changes expected in the coke treated. The weight loss is less than 10%.

Keywords: petroleum coke, desulphurisation, hydrodesulphurisation

1. Introduction

Hydrodesulphurisation (HDS) is a common process of desulphurisation in the oil industry, but it has not as yet found application in the treatment of petcoke.

Organic thiols, sulphides and disulphides as well as aromatic organic sulphur are susceptible to reduction by molecular or nascent hydrogen or hydrogen-donor systems:

$$R_1S_xR_2 + 4\,H \rightarrow R_1H + R_2H + H_2S_x$$

$$R_1S_xR_2 + 2\,R_3H \rightarrow H_2S_x$$

Sulphides and thiols would give H_2S. Disulphides may give hydrogen polysulphides (under mild reduction conditions) or H_2S (under more vigorous reducing conditions). Hydrogen polysulphides are unstable and tend to dissociate into H_2S and elemental sulphur. The elemental sulphur could be removed by vaporization or by solvent extraction (R. A. Meyers, 1977).

2. Hydrodesulphurisation of Petroleum Coke

In marked contrast to the HDS of liquids which must be contained at high pressures and are limited to processing temperatures below approx. 750 K, substantially higher temperatures can be used to achieve fairly rapid HDS of cokes, even at atmospheric pressure (E. S. Hall & E. L. Tollefson, 1985).

The HDS of petcoke can be visualized as having the following steps (Z. M. George, 1975):

a) The diffusion of hydrogen through the gas film boundary layer surrounding the coke granules.

b) Diffusion of hydrogen into the pores of the coke granules.

c) Reaction of hydrogen with sulphur

compounds to form H2S:

$$(C\text{-}S)_{solid} + H_2 \rightleftarrows C_{solid} + H_2S$$

a) Diffusion of H_2S from the outside of the granules to the fluid stream through the gas film boundary layer surrounding the coke granules.

b) Reaction of H_2S during its desorption with the coke particles to form new stable C-S compounds (The reverse reaction).

The diffusion of hydrogen through the gas film boundary layer is not the rate-controlling step. The rate-controlling step for the initial reaction is the diffusion of hydrogen into the pores of the granules (step b); the initial reaction rate increases with decreasing particle size. As the reaction progresses, the rate-controlling step shifts to the reaction of hydrogen with sulphur compounds (step c) (N. Takanari & T. Tanaka, 1973). At 900 K it may be inferred that the chemical surface reaction and not the physical processes is rate controlling (B. S. Parmar & E. L. Tollefson, 1977). At higher temperatures (> 1000 K) steps d & e would probably control the overall rate of desulphurisation with the reverse reaction (step e) Occurring more rapidly.

During the initial stages CH_4, C_2H_6, CO, CO_2, H_2O and H_2S are produced, but in the later stages only H_2O and H_2S are produced (Z. M. George, 1975). Some weight loss of the coke is caused by the formation of CH_4 and other compounds, as significant amounts of CH_4 are in fact produced (Z. M. George, L. CG. Schneider & E. L. Tollefson, 1978). A small fraction of the coke treated is transformed into well-crystallized graphite at higher temperatures. Small cracks or granulations form also in the coke (J. Gillot, B. Lux, P. Cornuault & F. Du Chaffaut, 1968). The extent of such formation is strongly dependent on temperature.

(1) In the simple HDS process, petcoke is heated in a fixed bed under an atmosphere of hydrogen. Table 1 shows the maximum desulphurisation obtained at different temperatures. This table which represents results extracted from the work of many workers clearly indicates that the rate of sulphur removal is greatest at about 1000 K, where about 50% of the sulphur is removed, but higher temperatures (~1600 K) are required for the removal of the more refractory sulphur. At temperatures above 1300 K and below 1450 K sulphur removal is not apparent (J. Gillot, B. Lux, P. Cornuault & F. Du Chaffaut, 1968). The value of the optimum temperature is dependent on the type of coke treated and other variables. The maximum desulphurisation at the optimum temperature can be explained by the fact that the net rate of desulphurisation is the result of two competing processes, namely the removal of the labile sulphur by hydrogen and the thermal fixation of sulphur by the reverse reaction which produces a more stable form of sulphur.

Table 1. Effect of temperature on HDS

Temp. K	Max. Desulph. %
810	6
860	6
870	18
920	41
980	50
1090	47
1120	40
1140	26
1170	21
1200	6
1270	0
1570	92

The reverse reaction becomes more rapid and rate controlling at temperatures in the range 1000–1300 K. It was shown by George et al. (Z. M. George, 1975) that adding a known amount of H2S to the hydrogen stream causes an inhibition in the degree of desulphurisation. As the partial pressure of H_2S was increased, the degree of desulphurisation decreased, and at about 0.32 bar of H_2S some sulphur incorporation was apparent. When a sample of some desulphurised coke (with 3.2% sulphur content) was used with 0.11 bar of H_2S, it was observed that the sulphur level increased to 4.0% indicating the occurrence of the reverse reaction (Z. M. George, 1975). However, at elevated temperatures (1500–1800 K) the presence of H_2S would induce sulphur removal, a fact which helps to explain the degree of desulphurisation achieved at 1600 K as can be seen from Table 1.

Other factors that may also explain the presence of a maximum in the temperature range 920–1120 K include the sintering of the coke particles at the higher temperatures which would limit the diffusion of H_2S out of the coke granules, making this diffusion rate controlling (E. S. Hall & E. L. Tollefson, 1985; Z. M.George, (1975; B. H. Mahmoud, S. Ayad & S. Y. Ezz, 1968).

The degree of HDS is dependent upon the sulphur content and type of petcoke. The degree of desulphurisation increases in general with increasing sulphur content, and it is easier to desulphurise fluid coke (with high sulphur content) than it is to desulphurise delayed coke (with less sulphur content), whereas the HDS of needle coke appears to be much more difficult (I. Mochida, T. Furuno, H. Fujitsu, T. Oyama & K Fujimoto, 1988). This effect is often obscured, however, by the influence of other process variables such as pressure, reaction time and hydrogen flow rate (see Tables 2 and 3).

Increasing the hydrogen flow rate will increase the degree of desulphurisation (Table 4). This increase may have, however, an upper limit as reported by George (Z. M. George, 1975) who found an optimum flow rate at 36 l/g coke/hr beyond which value the desulphurisation levels off.

Table 2. Effect of coke type on HDS

Type of coke	Desulph. %	S Content %	HDS Temp. K	Reaction Time (min.)	H2 flow rate l/g coke/hr	Ref.
Fluid	37	7.0	980	120	1.2	10
	31	7.3	970	120	1.4	11
	18 [1]	8.2	1120		0.5	6
Delayed	22	5.8	970	150	28.8	3
	3 [2]		970	120		12
Needle	55 [3]	0.5	970	120		9

(1) This relatively low value may be due to the low rate of hydrogen flow.

(2) This is an abnormally low value, which cannot be explained due to lack of relevant data on process variables.

(3) This high value is not easy to explain given the data available.

Table 3. Effect of initial sulphur content on HDS

S content	Desulph. %	Temp. K	Time (min.)	H2 flow rate l/g coke/hr	Ref.
0.4	9	1140	120	0.7	13
0.5	55 [1]	970	120		9
1.3	62 [2]	1570	750 h		7
1.5	26	1140	120	0.7	13
5.8	30	1120	150	29	3
7.0	24	1140	120	1.2	10
7.3	31	970	120	1.4	11
7.7	87 [3]	1070	120		4
8.2	18	1120		0.5	6

(1 & 2 & 3) All these values are unexpectedly high. (2) is explained by the long reaction time (750 hours) and the high temperature (1570 K), (3) is explained by the high pressure used (9.8

bars).

Table 4. Effect of hydrogen flow rate on degree of HDS

H2 flow rate l/g coke/hr	Desulph. %	Temp. K	Time (Min.)	Rate of heating K/min	S content Wt. %	Size (mm)	Ref.
0.03	13	980	120		7.0	0.3	10
0.45	13	1140	120		7.0	0.3	10
0.48	18	1120		21	8.2	0.2	6
0.70	26	1140	120	14	1.5	0.2	13
1.15	24	1140	120		7.0	0.3	10
1.44	31	970	120	23	7.3	0.3	11
28.80	30	1120	150	170	5.8	0.2	3

There is some indication of a general relationship between reaction time and desulphurisation level, although the effect may be masked by the influence of other variables. At one residence time of 120 min. the desulphurisation level was found to vary between 3 and 87%. A small fraction (10–16%) of the coke treated is transformed into a well-crystallized phase. This was found to depend upon reaction time, increasing at first with increasing time then decreasing (J. Gillot, B. Lux, P. Cornuault & F. Du Chaffaut, 1968).

Increasing the pressure seems to increase significantly the degree of desulphurisation (Table 5).

Table 5. Effect of pressure on degree of HDS

Pressure (bar)	Max. Desulph. %	Temp. K	Time (min)	S content (wt. %)	Ref.
1.0	31–36	1030-1090	120	7.0	10
1.0	55	970	120	0.5	9
3.5	57		60	7.0	10
6.1	70		60	7.0	10
9.8	87	1070	120	7.7	4

There does not seem to be any direct relationship between the rate of heating and degree of desulphurisation. However, few authors specify the rate of heating employed in their work (Table 6).

Table 6. Effect of the rate of heating on degree of HDS

Rate of heating K/min.	Desulph. %	Temp. K	Time Min.	S content %	Size mm	Ref.
14	26	1140	120	1.5	0.2	13
21	18	1120		8.2	0.2	6
23	31	970	120	7.3	0.3	11
30	55	970	120	0.5	< 0.1	9
100	17	970	120	0.5	30	9

170	30	1120	150	5.8	0.2	3
170	22	970	150	5.8	0.2	3

It might be expected that decreasing the coke particle size would in general improve the HDS efficiency, but this is not immediately apparent from the reported results (Table 7). Results obtained by Hall and Tollefson (E. S. Hall & E. L. Tollefson, 1985), however, show a substantial increase in the extent of desulphurisation as a result of particle size reduction. This effect was more pronounced for fluid oil sand coke than it was for delayed coke.

Table 7. Effect of coke particle size on degree of HDS

Particle size mm	Desulph. %	Ref.
30	10	9
> 2.8	21	9
1.8	32	9
0.7	5	3
0.5	1 – 30	2, 3
0.4	5	3
> 0.3	9	13
0.3	13–31	3, 10, 11
0.2	18–40	3, 6, 13
< 0.1	55-80	2, 9

The calorific value of coke was found to drop as a result of HDS from 35.1×10^3 KJ/Kg to 34.2×10^3 KJ/Kg (W. C. Shafer, 1952). HDS, on the other hand, would result in an increased porosity and surface area and improved reactivity. These properties seem to be a function of sulphur concentration and not of treatment temperature (B. H. Mahmoud, S. Ayad & S. Y. Ezz, 1968). The greater the amount of sulphur removed, the greater the structural changes expected in the coke treated. The coke density is expected to increase as a result of HDS, and there will be some weight loss (< 10%). The surface area of coke hydrodesulphurised at 1120 K increased from 4 to 11 m^2/g (Z. M. George, 1975).

(2) The use of fluidized bed desulphurisation leads to greater desulphurisation at reduced flow rates (Table 8). This is probably due to the more efficient contact between hydrogen and coke (Z. M. George & L. G. Schneider, 1982). Varying the bed depth within the range (7.6–15.2 cm) had no significant effect on desulphurization (B. S. Parmar & E. L. Tollefson, 1977). Decreasing the particle size improved desulphurization (B. S. Parmar & E. L. Tollefson, 1977). The extent of desulphurisation increased with temperature up to a maximum at 900–1000 K (B. S. Parmar & E. L. Tollefson, 1977; I. Mochida, T. Furuno, H. Fujitsu, T. Oyama & K Fujimoto, 1988), then it decreased in a manner similar to the desulphurisation in static beds. Weight loss as a result of the gasification of carbon by hydrogen increased with temperature (from about 2.4% at 870 K to 5% at 1090 K), but this additional gasification did not have a beneficial effect on desulphurisation (B. S. Parmar & E. L. Tollefson, 1977).

Table 8. HDS in static and fluidized beds

Temp. K	Max. Desulph. %	
	Fluid	Static
900	88	18
1000	74	49

Mochida et al. (I. Mochida, T. Furuno, H. Fujitsu, T. Oyama & K Fujimoto, 1988) found that cooling the coke to room temperature at different intervals during HDS improved the level of desulphurisation. From the evidence given it is apparent, however, that this inter-cooling is effective at certain critical temperatures only. Inter-cooling at 920 K and at 1120 K had no effect on desulphurisation. Inter-cooling at 1020 K, on the other hand, enhanced desulphurisation to a level of 60% (I. Mochida, T. Marutsuka, T. Furuno, Y. Korai & H. Fujitsu, 1987).

(3) Coke may be heated in an inert atmosphere (N_2, He) up to a specified temperature before the introduction of hydrogen. The effect of this treatment depends largely on the temperature at which the hydrogen is introduced. When the coke was heated in helium to 1120 K before the introduction of hydrogen, there was a decrease in the degree of desulphurisation as compared

with simple HDS (Z. M. George, 1975). George attributed this effect to changes in the coke structure that are likely to occur on heating and which make it difficult for H_2S to diffuse out of the coke granules. Also, the microcracks which are induced on the surface of the coke granules, and which very probably contribute to the access of sulphur atoms to hydrogen, tend to decrease in number as the temperature increases beyond 1120 K. Further, the increase in the surface area is much smaller at temperatures $\geq$ 1120 K than at lower temperatures (I. Mochida, T. Marutsuka, T. Furuno, Y. Korai & H. Fujitsu, 1987). Finally, more stable forms of sulphur may be formed which do not readily react with hydrogen to form H_2S. When the hydrogen was introduced at lower temperatures (~720 K), a general improvement in desulphurisation was observed and a maximum degree of desulphurisation of 92% at an HDS temperature of 920 was reported (F. Sef., 1960). The degree of HDS in the range 920–1120 K decreases slightly, or it levels off; but it decreases significantly above 1120 K.

The effect of the initial sulphur content is not evident from the reported results for reasons that are not unlike those discussed earlier (cf. Tables 2 & 3).

As with simple HDS increasing the hydrogen flow rate greatly improves desulphurisation (Table 9). A similar effect is evident on increasing the reaction time (Table 10) or the pressure (Table 11). Sef concluded that increasing the pressure beyond a certain critical value (6.6 bars) would have no effect on desulphurisation.

Table 9. Effect of hydrogen flow rate on HDS (F. Sef., 1960)

H2 flow rate l/g coke/hr	Desulph %	Pressure (bar)
0.5	34	1.0
1.0	40	1.0
2.0	46	1.0
4.0	52	1.0
7.0	52	1.0
18.0	80	3.7
20.5	92	6.6

Table 10. Effect of reaction time on HDS at 1120 K

Time (min.)	Desulph. (%)	Size (mm)	S content (wt. %)	Ref.
30	35	0.06	6.0	14
60	72	0.05	2.4	16
150	36	0.22	5.8	3
160	34–52	0.12	1.9	15
360	45	0.06	6.0	14
600	60	0.14	2.4	16

Table 11. Effect of pressure on HDS at 1120 K

Pressure bar	Desulph. %	S content Wt. %	Time min	Size Mm	Ref.
1.0	46	1.9	160	0.12	15
1.0	35-45	6.0	30–360	0.06	14
2.2	57	1.9	160	0.12	15
3.7	67	1.9	160	0.12	15
6.6	74	1.9	160	0.12	15

With increasing particle size desulphurisation decreases. Sef (F. Sef., 1960) found that increasing particle size up to 0.6 mm decreases rapidly the amount of sulphur removal, but a further increase in particle size had a comparatively small effect. Increasing particle size leads to the decrease of the external surface of the sample, but as the particle size increases beyond 0.6 mm the effect of rough porosity becomes apparent. The effect of particle size is also dependent on temperature, and at 1020 K this effect is rather limited (I. Mochida, T.

Marutsuka, T. Furuno, Y. Korai & H. Fujitsu, 1987) (See also Table 12).

Table 12. Effect of particle size on HDS at 1120 K

Size mm	Desulph. %	Time min.	S content Wt. %	Ref.
0.005	72	60	2.4	16
0.06	35–45	30–360	6.0	14
0.12	46	160	1.9	15
0.14	60	600	2.4	16
0.22	36	150	5.8	3
0.30	26	160	1.8	15
0.62	21	160	2.0	15
1.24	17	160	2.0	15
2.81	13	160	2.0	15
15	23	300	6.0	14

(4) When petcoke is heated in an inert atmosphere to a specified temperature, cooled and then heated in hydrogen, the level of desulphurisation achieved is either decreased (Z. M. George, 1975) or greatly enhanced (I. Mochida, T. Marutsuka, Y. Korai & H. Fujitsu, 1986) in comparison with simple HDS. Again, the reason for this apparent contradiction must be sought in the heat treatment temperature prior to HDS. This is also confirmed by Mochida et al. (I. Mochida, T. Marutsuka, Y. Korai & H. Fujitsu, 1986) who found the temperature of pre-heating very influential on the final desulphurisation level. When coke is preheated to 920 K (I. Mochida, T. Marutsuka, T. Furuno, Y. Korai & H. Fujitsu, 1987) or 1270 K (I. Mochida, T. Marutsuka, Y. Korai & H. Fujitsu, 1986) improved desulphurisation level is reported, but when the coke is heated to 1120 K, the final desulphurisation level is reduced (Z. M. George, 1975; I. Mochida, T. Marutsuka, T. Furuno, Y. Korai & H. Fujitsu, 1987). Enough has already been said on the effects of thermal treatment on coke structure in this temperature range to make the effect of heat treatment temperature on the final desulphurisation level clear and understandable (Table 13).

Table 13. Effect of heat treatment temperature (HTT) on HDS

HTT, K	Desulph. %	Ref.
870	20	17
920	79	14
1070	68	16
1120	22–38	3, 14
1170	60	16
1270	78	16

HDS temperature affects also the final desulphurisation level, which increases with temperature increase up to 1020–1070 K then it decreases. The initial increase may be related to the activation energy, while the final decrease may be due to the onset of sintering (Z. M. George, 1975; B. H. Mahmoud, S. Ayad & S. Y. Ezz, 1968) (Table 14).

Increasing the hydrogen flow rate increases the concentration of hydrogen at the surface of particles and decreases the thickness of the boundary layer around these particles thus promoting the diffusion of gases in and out of the coke particles and increasing the level of desulphurization (B. H. Mahmoud, S. Ayad & S. Y. Ezz, 1968). The heating rate, on the other hand, does not essentially affect the desulphurisation level (I. Mochida, T. Marutsuka, Y. Korai & H. Fujitsu, 1986). Decreasing coke particle size tends in general to improve HDS. The weight loss on HDS varied between 9–15% (I. Mochida, T. Marutsuka, T. Furuno, Y. Korai & H. Fujitsu, 1987).

Table 14. Effect of HDS temperature on degree of desulphurisation

Temp. K	Max. Desulph. %	Ref.
970	24	17
1020	30	17
1020	78	16
1070	79	14
1100	22	3

(5) While the thermal treatment of petcoke in an oxidizing atmosphere of oxygen or air was not found to be an effective desulphurisation process on itself, there is evidence to indicate that pre-oxidizing the coke at moderate

temperatures renders it more amenable to HDS (B. S. Parmar & E. L. Tollefson, 1977; R. B. Mason, 1959). Pre-oxidation will also be accompanied by some sulphur reduction as well. The amount of sulphur removal is related to the weight loss regardless of temperature, but the rate of sulphur reduction is greater at lower temperatures, a fact which indicates, according to some, a more selective SO_2 formation at lower temperatures. This preferential oxidation of sulphur as compared with carbon, which takes place at lower temperatures, allows more effective desulphurisation with a lower consumption of coke.

The beneficial effect of pre-oxidation is probably due to the oxidation of the sulphur bonded into the coke matrix thereby weakening the C-S bonds. Further, some increase in the surface area on pre-oxidation is to be expected, particularly at low temperatures (< 700 K) (Table 15). This may be due to the opening up of micropores in the coke matrix or the spreading apart of planes of largely polycyclic carbon causing the exposure of a larger surface area (B. S. Parmar & E. L. Tollefson, 1977; I. Mochida, T. Marutsuka, Y. Korai & H. Fujitsu, 1987). However, this increase in surface area does not necessarily mean improved desulphurisation. Mason reported (R. B. Mason, 1959) an increase in the surface area that produced only slight improvement in desulphurisation. Pre-oxidation induces also many large cracks in almost all grain cokes at temperatures less than 700 K (I. Mochida, T. Marutsuka, Y. Korai & H. Fujitsu, 1987). When lump coke was pre-oxidized, a large number of small cracks was induced in the coke surface, but these were removed on polishing which indicates that they were very shallow in comparison with grain size (I. Mochida, T. Marutsuka, T. Furuno, Y. Korai & H. Fujitsu, 1987).

Table 15. Variation of surface area with pre-oxidation temperature (R. B. Mason, 1959)

Temp. K	Surface area (m^2/g)
Initial value	7.0
610	163
640	339
670	199
730	83
860	10

Up to 75% of the sulphur present in oil sands coke was removed when the coke was pre-oxidized at 550 K for eight hours followed by hydrodesulphurisation with hydrogen at 920 K for eight hours (B. S. Parmar & E. L. Tollefson, 1977). It has been suggested that the physical basis for this may be based on the chemistry of such thiophenic compounds in coke that are most resistant to conversion by hydrodesulphurisation but are most readily amenable to oxidation and extractive desulphurisation.

As has been pointed out by several workers, any improvement that is likely to occur as a result of pre-oxidation is offset by the increased weight loss. Weight loss can indeed be substantial if pre-oxidation is prolonged. Mason reported 38% weight loss after pre-oxidation at 640 K for 1020 minutes (R. B. Mason, 1959). Effective improvement in HDS can, however, be achieved after less periods of time at considerably less weight loss (max. 7%). Lower temperature pre-oxidation promotes higher levels of HDS as well. The optimum temperature for pre-oxidation was found to be in the range 570–620 K (R. B. Mason, 1959; I. Mochida, T. Marutsuka, T. Furuno, Y. Korai & H. Fujitsu, 1987; I. Mochida, T. Marutsuka, Y. Korai & H. Fujitsu, 1987; Z. M. George, B. S. Parmar & E. L. Tollefson, 1977). Pre-oxidizing the coke at a lower temperature (550 K) did not have a beneficial effect on HDS (B. S. Parmar & E. L. Tollefson, 1977). The reaction was found to be too slow at 630 K also (R. B. Mason, 1959).

It was shown by Mason (R. B. Mason, 1959) that HDS of pre-oxidized coke is less affected by pressure increase and is less sensitive to temperature increase above the optimum observed for non-preoxidised coke. Higher temperatures can therefore be employed to good effect. This may be explained in terms of the change in the nature of sulphur present in the coke due to the oxidation resulting from the pre-treatment. The presence of oxygen atoms may also strengthen the coke structure sufficiently to make the coke less susceptible to sintering (B. S. Parmar & E. L. Tollefson, 1977).

The addition of water during the pre-oxidation treatment accelerates oxidation especially at lower temperatures, probably by accelerating the liberation of oxidized carbon from the coke surface, thus increasing the surface area of the coke. Oxidative desulphurisation is, however, slightly retarded by water, but this does not affect the overall desulphurisation which is in fact improved as a result of enhanced HDS (I. Mochida, T. Marutsuka, Y. Korai & H. Fujitsu, 1987). There are conflicting reports on the role of varying the amount of water on desulphurisation. Mochida et al. (I. Mochida, T. Marutsuka, Y. Korai & H. Fujitsu, 1987) using ground coke found this role to be small, but when lump coke was used varying the amount of water slightly reduced the desulphurisation level significantly (I. Mochida, T. Furuno, H. Fujitsu, T. Oyama & K Fujimoto, 1988) (Table 16).

Table 16. Effect of the addition of water (during the pre-oxidatin of coke) on HDS

Pre-treatment				HDS			Ref.
Temp. K	Time, min.	Desulph. %	Wt. Loss %	Temp. K	Desulph. %	Wt. Loss %	
720	15	19	27	1020	61		18
720	45	5	4	970	47	10	9
670	35	23	24	1020	72		18
620	65	5	4	1020	65	7	14
620	125	25	21	1020	88		18

(6) Lowering the partial pressure of hydrogen by dilution with helium gave a proportional decrease in the degree of desulphurisation at the same total flow rate (Z. M. George, 1975). Similar results were reported when hydrogen was diluted with nitrogen (R. B. Mason, 1959) (Table 17).

Table 17. Effect of diluting the hydrogen with nitrogen on HDS (Temp. 980 K, flow rate 1.15 l/g coke/hr) (R. B. Mason, 1959)

Gas used	Residence time (min.)					
	10	20	30	60	110	120
H_2	0	13	16	20	27	36
$H_2 + N_2$ (50-50 ratio)	0	10	13	14	17	19

(7) The presence of steam in HDS can have variable effects depending on the temperature and/or steam flow rate (Z. M. George, 1975; I. Mochida, T. Furuno, H. Fujitsu, T. Oyama & K Fujimoto, 1988; R. B. Mason, 1959) (Tables 18 & 19).

Table 18. Effect of steam flow rate on HDS (I. Mochida, T. Furuno, H. Fujitsu, T. Oyama & K Fujimoto, 1988)

Steam flow rate, (l/h)	Max. Desulph. %
-	32
0.45	37
2.4	22

Table 19. Effect of temperature on HDS with steam (R. B. Mason, 1959)

Temp. K	Max. desulph. %	
	With steam	Without steam
1090	20	23
1140	20	13
1200	13	6

(8) The addition of H2S has a retarding effect on HDS, and increasing the partial pressure of H_2S beyond a certain value may lead to sulphur incorporation as is reported by George (Z. M. George, 1975). Similar results were also obtained by Mason (R. B. Mason, 1959) when H_2S was added to hydrogen at 980 K, and a sulphur

increase of 14% was observed.

(9) Finally it appears that impregnating the coke with an aqueous solution of NaOH prior to HDS enhances the desulphurisation (Table 20). Ground coke is mixed with aqueous NaOH and the mixture is stirred and heated to dryness. George et al. (Z. M. George & L. G. Schneider, 1982) reported that the optimum temperature for drying was about 350 K and that higher or lower temperatures reduced the efficiency of desulphurisation. When Mason (R. B. Mason, 1959) used higher temperatures (520 K), however, he achieved a high degree of desulphurisation (95%). Impregnation in air or in an inert atmosphere had no effect on HDS (Z. M. George & L. G. Schneider, 1982). Coke can also be mixed with NaOH powder (N. Miyoshi, S. Tsutsumi & N. Sonoda, 1975).

Table 20. Effect of NaOH-impregnation on HDS (Z. M. George & L. G. Schneider, 1982)

Process	Max. Desulph. %
Simple HDS	31
HDS with NaOH impregnation	95
HDS with wet H2 and NaOH impregnation	85

The most significant variables in this process are temperature, time and NaOH/coke ratio.

An optimum temperature (~1000 K) was reported (Z. M. George & L. G. Schneider, 1982; N. Miyoshi, S. Tsutsumi & N. Sonoda, 1975) at which maximum desulphurisation was achieved. But, whereas George et al. (Z. M. George & L. G. Schneider, 1982) reported a desulphurisation increase with reaction time at 1000 K up to 120 min. others found a desulphurisation decrease (N. Miyoshi, S. Tsutsumi & N. Sonoda, 1975) (Table 21). This might be due to an unfavourable reaction between the coke and sodium sulphide.

Trace amounts of NaOH could have a very pronounced effect on desulphurisation, and maximum desulphurisation was obtained at an NaOH/coke ratio of 0.04 (at 1000 K). When a lower ratio (0.01) was used with delayed coke only 25% desulphurisation was reported (Z. M. George, B. S. Parmar & E. L. Tollefson, 1977). Higher ratios were used for effective desulphurisation (0.14 with delayed coke and 0.21 with fluid coke) (Z. M. George, B. S. Parmar & E. L. Tollefson, 1977), but these higher ratios were probably not necessary in view of the results reported in (Z. M. George & L. G. Schneider, 1982).

Table 21. Effect of reaction time on HDS with NaOH impregnation (Temp. 1020 K, NaOH/coke 0.22) (N. Miyoshi, S. Tsutsumi & N. Sonoda, 1975)

Time, min.	Desulph. %	Wt. Loss %
5	79	10
10	86	10
15	84	10
30	82	10

The weight loss on HDS amounted to 10–15% (Z. M. George & L. G. Schneider, 1982; N. Miyoshi, S. Tsutsumi & N. Sonoda, 1975).

Reducing the hydrogen partial pressure by dilution with helium had a retarding effect on desulphurisation. The use of steam with hydrogen resulted in little or no reduction in the level of desulphurization (Z. M. George & L. G. Schneider, 1982; N. Miyoshi, S. Tsutsumi & N. Sonoda, 1975).

Whereas HDS is coke-particle-size dependent (to some extent) and diffusion-controlled, impregnation with NaOH eliminated this effect and no variation of the level of desulphurisation with particle size was observed, and pore diffusion was found not to be significant. Although deep cracks were observed on the treated coke, no indications of the opening up of pores were evident.

Impregnation with NaOH resulted in significant loss of surface area due to the filling up of pores with adsorbed NaOH, and the surface area remained negligible after HDS and the removal of ~96% sulphur (Z. M. George & L. G. Schneider, 1982). Other workers reported a six-fold increase of surface area as a result of HDS (R. A. Ridley, 1970).

The explanation for the enhancement of desulphurisation as a result of the impregnation with NaOH is given by George and Schneider (Z. M. George & L. G. Schneider, 1982) as follows: It is possible according to them "that during impregnation and drying, which may be considered as an activation process for this reaction, the C-S bonds are weakened and these reactive sulphur compounds may diffuse towards the surface of the granules where they react readily with hydrogen to form H_2S. As H_2S is now formed on the external surface of the granules, the rate may be limited by film and not by pore diffusion as observed. The following tentative mechanism may explain desulphurisation of the coke. It is probable that sulphur compounds in the coke may be present as organic sulphides of the type R-S-R, where R could be an aromatic or aliphatic group.

$$\text{R-S-R} + \text{HO}^- \text{Na}^+ \Longrightarrow \text{R-S-Na}^+ + \text{ROH}$$

$$\text{R-S-Na}^+ + \text{ROH} \Longrightarrow \text{RONa}^+ + \text{RSH}$$

$$\text{ROH} + \text{H}_2 \Longrightarrow \text{RH} + \text{H}_2\text{O}$$

$$\text{R-S-H} + \text{H}_2 \Longrightarrow \text{RH} + \text{H}_2\text{S}$$

$$\text{R-O-Na}^+ + \text{H}_2\text{O} \Longrightarrow \text{ROH} + \text{NaOH}$$

(It) is possible that the NaOH generated in situ by the last reaction could aid in enhanced desulphurisation.

Alkaline reagents, other than NaOH, were used and the few experiments conducted indicate that the effectiveness of the reagents decreases in the order NaOH > LiOH > KOH, the respective desulphurisation levels being 88, 61 and 53 (Z. M. George & L. G. Schneider, 1982).

Miyoshi et al. found that alkali desulphurisation proceeded smoothly under hydrogen when the coke was exposed to microwave radiation (N. Miyoshi, S. Tsutsumi & N. Sonoda, 1975). Up to 96% sulphur was achieved with a hydrogen flow rate of 0.4.

George and Schneider mixed Na2CO3 mechanically with coke and found that effective desulphurisation can be achieved by using a higher weight ratio (0.08) than was necessary with NaOH (Z. M. George & L. G. Schneider, 1982). When coke particles were impregnated with aqueous Na_2CO_3 and the mixture fluidized by hydrogen at atmospheric pressure at 920 K for four hours, 67% of the sulphur was removed and a higher coke yield obtained than by solid Na2CO3 (M. T. Thakker, 1973).

3. Conclusions

Given the fact that the consumption of great amounts of alkali metal compounds is required for effective desulphurisation and that preoxidation reduces the coke yield it becomes evident that hydrodesulphurisation in a fluidized bed offers the most attractive desulphurisation process. This process is expected to be more effective with cokes of high sulphur content and high ash and heavy metals content, as at temperatures less than 1100 K the adverse effects of high ash and heavy metals content on desulphurisation are largely avoided. The process would result in an increased porosity and surface area and improved reactivity. These properties are dependent on the sulphur concentration. The greater the amount of sulphur removed, the greater the structural changes expected in the coke treated. The coke density is expected to increase as a result of the treatment, and there will be some weight loss (< 10%).

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