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The role of sulfur in commercial iron-based Fischer–Tropsch catalysis with focus on C_2-product selectivity and yield

Johan Andries Kritzinger*

Sasol Technology Pty Ltd., Private Bag X1034, Secunda 2302, South Africa

Abstract

This paper presents some insight into the role of sulfur, a well-known Fischer–Tropsch (FT) catalyst poison, regarding the selectivity of ethylene:ethane and C_2-product yield in a commercial, Fe-based, high-temperature, 2-phase FT process.

It is well known that in these kind of processes, the level of sulfur allowed in the feed gas is normally very low (ppb range) and aggressively kept low due to the poisoning effects. The practice generally is to get sulfur levels down as close as possible to zero.

The poisoning effects are well studied in research work and significant information exists in that regard. It is, e.g. known that the poisoning action of sulfur would typically increase selectivity towards more hydrogenated ethane relative to ethylene (the more attractive product). At high enough levels it would kill catalyst activity completely.

This paper highlights the role of sulfur in a typical commercial operation. Data from a period of almost 2 years was used. It was found that under the prevailing actual commercial scale operating conditions, sulfur did not behave as a poison to the catalyst. However, its effect did not become completely negligible either. There were strong indications of sulfur promoting selectivity shifts towards more olefinic C_2-product. These results were also independently confirmed on a different set of data and a different kind of commercial reactor. © 2002 Published by Elsevier Science B.V.

Keywords: Sulfur; Fischer–Tropsch catalysis; Selectivity; Activity

1. Introduction

Sasol is a leader in the field of Fischer–Tropsch (FT) technology and has done substantial research and development on FT catalysts. A valuable part of the FT product spectrum is the ethylene in the C_2-fraction. As ethylene is the more desirable product (over ethane), it is worthwhile to develop some handles to maximize the C_2-olefinity without negatively impacting on the product yields.

As the C_2-fraction is a relatively small part of the product slate, one would expect it to be very sensitive to operational changes. In this regard, the potential impact of syngas sulfur fluctuations on the controllability of the ethylene content in the product slate has always been a topic for debate.

It is rather well known in FT circles that sulfur is a poison to the FT catalyst at low concentration levels in the synthesis gas. Substantial work has been done in the past to establish the effects of sulfur—particularly on a fused iron catalyst as is used in the Sasol Secunda Complex. The majority of research indicated that sulfur deactivates the FT catalyst and also causes some selectivity shifts towards less olefinic (more parafinic products). It has been shown that H_2S adsorbs on the catalyst surface in a rather permanent way, deactivating catalytic sites by accumulating on the catalyst.

Due to this tendency to accumulate and deactivate the catalyst and due to the relatively long catalyst life-

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* Tel.: +27-17-619-2269; fax: +27-17-619-2798.
E-mail address: dawid.duvenhage@sasol.com (J.A. Kritzinger).

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times, most research on sulfur poisoning was done in an accelerated way. Sulfur levels in the syngas were normally much higher than actual values in the plant. Until recently, it was also very difficult to do bench scale work at the low sulfur levels practically experienced in commercial operation.

Based on research results, the typical operating philosophy has always been to maintain sulfur levels as low as possible to protect the catalyst. Typical sulfur levels currently allowed for Fe-based FT are <5 ppb in syngas feed to the reactor.

In the past, some internal Sasol studies did indicate an opposite effect of sulfur, i.e. low-level sulfur would have no negative effect or rather some positive effect on activity and product spectrum. However, in the opinion of this author (and in hindsight to this investigation), these studies did not always get the attention they deserved.

2. Research objectives

As part of developing handles to improve control over C_2-olefinity, it was decided to look at the actual commercial scale impact of sulfur on the catalyst surface. The study had the following objectives:

- To determine the active sulfur levels in the reactors over time, taking into account the different sources of sulfur as well as the net effect of actual SOLCRA (Synthol on-line catalyst removal and addition) activities.
- To relate the sulfur on the catalyst to the variations in C_2-olefinity (selectivity).
- To relate the sulfur on the catalyst to the variations in C_2-product yields (activity).

3. Data analysis

3.1. Data used in investigation

The investigation was done on plant scale and had to tolerate normal production instability and variations. The luxury of laboratory style-controlled conditions and measurements did not exist. The data used covered the period November 1996–September 1998 and included only the eight CFB reactors of one of the Secunda plants (Western Plant). No additional sulfur was added to the reagents in this study, i.e. the feed gas sulfur level and variation were those typically experienced in the plant.

3.2. Assumptions

Some important assumptions that were made to enable numerical representation of the system, are listed below.

1. It is assumed that the catalyst site area is proportional to the atomic surface area of atoms present. (Used when predicting the fraction of sites influenced by sulfur and the base level of sulfur exposed in the reactor.)
2. The effect of carbon formation on the actual number of available sites and the extent thereof as well as variations therein, is not known. (Affects the number of real sites available for reaction and therefore the seriousness of site occupation by sulfur—various calculations with different values were used to show the possible range of effects.)
3. It is assumed that the sulfur that remains in the fresh catalyst after reduction is affected as follows but should be checked by further research:
    - Matrix sulfur not exposed during the reduction process (in the creation of pores and thus more (new) surface area) is assumed to be unaffected and shielded from reagents. This sulfur therefore is practically ignored.
    - Matrix sulfur on the catalyst surface (including the surface created by reduction) is assumed to be removed proportionally to the reduction level. This means that if the reduction level is 70%, then 70% of the exposed sulfur is assumed to be removed. This is not critical as the level of sulfur in the catalyst is assumed at a constant value due to the lack of data.

4. Some sulfur deep in the metal matrix is assumed not to be removed during reduction and this is calculated to be around 94% of the catalyst sulfur content (only 6% regarded as surface sulfur). It is taken as valid to disregard this sulfur. As the particle core shrinks and exposes more S, some sulfur on the surface will split off and become inactive in the reactions and therefore it is assumed that this effect will balance the effect of matrix sulfur being exposed.

5. It is assumed that the catalyst matrix sulfur behaves in the same way than sulfur in the feed gas as far as interference with reactions is concerned. This is highly debatable however.
6. All synthesis gas sulfur is assumed to attach to the catalyst and remain there. This assumption elevates the calculated levels of sulfur on the catalyst and therefore the fraction of sites affected but does not influence the relative effect of sulfur seriously.
7. A typical analysis of an equilibrium catalyst was used as basis to approximate the effect of carbide formation and its dependency on reduction level of the fresh catalyst. This would have some slight impact on the calculated number of sites available.
8. The effect of oxidation of catalyst after the initial move to equilibrium catalyst is not included. No further oxidation is assumed. This is an optimistic assumption in terms of available sites.

3.3. Calculation approach

The calculation approach was as follows. All calculations are based on the entire plant unit. No attempt was made to distinguish amongst different reactors, as the required information on a single reactor basis is just not available. This approach is therefore one of taking a global view on the system.

The sulfur feed into the system is based on analyzer data, synthesis gas flow rates and on catalyst analysis (little information available). The potential influence of sulfur on the catalytic sites was estimated by using atomic volumes and assuming homogenous distributions. This was necessary to make an estimate of what proportion of the relatively high sulfur in the fresh catalyst influences the reactions.

Some allowance was made for other compounds like carbon interfering with the sites and deactivating them. With the number of sites available and the total sulfur accumulation including the active part of the contribution from fresh catalyst, some estimates could be made about the influence of sulfur on the C_2-products.

To estimate the effect of carbon formation on the catalyst inventory, the total mass into and out of each reactor was balanced on a monthly basis to get the actual carbon formation factor. From these calculations that were repeated for each day in the data period, various relationships could be explored.

4. Results and observations

4.1. Available catalytic sites

Traditionally the sulfur carry-over from the gas production units to the FT unit is a critical control parameter. From both sides there is always pressure (and action) to reduce the carry-over as far as possible to guard against catalyst poisoning and complete activity loss. It sometimes happens that plant throughput is constrained or syngas is flared when the required low sulfur specifications cannot be met. However, this is done without knowing how far the operating point is from the threshold value.

To get a grip on this, one could consider a different perspective. One should estimate the number of actual catalytic sites available at any point in time in the reactors and relate that to the sulfur that enters/accumulates in the reactors. One should also distinguish between the effects of sulfur on the site to which it adsorbs (killing it) and on the sites surrounding that site, where it could interfere but may not kill the site. In that way, one would develop some idea about the actual poisoning effect you could expect in relation to contamination levels.

Based on the assumptions already given, the total number of potentially active sites in the system was calculated. This number included the effect of less than 100% reduction as well as oxidation during establishment of equilibrium catalyst. It was further deducted from some calculations done on the plant data that a reasonable stab at the amount of sites that get destroyed by carbon (inclusive of other effects) is possible and an adjustment was made for that.

The next question is: how many sites are affected by a single sulfur atom? The assumption made here is that with a single sulfur atom, a single site will be killed permanently and that the Fe atoms next to the killed one as well as the ones next to those four will be electronically interfered with and thus influenced. Thus, the assumption was made that a single sulfur atom could influence around 10 sites and all calculations around estimated selectivity effects used a value of 10.

Based on this approach, the estimated sulfur level calculated from the plant data is given in Fig. 1. At the worst contamination seen during the 2-year period investigated, about 4% of the available sites could have been influenced and 0.4% killed by sulfur. On average, less than 2% (0.1% of original sites) is influenced and less than 0.2% (0.01%) killed. One must keep in mind that in this result the effects of aging and sulfur accumulation have been discounted as well as reduction level. From this, one could expect that the influence on product spectrum would be fairly small but measurable. One could also deduct that the maximum potential reduction in yield would be about 0.5% (only under circumstances where the reactors are all kinetically limited by the catalytic sites available).

4.2. Effect of sulfur on C_2-olefinity

The generally accepted effect of sulfur poisoning on olefin selectivity (below the threshold that would kill the catalyst) is that higher sulfur levels decrease olefinity and carbon number distribution or the alpha value of the Schulz–Flory distribution (less olefins and lighter product spectrum). High poisoning levels could kill catalyst activity completely and immediately.

One could argue that it is not the sulfur in the feed that affects the olefinity but the sulfur adsorbed on the catalyst. Therefore, the correct way to view this is to address the actual level of sulfur on the catalyst taking into account the sulfur in the feed as well as the effects of catalyst mass, age, SOLCRA, effective reduction levels and carbon formation. Only then can one give a reasonable account of what the actual situation in terms of poisoning is. This was done and the results shown in Fig. 2 as a plot of olefinity against the total mass of sulfur in the reactors. It can be seen that there is a direct proportionality between olefinity and sulfur. The effect is fairly strong with olefinity changing on average with 5% points over the sulfur range that was experienced. The direction of this proportionality, however, is opposite to general perception. The large amount of scattering is obviously due to the other factors also at play.

One dilemma in interpreting this result is that one may argue that higher sulfur may be advantageous under specific circumstances like having a high catalyst inventory or high level of reduction but that the effect may reverse quickly under another set of conditions. To shed some light on this, the data presented in Fig. 2 was also separated into different time zones. Fig. 3 contains the data during a period that the C_2-olefinity was low and where one could expect to see an inverse proportionality if sulfur exhibited some poisoning behaviour. Interesting is that also during this period, the relationship stayed directly proportional. This holds for all the intervals that were used. This is strong evidence that the observed relationships could be accepted as representative of reality.

This result is quite surprising and, to some extent, unexpected. It also could change the view on the role of sulfur in FT. This gave a different perspective on numerous studies that reported the positive effects of low-level sulfur poisoning on olefinity.

It has been reported that, at low levels, sulfur has some selectivity modification effects that may enhance olefinity. When one scan the reported studies on this topic, it becomes clear that the syngas sulfur levels that those authors reported as being in the threshold range, in fact are an order (or more) higher than what Sasol experience in practice. Without going into too much detail of reported literature, it could be summarized as follows.

Duvenhage [1] provides an extensive review of literature on the poisoning effects of H_2S and other sulfur compounds. Various authors are cited (will not be repeated here) and this literature can be summarized as follows (for the purpose of this study):

- No deactivation was observed in an iron catalyst over 8 weeks operating at a H_2S concentration of 32 ppm (32 000 ppb) [2+ Refs.].
- Beneficial effects of sulfur are reported in many cases [10+ Refs.].
- Sulfur plus alkali promoters extend life of group VIII metal catalysts and enhance olefin production [3+ Refs.].
- With 0.8 mass% sulfur in Co catalyst selectivity shifts to heavier products are reported. Above 0.8% deactivation occurred [3+ Refs.].
- Increased oil yields and olefin selectivity is reported in many cases.

Bromfield [2] also reported recently similar effects of low-level sulfur on Iron catalyst.

In conclusion of this literature overview it appears as if low levels of sulfur (0.05–0.8 mass% on the catalyst) actually could have promoting effects towards olefins as well as yields while levels larger than 1% deactivate the catalyst. In this light, we have to deduct that what is observed in this study is well in line with published literature.

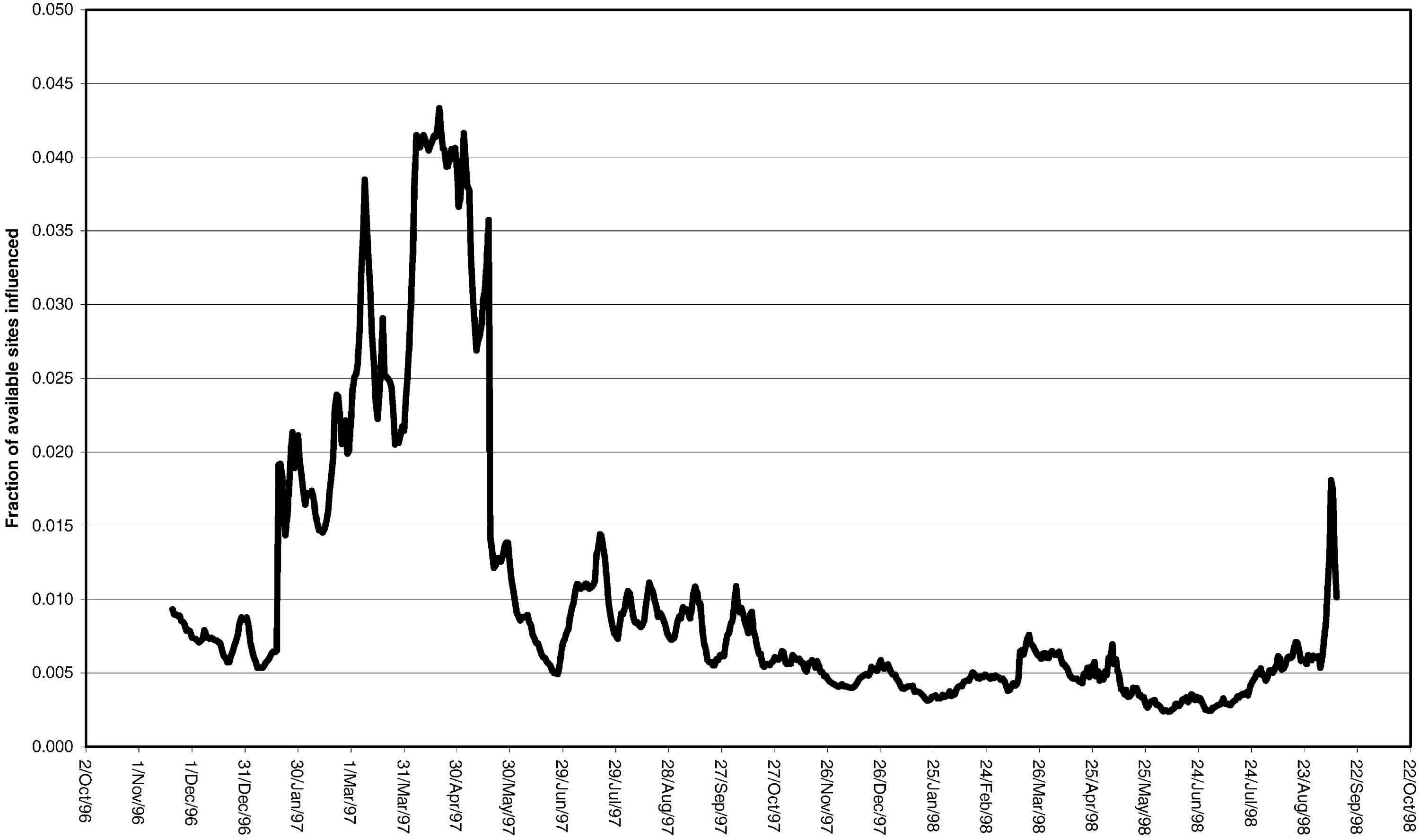

Fig. 1. S influence on available catalyst sites.

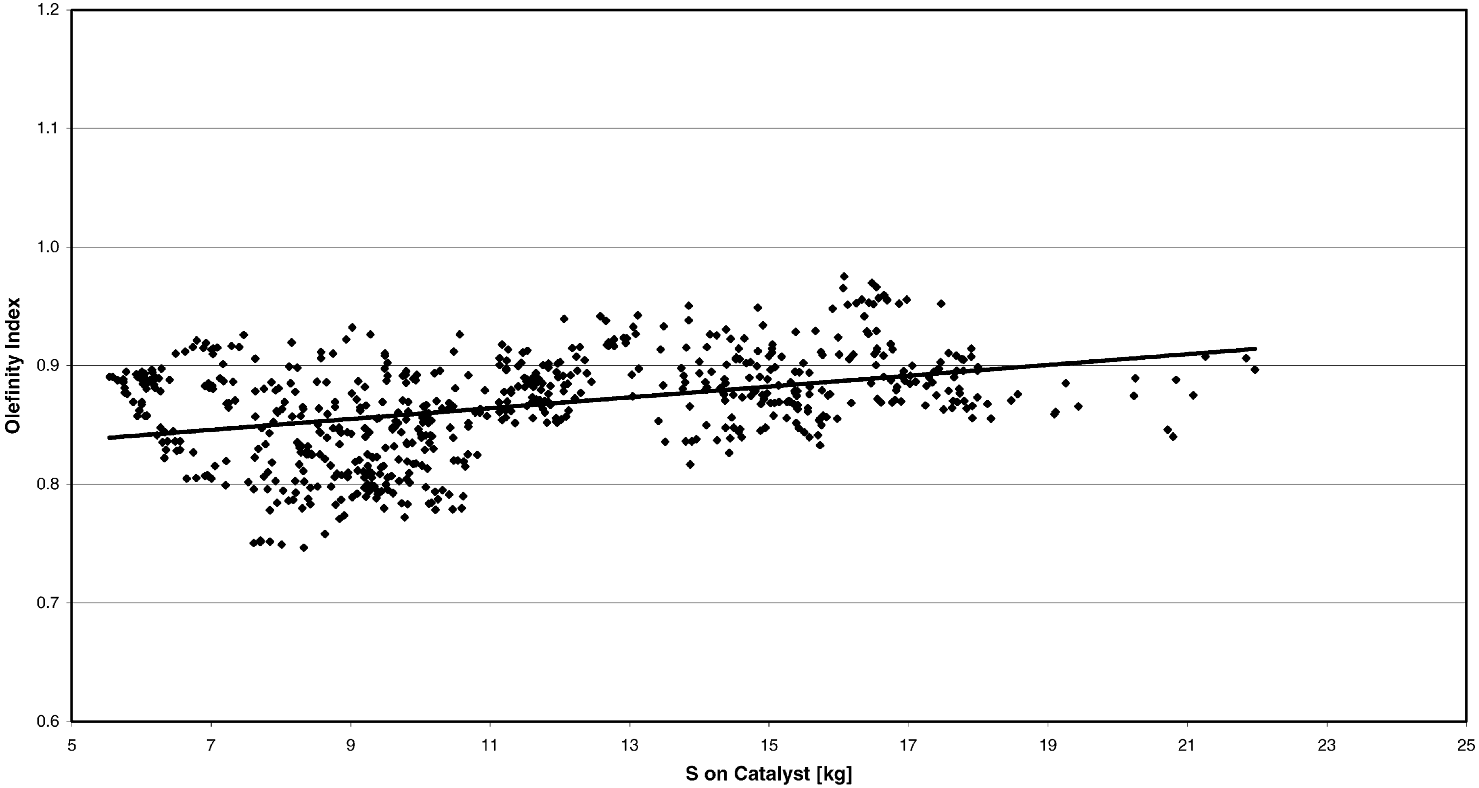

Fig. 2. Olefinity (C_2H_4%) vs S on catalyst (full period).

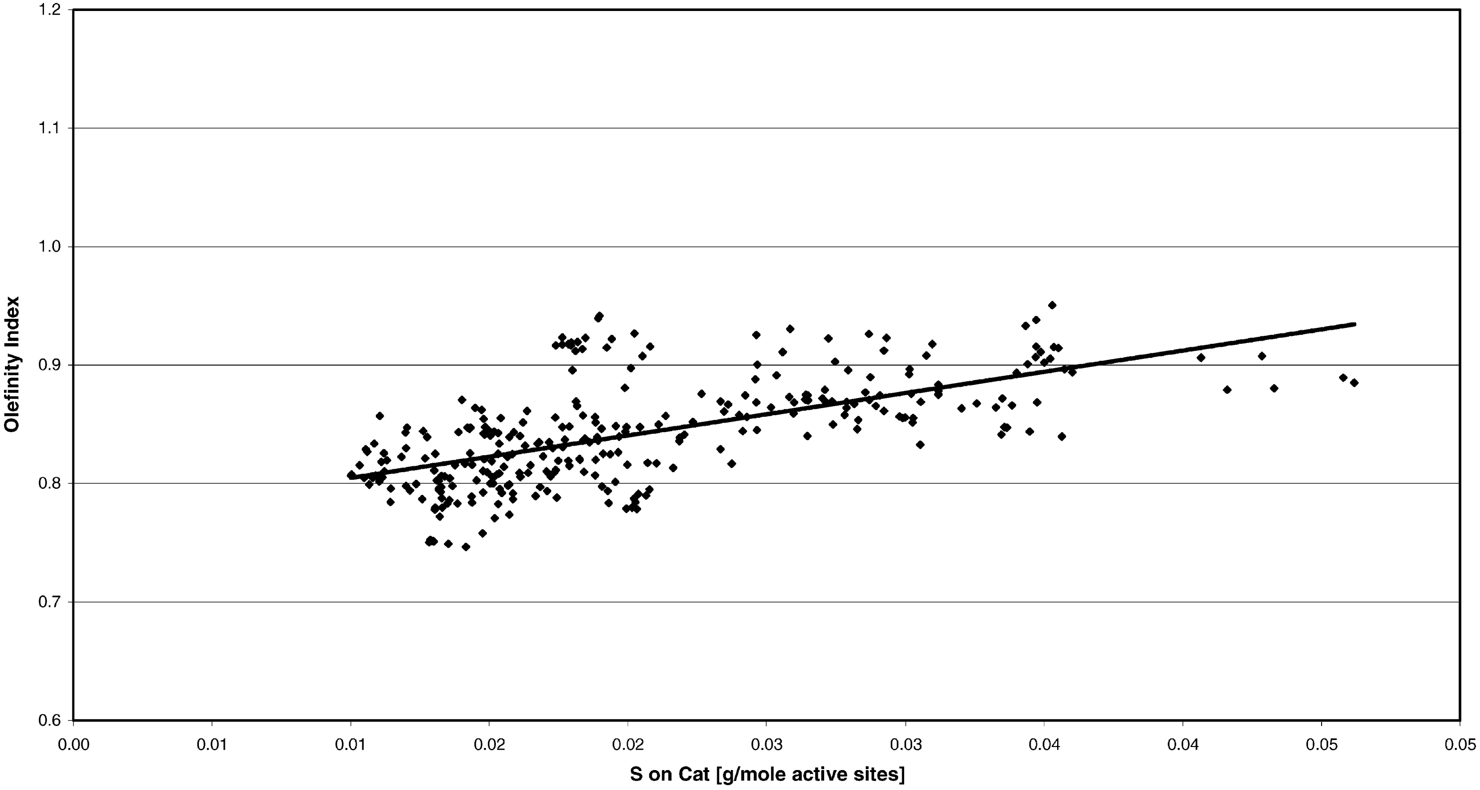

Fig. 3. Olefinity (C_2H_4%) vs S concentration on catalyst (during low C_2 period).

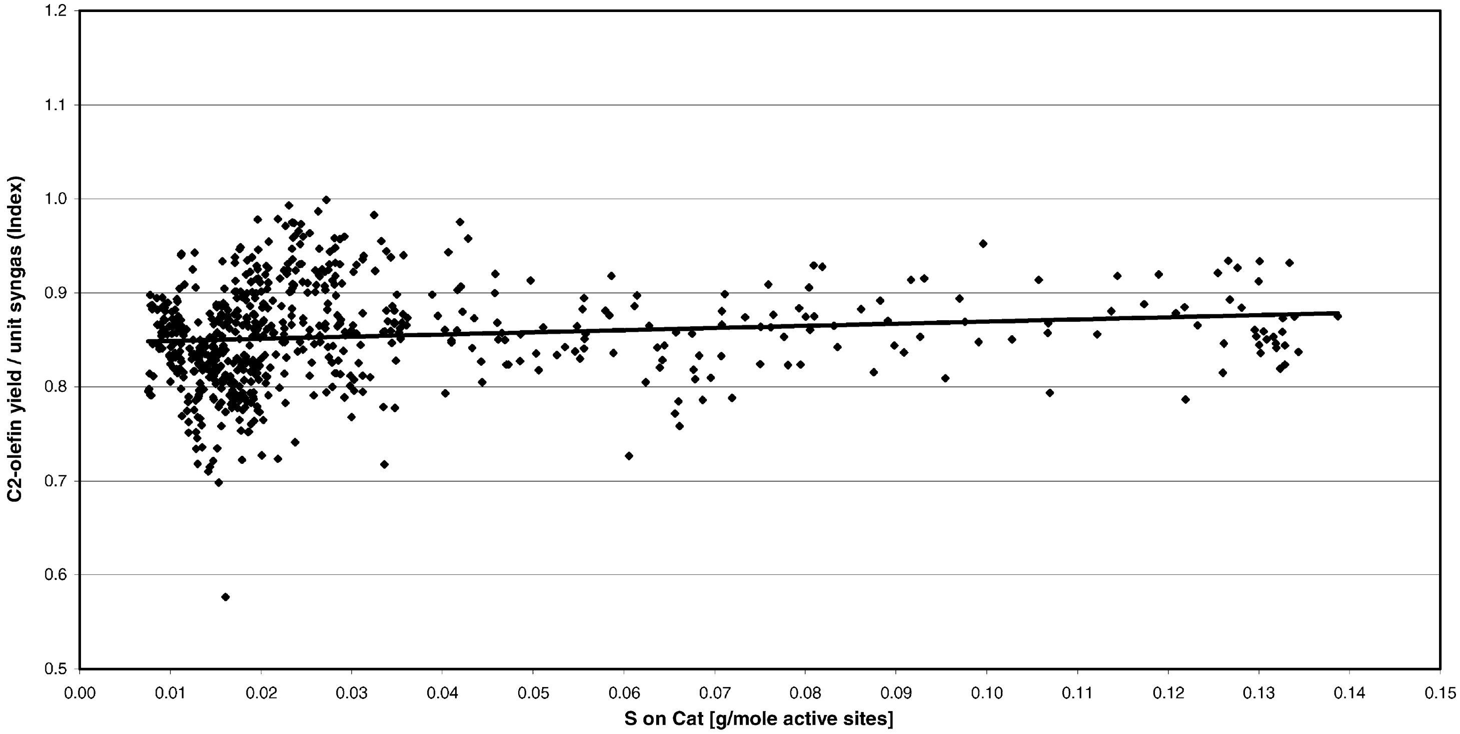

Fig. 4. Activity: C_2-olefin yield vs [S] on catalyst.

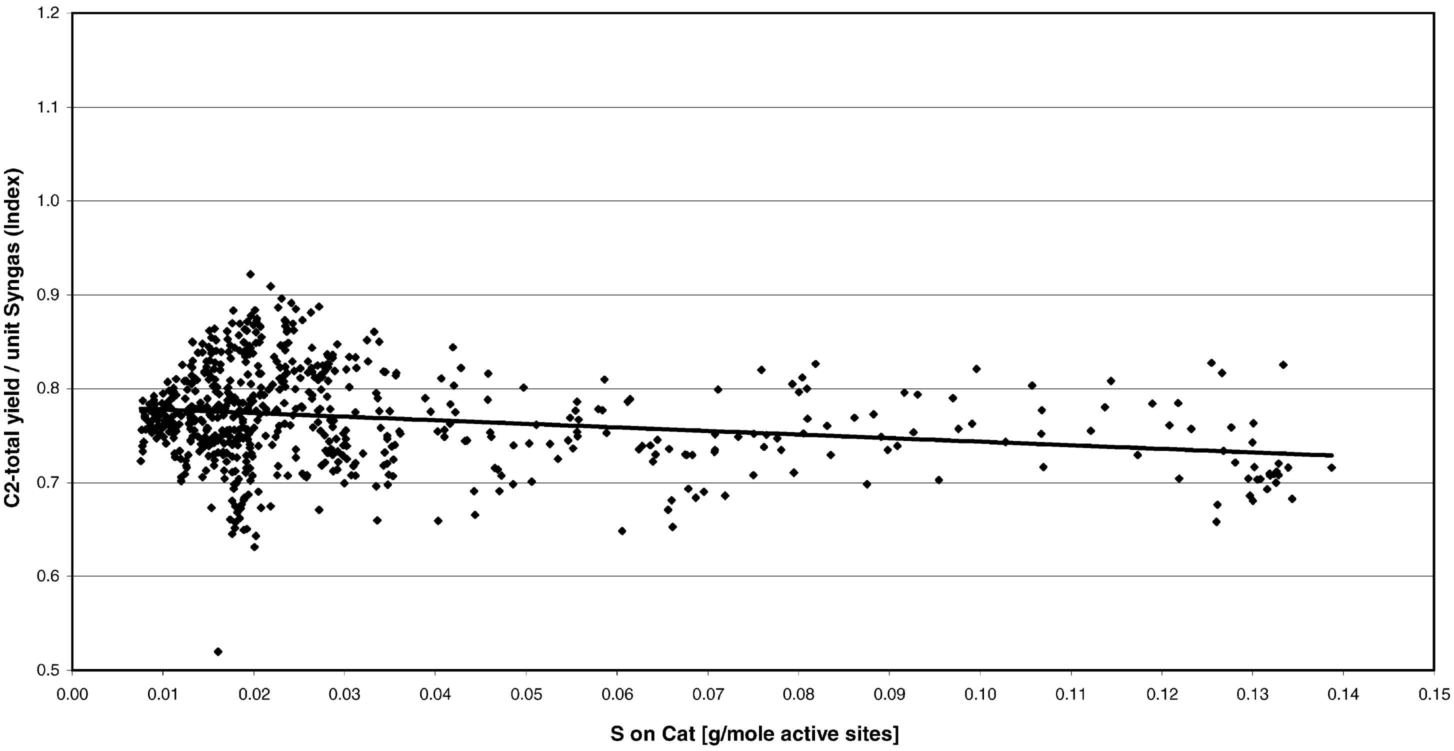

Fig. 5. Activity: C_2 total yield vs S on catalyst.

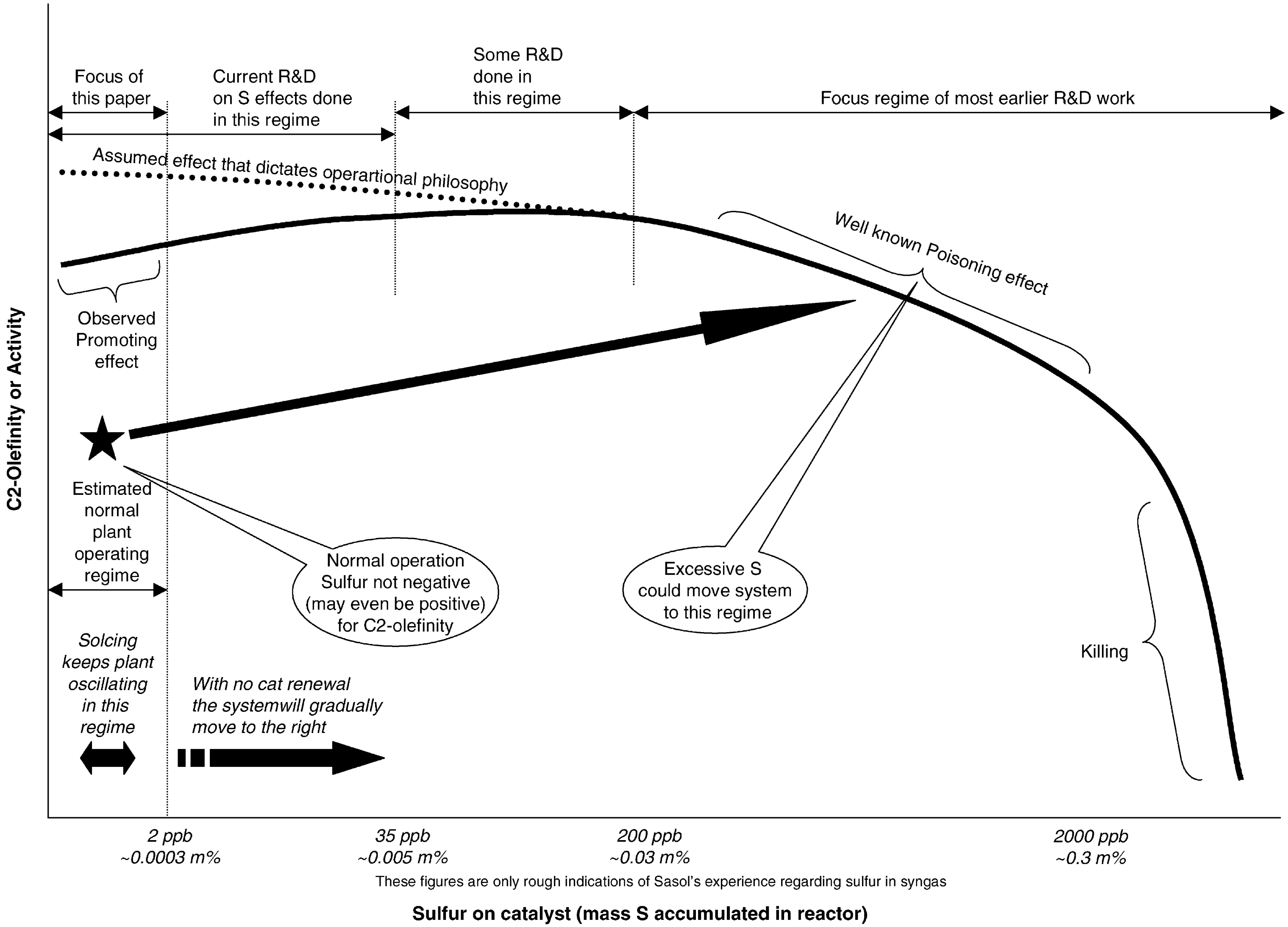

Fig. 6. Sulfur on Fe FT catalyst vs olefinity and activity.

If we now compare the literature figures with those found in this study, we can put things in perspective. The peak sulfur level on the catalyst over 2 years was 0.003 mass% and on average it was 0.002%. This is 16 times lower than the lower limit reported in the above literature.

4.3. *Effect of sulfur on C_2-yields*

In general, it is accepted that increased sulfur levels would affect selectivity (thus increasing the yield of low carbon number products at the expense of the longer chain products) and also activity (especially when serious poisoning is experienced—the yields would drop across the carbon number spectrum). Fig. 4 plots C_2-olefin yield (per unit pure gas) and Fig. 5 the C_2-total yield against sulfur concentration on the catalyst. It is evident that there is only a weak positive slope in the olefin yield and a weak negative slope in the total C_2-yield.

One could conclude that the effect of sulfur on the yield of C_2's is weak but rather positive than negative for the C_2-olefins and rather negative than positive for the total C_2-yield. This is, thus also opposite to general belief but again in line with what is reported in the mentioned literature.

4.4. *Handles for C_2-olefinity*

A regression model was fitted to the data to test the net effect of sulfur on catalyst as well as other variables like reduction level, catalyst promotion, catalyst age and mass of catalyst in the reactors. The amount of sulfur on the catalyst was used rather than the sulfur concentration on the catalyst surface as the latter is to some extend dependent on age as well as mass and reduction level (i.e. not independent). One concern is that age and sulfur on catalyst is not independent. This was checked and can be assumed as such. The sulfur variations in the feed gas has a large influence on sulfur on the catalyst whilst the SOLCRA strategy has the larger influence on catalyst age.

The derived model could explain a significant part of the normal operational fluctuations. From the model, it is concluded with a high degree of confidence (based on *f*- and *t*-statistics and standard errors) that—for the typical commercial operating regime as applied by Sasol (and with all else constant)—olefinity is:

- directly proportional to the catalyst age,
- directly proportional to the amount of sulfur on the catalyst,
- inversely proportional to the reduction level,
- inversely proportional to the amount of catalyst,
- the effect of catalyst promotion depends on the kind of promotion used and was in line with what was expected.

With this analysis, the core of the C_2-selectivity variation could be explained successfully and the main handles for optimization were thus defined. It is important to note that these effects apply to the specific operating regime and could be different in other regimes (as indicated in Fig. 6).

5. Conclusions

5.1. *Available catalytic sites*

It appears that, for normal operation at Sasol, at worst less than 0.2% of the available catalyst sites are killed by sulfur and less than 2% are influenced by it.

5.2. *Effect of sulfur on selectivity and activity*

There is good evidence that, in the regime that Sasol operates, the sulfur on the catalyst is not detrimental to C_2-olefinity (with the possibility that it may even be advantageous). This conclusion is also supported in literature and by Sasol pilot plant studies in the 1980s.

There is no evidence that the plants operate close to the point where catalyst activity is negatively impacted by build-up of sulfur over time.

It is concluded that the role of sulfur as a potential handle in C_2-olefinity maximization could be that of promoting olefinity and not decreasing it. Fig. 6 attempts to provide an overall perspective on this.

5.3. *Explaining C_2-selectivity variation*

The main operational handles for C_2-olefinity were identified as reduction level, catalyst age, sulfur on the catalyst, mass of catalyst in the reactor and also the normal promoters used.

It is also concluded that the attention given to driving down H_2S in the syngas could work against the objective of maximizing ethylene in the C_2-fraction.

6. Continued research

After internally publishing these results, an independent evaluation was done by Espinoza [3]. This evaluation was, however, applied to SAS reactor operation. It confirmed the relationships found during this study (although some absolute values varied due to the different SAS product selectivity) and specifically the "promoting" effect of the sulfur.

An extensive commercial scale FT test run was initiated after this study to prove these conclusions and to evaluate the risks involved in using these findings as an opportunity to optimize reactor FT operations. It deliberately and continuously introduced sulfur into one reactor over a period of 6 months. The dose was also increased stepwise in the hope of reaching the turning point between the promoting and poisoning regimes. Sulfur levels on the catalyst as high as 10–15 times that seen in normal operation (and reported in this paper) were reached. This work is now in the final evaluation stage and it can be reported already that no significant negative effects were found even at the (relatively) high levels of sulfur introduction. (These levels are still below those reported in the mentioned literature as the regime where deactivation steps in.)

Research work has also been started to further confirm these effects in controlled lab scale studies and also to understand the mechanisms at play in generating these effects. Three possible explanations are currently being considered:

- The positive effect on olefinity could be because of selective poisoning of highly active catalyst sites thereby preventing hydrogenation of ethylene.
- It could also be general mild poisoning of the catalyst surface resulting in early departure of species from the surface before full hydrogenation could take place.
- Thirdly it could be the sulfide species stabilizing the Hagg carbide phase of the catalyst in a similar way than how H_2S prevents metal dusting in reformers [4].

Acknowledgements

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