

01-11947

ERL 88-24(J)

Effect of Oxygen Concentration on Temperature Runaway During Regeneration of Hydrotreating Catalyst

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(Received 16 March 1988, revised manuscript received 10 June 1988)

ABSTRACT

Spent Shell 424 nickel-molybdate catalyst supported on γ -alumina, which was used to hydro-treat a synfuel distillate, was regenerated by burnoff using a wide oxygen concentration range medium. A linear correlation was established between oxygen concentration and the ΔT parameter reflecting the temperature runaway on the oxidizing gas admission. The addition of steam or carbon dioxide resulted in a dilution effect only. Catalyst pretreatment by extraction and reduction resulted in a significant increase in the initial rate of sulfur dioxide formation and a decrease in carbon monoxide and carbon dioxide yields.

INTRODUCTION

A continuous decline in catalyst activity during hydroprocessing and hydro-treating operations is a generally known phenomenon. The activity loss results from blocking active sites and plugging the catalyst pores by basic and polynuclear aromatic species and high-molecular-weight compounds [1]. At a certain stage the catalyst has to be either replaced or regenerated. For processes employing a fixed bed the catalyst replacement or regeneration usually requires a temporary shutdown of the operation. The shutdown frequency depends on feedstock properties. For light feeds the operation may continue for a long period. In this case the catalyst replacement or regeneration may be combined with planned shutdowns for periodic inspection and/or repairs of the unit.

It is generally known that the activity recovery during regeneration depends on the extent of catalyst deactivation. Thus, for catalysts used to hydrotreat light or medium distillate fractions almost complete activity recovery may be achieved. On the other hand the activity of catalysts used for hydroprocessing heavy residues may be only partly recovered. In this case only a limited number of utilization-regeneration cycles may be performed.

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The coke deposit removal is an essential step for catalyst reactivation. The oxidative burnoff is the most frequently used method for coke removal. The early stages of the contact between oxidizing medium and coke are of crucial importance since the burnoff of the most reactive parts of coke molecules may result in temperature runaway causing undesirable changes to catalyst material. Some precautions have to be taken to contain the temperature rise within acceptable limits. Although regeneration of hydrotreating catalysts has been performed commercially, no experimental data of this nature were published in the scientific literature.

In the present work the attention was focussed on the early stages of the burnoff of a nickel-molybdate catalyst used to hydrotreat Syncrude distillates. The aim was to determine the effect of oxygen concentration in oxidizing gas on temperature rise. The effect of catalyst pretreatment such as extraction and heating in hydrogen was also investigated. The aim was to simulate the effect of de-oiling catalyst bed at the end of operation on burnoff temperature profile. The addition of steam and carbon dioxide to oxidizing mixture and their effects on burnoff profile were explored as well. The work was carried out in a specially designed reactor equipped with two sets of four thermocouples for a continuous temperature recording in the bed and on the reactor walls.

EXPERIMENTAL

Catalyst

A trilobe Shell 424 nickel-molybdate catalyst supported on γ -alumina, which was used to hydrotreat synthetic distillates obtained from flexicoking of Athabasa bitumen was used. The as received catalyst was screened to remove fines. The experiments were carried out on as received as well as pretreated catalysts. The pretreatment included either tetrahydrofuran (THF) extraction or de-oiling in hydrogen. For the former the catalyst was extracted in the Soxhlet apparatus until disappearance of the solvent discoloration. For de-oiling the catalyst was heated from room temperature to 200°C in a flow of nitrogen. At this point nitrogen was replaced by hydrogen and heating continued to 400°C

TABLE 1

Analysis of catalysts (wt.-%)

	As received	Extracted	H ₂ treated
Carbon	7.4	5.2	4.6
Hydrogen	1.2	1.0	0.2
Nitrogen	0.40	0.46	0.2
Sulphur	7.13	7.20	7.10

with an additional 30 min hold at this temperature. Some properties of the catalyst (as received and pretreated) are shown in Table 1.

Apparatus and procedure

The externally heated reactor (15 mm I.D.) was made of stainless steel. The simplified diagram of the reactor is shown in Fig. 1. A 200-mesh sieve was placed on the distributor plate to support the catalyst load. With this arrangement and using the prescreened catalyst, the reproducibility of temperature profiles significantly improved presumably because of diminishing the non-uniform flows through the bed. The temperature was measured by a set of four thermocouples placed at different heights at the centre of the bed. For this set the thermocouple wells entered through reactor walls at right angles. Another set of four thermocouples at the same bed heights was placed on the reactor walls. All thermocouples were connected to digichannels for continuous temperature recording.

The experiments were carried out with 20 g of catalyst extrudates. This amount gave about 80 mm bed height. The oxidizing medium entered at the bottom. Total flow of nitrogen-oxygen mixtures was always 2 l/min. Whenever steam was used, its feed rate was always 1 g/min. Prior to the admission of oxidizing gas the catalyst bed was heated in nitrogen stream until the burnoff temperature was reached and stabilized. For most of the experiments the burnoff temperature was 350°C. For the catalyst de-oiled in hydrogen the hy-

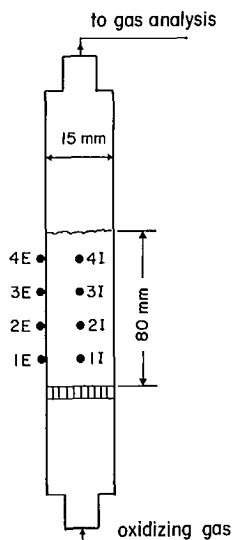


Fig. 1. Simplified arrangement of the fixed bed reactor.

drogen flow was replaced at 400°C by N₂. This was followed by a temperature adjustment.

Analysis

The burnoff products exiting at the top of the reactor were split for simultaneous analyses using an on-line mass spectrometer and infrared analyzer. These systems were connected to datalogs which could record and print the product composition every 20 s.

RESULTS AND DISCUSSION

A proper measurement of temperature is crucial for obtaining reliable data on spent catalyst burnoff. As expected the temperature maximum measured on reactor walls was consistently lower than that measured in the bed (Table 2). Moreover, for the former the occurrence of maxima was delayed by several minutes. This is attributed to heat losses and/or a radial temperature gradient. For 2 vol% oxygen the difference between the inner and outer temperature was much smaller than that for air. It is believed that for 2 vol% oxygen the burnoff is chemically controlled and the temperature measured in the bed approaches that of the pellet [2]. However, for air the burnoff of the last part of coke at the pellet centre may result in a higher interior temperature compared with the pellet skin temperature [3] especially in later burnoff stages. In this case the temperature measured in the bed, although more reliable than the external temperature may not reflect the actual temperature of a single pellet. Such conditions may be approached during diffusion controlled burnoff.

The internal temperature profiles from catalyst burnoff in air and nitrogen-oxygen mixture containing 2 vol% oxygen are shown in Fig. 2A and B, respectively. The catalyst bed temperature before the admission of the oxidizing gas was 350°C. For air the temperature increased dramatically and then decreased

TABLE 2

Effect of oxygen concentration on the outer and inner temperature (°C)

Thermocouple	Oxygen concentration			
	2 vol%		21 vol%	
	Inner	Outer	Inner	Outer
1	388	384	816	464
2	410	402	747	508
3	410	405	680	526
4	407	398	624	506

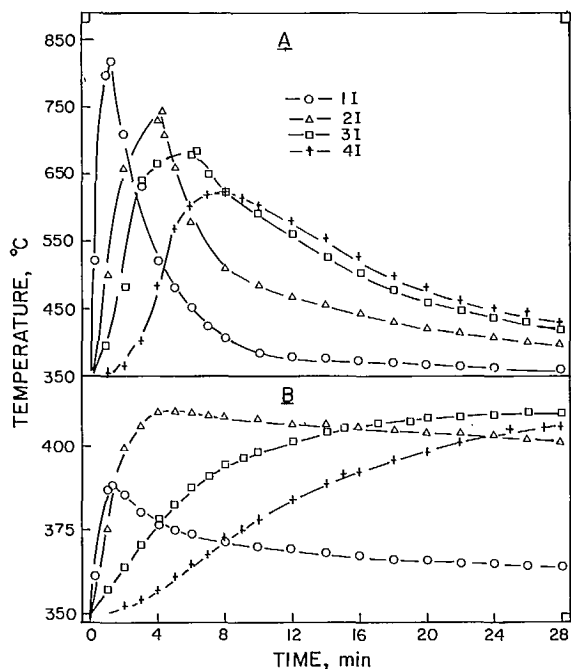


Fig. 2. Effect of oxygen concentration on temperature profile (catalyst bed at 350°C before admission of oxidizing gas). (A) 2 l air/min; (B) 2 l nitrogen-oxygen (98:2, v/v)/min.

after reaching a maximum. The most abrupt temperature change occurred at the bottom of the bed. The occurrence of maxima at different times for different thermocouples indicates the progress of burning zone. The lower maximal temperatures at the top are attributed to dilution of air by carbon dioxide produced at the bottom of the bed. As expected for 2 vol% oxygen the temperature runaway was much smaller than that for air.

The effect of oxygen concentration on burnoff is evident from the marked difference in product yields for air and 2 vol% oxygen (Fig. 3) though the carbon dioxide/carbon monoxide ratio in burnoff products was similar. This suggests that a complete carbon combustion dominates the coke burnoff even at low oxygen concentrations. The amount of coke and sulphur content of the catalyst (Table 1) confirm that most of the sulphur dioxide was produced during oxidation of Mo and Ni sulphides to corresponding oxides [4]. For the burnoff in air, the oxygen appeared in the exiting gas after about 2 min and its concentration steadily increased to about 18 vol% at the end of the run. For the burnoff in 2 vol% oxygen gas, the oxygen appeared only after about 20 min and at the end of the run its concentration reached about 0.3 vol%.

The parameter ΔT was chosen to study the effect of oxygen concentration, expressed as the volume of oxygen flowing per unit time and unit weight of

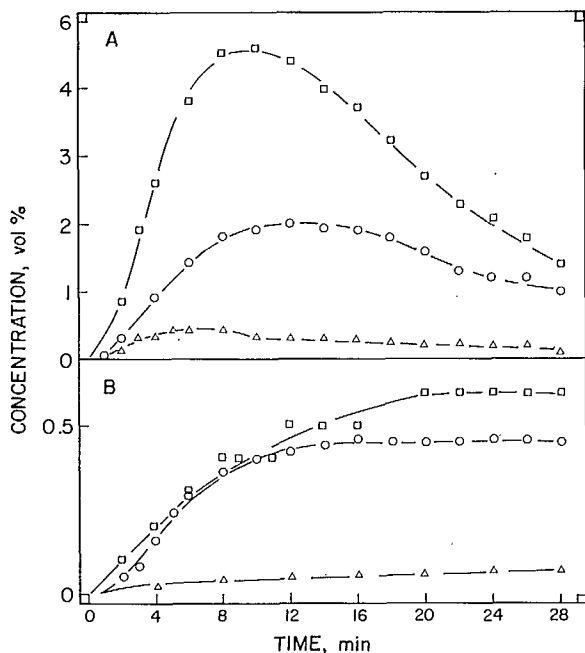


Fig. 3. Effect of oxygen concentration on yield of burnoff products (conditions A and B the same as those in Fig. 2). (□) CO₂; (○) SO₂; (△) CO.

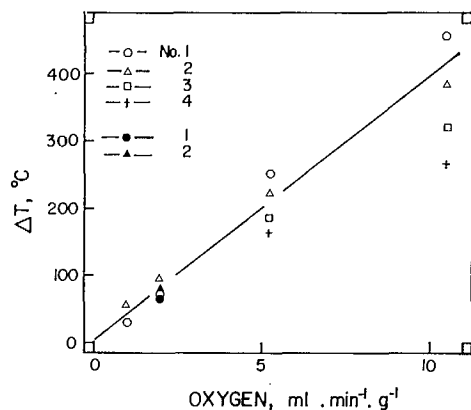


Fig. 4. Effect of oxygen concentration on temperature runaway (solid points for THF extracted catalyst).

catalyst, on the temperature runaway. This parameter represents the difference between the maximal temperature and the bed temperature before the admission of oxidizing gas. The oxygen concentration effect on this parameter for bed held at 350°C is shown in Fig. 4. For thermocouples 1 and 2 linear

correlation was observed. These results suggest that an undesirable catalyst overheating may be prevented at very low oxygen concentrations. Thus, it is preferred to maintain the maximum temperature below 500°C to prevent catalyst sintering [5]. The first contact of oxygen with coke is crucial because the most reactive parts of molecules burn at high rates. Therefore, the first stage of burnoff should be performed with very diluted oxidizing gas. Also, the catalyst bed temperature before admission of oxidizing gas should not be higher than 350°C [6]. It is believed that ΔT parameter depends on the amount and type of the coke deposited on catalyst surface. Thus, a "hard" coke formed during cracking operations is expected to be less reactive than the "soft" coke formed during hydrotreating operations [7].

The addition of steam to oxidizing gas resulted in a decrease of ΔT parameter as indicated by results in Table 3. This was complemented by a decrease of burnoff products yield. An example of steam effect is shown in Fig. 5 for 4 vol% oxygen although the same trends were confirmed in the whole oxygen concentration range. It is obvious that the ΔT lowering was caused by the decrease of burnoff rate. This could have been caused by shortening the contact time between oxygen and coke due to increase of linear velocity as well as the oxygen dilution on steam addition.

Also, a non-activated adsorption of water molecules at burnoff sites cannot be ruled out completely. The presence of these effects is supported by the earlier appearance of oxygen (by about 3 min) in burnoff products in the presence of steam compared with that in the absence of steam (Fig. 5A and B). The chemical reaction of water with carbon was negligible as was indicated by little difference in hydrogen yields in the presence and absence of steam. It is well known that a much higher temperature is required for such reaction to occur at a measurable rate.

The carbon dioxide addition to the oxidizing gas with the aim to decrease the ΔT parameter was also explored. In this case the catalyst bed was held at

TABLE 3

Inner maximum temperatures (°C)

Oxidation gas contained 4 vol% oxygen

Thermocouple	Catalyst		As received* (steam)
	As received	Reduced	
1	427	427	383
2	449	434	398
3	448	425	400
4	444	417	398

*1 g/min steam added to 2 l/min nitrogen + oxygen mixture containing 4 vol% oxygen.

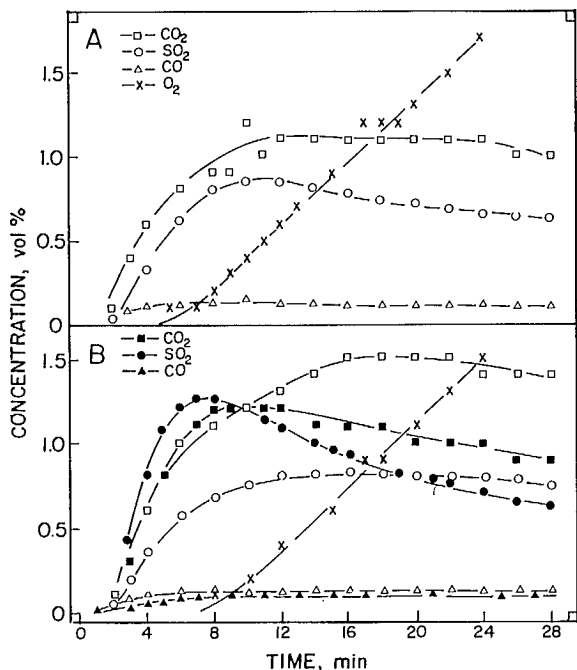


Fig. 5. Effect of steam addition to oxidizing gas on yields of burnoff products (solid points for THF extracted catalyst).

450°C prior to the admission of oxidizing gas. Only an oxygen dilution effect was observed. Thus, the burnoff profiles for air diluted by carbon dioxide and nitrogen to the same oxygen concentration were similar. This supports the results published recently which show that in pure carbon dioxide a temperature higher than 750°C and a long contact time was required to attain carbon conversions which were comparable to those in air at about 300°C [8].

The catalyst pretreated by solvent extraction was also investigated to assess the effect of de-oiling on the burnoff profile. As expected the carbon monoxide and carbon dioxide yields for the extracted catalyst were smaller than these for the catalyst as received (Fig. 5B). However, for the former the initial rate of sulphur dioxide formation and the overall sulphur dioxide yield during the indicated burnoff period was larger. This suggests that coke molecules may have initially hindered the access of oxygen to the metal sulphide sulphur from which most of the sulphur dioxide originated. The extraction had little effect on the ΔT parameter (Fig. 4). This is quite surprising as one would expect this parameter to be lower. Thus the extraction should result in removal of reactive species leaving behind non-reactive coke molecules. This observation may be attributed to a greater contribution of sulphur dioxide forming reactions to the

temperature increase. Also, the extraction may improve the oxygen diffusion into particles interior due to reopening of the catalyst pores.

The effect of the spent catalyst reduction on temperature runaway was evaluated using 4 vol% oxygen mixture. The inner maximum temperatures for the catalyst as received and reduced are shown in Table 3. Considering relatively large removal of coke on reduction (Table 1), the temperature lowering was insignificant. This is attributed to a larger contribution of sulphide oxidation reactions to the evolved heat as observed for extracted catalyst (Fig. 5). Thus, a steep sulphur dioxide buildup during early burnoff stages was also observed for the reduced catalyst. The carbon removal during treatment of the reduced catalyst in steam (1 g/min) and carbon dioxide (2 l/min) at 400°C for 60 min was negligible as indicated by the same carbon content of the reduced and treated catalysts.

CONCLUSIONS

The de-oiling of spent catalyst may be achieved by an extraction and reduction. However, the partial coke removal had little effect on temperature runaway during early stages of burnoff. This may be attributed to a greater contribution of sulphur dioxide forming reactions to the overall heat of burnoff. Also, a partial reopening of pores on de-oiling improved the access of oxygen to coke. For the same oxygen content in the oxidizing gas the de-oiling resulted in an increased oxygen/coke ratio compared with the as received catalyst.

For spent catalysts from fluid cracking, the temperature runaway may be accurately predicted using mathematical models whereas that for spent hydrotreating catalysts contains additional elements such as S, N and O as well as transition metals such as V, Ni, Ti and Fe. Moreover, the sulphided form of spent hydrotreating catalysts is converted to an oxidic form during regeneration. Under similar conditions the chemical changes incurred by fluid cracking catalysts are insignificant. Therefore, the use of a laboratory technique such as used in the present work may be needed to select optimal conditions for regeneration of hydrotreating catalysts.

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