

Emission challenges in partial burn FCC operation



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Partial burn regenerator operation offers the possibility to process lower cost crudes. This makes partial burn operation very competitive for conversion of sour high Concarbon crude into fuels and petrochemicals. Partial burn operation means using less oxygen than stoichiometrically required for complete coke combustion. The main products of coke combustion are: water, CO and CO₂. Hydrogen in coke is oxidised to water, but there is insufficient oxygen to burn all carbon to CO_{2} , so a part of the carbon from coke is converted to CO. Oxidation to CO is far less exothermic than oxidation to CO₂, therefore the heat produced is substantially lower than in full burn operations. Heat balance therefore demands higher coke make to supply the energy required to vaporise and crack feed at the required riser outlet temperature, allowing cheaper, more refractory, feedstocks to be processed.

Partial burn operating mode is popular in Europe, Asia, South America and Canada, but not common in the US. Because of the shale oil revolution in the US feedstocks are amongst the lightest in the world, so the advantages of partial burn are low in this case. However, the under representation of partial burn units in the US pre-dates the shale oil revolution: so what is the difference between the US and the rest of the world that makes partial burn operation less favourable? A major difference is the cost effectiveness of controlling environmental emissions such as SOx and NOx. Legislation outside the US typically takes one or more decades to catch up compared to many consent decrees already actively in force in the US. For full burn operations there are highly effective FCC additive solutions available to control emissions, however in partial burn operations FCC additives are typically less effective and therefore costlier hardware solutions are required.

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In recent years research efforts into partial burn chemistry have made big steps forward in gaining insight into coke combustion under sub-stoichiometric oxygen conditions and its effect on contaminant nitrogen and sulphur species (see Figures 1 and 2). In partial burn there is an apparent advantage for NOx generation in the regenerator: much less NO is formed compared to full burn operation; and most of the nitrogen species formed are present in 'reduced' forms: ammonia and hydrogen cyanide (HCN). HCN is the primary product of combustion of nitrogen in coke. HCN is not thermodynamically stable at high temperatures in the presence of oxygen, so in full burn operations (excess oxygen present) HCN is mostly oxidised to N_2 or NOx. However, in partial burn (sub-stoichiometric oxygen) different pathways are open to HCN conversion, for instance hydrolysis to ammonia, which can be subsequently oxidised to NO. Oxidation of N-species depends on the availability of oxygen and presence of catalysts (for instance platinum – present in combustion promoters). The apparent NOx advantage, however, disappears once the full process is considered; in the CO boiler HCN and ammonia are oxidised mainly to NO.





Figure 1. Reaction pathways for nitrogen combustion in the FCC regenerator



Figure 2. Reaction pathways for sulphur combustion in the FCC regenerator

Full burn SOx chemistry is relatively easy to understand and well documented. But what happens if there is insufficient oxygen present for full coke oxidation? H₂S is the primary product of combustion of sulphur in coke. H₂S readily reacts with CO or O₂ to form COS or SO₂ respectively; SO₂ then reacts further with O₂ to establish an SO₂/SO₂ equilibrium mixture. The fraction converted to SOx depends heavily on the depth of partial burn operation. In shallow partial burn (lower CO levels) more SOx is present vs COS, whereas in deeper partial burn (higher CO levels) formation of COS is dominant and the fraction of SOx is much smaller (see Figure 3). Deeper partial burn operation leaves a substantial part of sulphur species in their reduced forms (H₂S and COS). Observation shows that H₂S is predominantly present in shallow partial burn, whereas COS is the major fraction in deep partial burn. The CO boiler downstream of the FCC regenerator effectively converts flue gas COS and H₂S to SOx. Only SO₂ in the regenerator is captured by FCC SOx additives. Therefore, conventional SOx additives are generally less effective in partial burn than in full burn. However, understanding of the chemistry has allowed partial burn (PB) SOx additives to be dramatically improved in the past years. State-of-the-art PB-SOx additives typically require less than half the addition rate compared with previous PB-SOx additives (as measured in pick-up factor, lb of SOx captured per lb of additive).

Partial burn SOx chemistry today is in the same position as full burn SOx chemistry was in the 1990s. One hundred percent SOx removal in partial burn is still some way off, but for some areas in the world the latest generation PB-SOx additives are already acknowledged as the most cost effective environmental solution. Today in the US, PB-SOx additives are also being used to reduce flue gas scrubber operating costs. In a few years the effectiveness of SOx additives in partial burn operations may be equal to full burn additives of today.



Figure 3. Fraction of sulphur species present as SOx in partial burn FCC regenerators

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