Crude oil refining is an energy intensive process. On average, the thermal energy consumption of a refinery is in the order of 350-400 MJ/bbl, based on 2017 data from environmental agencies in the Netherlands, with some refiners achieving a higher energy efficiency than others. In order to reduce operational expenditure as well as the carbon footprint, refiners engage in projects to improve energy efficiency and process sustainability.

For a 100 000 b/d refinery, the typical thermal energy consumption equates to 400 MW. Of this energy, most is consumed in endothermic processes. Approximately 10% however is lost through the stack as waste heat. Historically, these stack losses of flue gas being emitted at high temperatures were accepted as a given because further heat recovery would lead to acid corrosion and related operational reliability issues. These corrosion and reliability concerns can now be overcome, allowing refiners to recover about a third of the waste heat from their flue gases (14 MW/100 000 b/d) in an economical way. As a result, an improvement of the overall refinery energy efficiency of 3-4% can be achieved.

In this article, we look at the issues traditionally linked to recovering heat from flue gases. We review the solution that allows more heat to be recovered by cooling the flue gas down to temperatures below the acid dew point, and we discuss what the implications are for existing downstream equipment.

**What is the issue with corrosive flue gas?**

In refineries, a wide range of fuels are combusted in thermal processes, ranging from natural gas, off-gases, LPG to naphtha and fuel oil. Most of these fuels contain sulphur components like H₂S, mercaptans and thiophenes, which are readily converted to SOx in the combustion chamber. Mainly SO₂ is formed, but part of this SO₂ (typically about 2-4%) oxidises further to SO₃. This SO₃ reacts with H₂O in a condensing reaction to form sulphuric acid, when the flue gas cools below the acid dew point (ADP):

$$\text{SO}_3_{(g)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{H}_2\text{SO}_4_{(l)} \quad [1]$$

The acid dew point temperature depends on the levels of reactants present in the flue gas. It generally lies in the range 100-150°C. Figure 1 shows the relationship between the ADP and the SO₃ level, calculated at a typical H₂O level of 15 vol% by using a number of different approaches proposed in the literature.

Sulphuric acid is highly corrosive and affects susceptible equipment surfaces. For example, on cold surfaces in metal air preheaters, local temperatures drop below the ADP, leading to sulphuric acid condensation, which results in rapid corrosion and breakdown of plates and
costs of steam and reduces the heat recovery. Both of these mitigation approaches still limit the recovery of the heat in the flue gas to approximately 20°C above the acid dew point.

To recover more energy from the flue gas, it has to be cooled down below the original acid dew point. Around the acid dew point, corrosion rates are high, but as the flue gas is cooled further down through the corrosive temperature range (see Figure 2), rates of corrosion become manageable again. Below 90-100°C, the corrosiveness of the flue gas is significantly lower compared to the corrosiveness just below the acid dew point temperature.

Under the acid condensing conditions arising from cooling down through the acid dew point, standard metal heat exchangers are not suitable. Special alloys need to be used. The cost of these, however, makes the heat recovery uneconomical. Alternative materials of construction like glass or enamel coated metal have been implemented at times. These solutions are, however, susceptible to flow induced vibrations and thermal shocks, which lead to damaged enamel coatings (allowing the acid to reach the underlying metal surface and corrode it away), tube breakage or rupture. The subsequent short cut between combustion air and flue gas reduces heat recovery and increases the load on the air fan as described before.

**Polymer heat exchanging tube bundles**

HeatMatrix Group has developed an innovative polymer based heat exchange technology that allows recovery of heat from corrosive and/or fouling flue and exhaust gases, to preheat combustion air and thereby improve overall process energy efficiency. This technology allows operators to recover even more heat from the flue gas down to temperatures well below the acid dew point, or replace their existing glass tube or glass lined air preheater or steam air preheater with a reliable, more efficient solution.
The HeatMatrix APH air preheater is based on Polymer Honeycomb technology. In this technology, multiple tubes are connected to each other over a significant length of the tube, forming a honeycomb modular bundle (see Figure 3, left). Multiple corrosion resistant polymer tube bundles are mounted into a metal casing (see Figure 3, right) to give the required heat exchange area.

Polymer Honeycomb technology provides a strong and rigid heat exchange matrix that is able to resist high gas velocities and thermal shocks. The geometry creates a 100% counter current flow configuration between the flue gas and air streams. This configuration improves the heat transfer by up to 20% compared to cross flow type exchangers. Flue gas flows from top to bottom through the tubes (see Figure 3, red arrow) and combustion air flows in the opposite direction around the tubes (see Figure 3, blue arrow). Inside the polymer tubes, the flue gas will go through its acid dew point and acid condenses on the tube wall. At the ADP, the concentration of sulphuric acid is high. As the acid travels down the tube, it will absorb water and the resulting condensate is collected in and drained from the bottom section of the air preheater. This bottom section has been designed to disengage condensate from the flue gas. Whereas the top three sections of the exchanger are carbon steel based, the bottom section is specifically designed to withstand the diluted acidic condensate (approximately 1% H$_2$SO$_4$ content).

In addition to corrosion resistance, the application of polymer offers benefits in fouling conditions. Polymers have very smooth surfaces and have low affinity for binding with dust, soot, salts and particulates. The positioning of the tubes in a vertical flow direction means that there are no dead zones inside the tubes where fouling can accumulate. As a result, fouling build-up is reduced. In cases of extremely fouling flue gases, each bundle can be equipped with an in-line spraying nozzle, which cleans each bundle in an alternating cleaning sequence during operation. The bundles can be washed with water. The chemical properties of the polymer allow for even more aggressive cleaning with detergents, acids or caustic if the duty requires this.

The low weight of the polymer bundles allows flexible installation of the heat exchanger, even at height, when plot space is limited. The lightweight bundles are retractable from the top and can be cleaned or replaced without demounting the complete exchanger.

What about downstream?

Acid removal

The HeatMatrix exchanger has been designed to cool the flue gas down through the acid dew point. Sulphuric acid condenses on the tube wall in the polymer heat exchanger. The highly hygroscopic acid absorbs water as it moves down the tube and drops into the bottom basin. It is worth noting that the temperatures remain above the water dew point.

Research

The condensation of sulphuric acid means that SO$_3$ is selectively removed from the flue gas. Hence the acid dew point of the exit flue gas is reduced accordingly. To confirm that SO$_3$ is indeed removed and to what extent, a research project was set up in conjunction with the TNO research institute in the

![Figure 4 HeatMatrix APH examples: cylindrical (L) and box (R)](image)

![Figure 5 ADP reduction in a Polymer Honeycomb](image)
Netherlands. In the test programme, gas with $\text{SO}_3$ was passed through the polymer tubes at typical gas velocities. The inlet and exit $\text{SO}_3$ levels were measured. The testing showed that 80 to 90% of the $\text{SO}_3$ will be removed in HeatMatrix Polymer Honeycomb technology.

As $\text{SO}_3$ is removed, the acid dew point is lowered accordingly. Taking for example the Okkes equation and starting with a $\text{SO}_x$ level of 200 mg/Nm$^3$, an $\text{SO}_3$ level of 1.4 ppmv (assuming 2 vol% $\text{SO}_3$) gives an ADP of 123°C. After 80-90% has condensed out, the $\text{SO}_3$ level in the cooled gas drops to 0.14-0.28 ppmv, which equates to an ADP of 108-112°C, so a drop of 11-15°C (see Figure 5).

Impact on corrosion rate
A lower acid dew point corresponds to a lower corrosivity of the flue gas. Figure 6 shows the corrosion rate of carbon steel as a function of the acid dew point. The graph shows that as soon as the acid dew point drops below 105°C, the corrosion rate reduces to less than 0.1 mm/year, which is a typical design corrosion rate. This shows that cooled flue gas is significantly less corrosive and that the corresponding corrosion rates are within the design parameters for the materials of construction used downstream of the air preheater.

Proof from the field
At an operating unit, a carbon steel material coupon was installed in the exit of the HeatMatrix polymer APH. The flue gas $\text{SO}_x$ level in this unit is 500 mg/Nm$^3$, corresponding to a $\text{SO}_3$ level of 3.5 ppmv, which means an ADP (Okkes, ZareNezhad) of 130°C. With 80-90% of the $\text{SO}_3$ condensing out, the $\text{SO}_3$ level in the cooled gas is in the range 0.35-0.7 ppmv, which equates to an ADP of 113-118°C (Okkes) or 107-114°C (ZareNezhad). In line with Figure 6, a corrosion rate of 0.1-0.3 mm/year would be expected. Over the period of a year, the corrosion coupon was monitored for any signs of corrosion or weight change. No significant impact was discernible. In Figure 7, development of the plate thickness and material loss is shown for the carbon steel coupon.

The analysis confirms that downstream of the HeatMatrix air preheater, the resulting acid dew point of the flue gas has been lowered to such an extent by the condensation of sulphuric acid in the heat exchanger that the corrosion rate has dropped to levels well below the design corrosion rate of 0.1 mm/year.

Case study: CDU furnace
HeatMatrix technology has been proven in a wide range of applications, including methane steam reformer and oil refinery furnaces. Here is a case study in a refinery. On a CDU furnace, an existing metal air preheater (APH) recovered part of the heat in the flue gas. The acid dew point of the flue gas was 129°C (Okkes, ZareNezhad). To protect the existing metal APH against cold spot corrosion and to improve the refinery’s energy performance, an additional metal APH in combination with a HeatMatrix polymer APH was installed. The polymer APH protects the metal APH from cold spot corrosion. The combined additional recovery amounted to an energy saving of 9 MW, of which about 30% is recovered in the polymer APH.

The overall pay-back time for this project is less than five years.

Conclusion
Crude oil refineries are large consumers of energy in their thermal processes. Of the energy used in combustion, about 10% is lost through the stack. Concerns about
acid dew point corrosion have held refiners back in recovering more waste heat from the flue gases. Traditional solutions like glass tubes or enamel coated tubes have caused reliability issues and are therefore less frequently applied. Operators tend to stay well above the acid dew point after their air preheaters. However, variations in fuel sulphur content and low ambient air temperatures in winter can still lead to cold spot corrosion in the existing metal air preheaters. To mitigate against this cold spot corrosion, some operators choose to preheat the combustion air with steam, which implies costs for steam and reduces the overall heat recovery.

Polymer based heat exchange technology allows operators to recover more heat from the flue gas by addressing acid corrosion concerns. Moreover, in the HeatMatrix polymer honeycomb heat exchanger, most of the sulphuric acid is removed from the flue gas, which makes the cooled flue gas much more benign to equipment downstream from the polymer APH.

The extra heat recovered from the flue gas can be used to preheat the combustion air which in turn leads to a reduction in the consumption of combustion fuel. Overall, this solution allows refiners to improve their sites’ energy efficiency by up to 4%. The many references of the HeatMatrix technology have proven that concerns around acid dew point should no longer be a showstopper for this kind of energy saving.

References
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Figure 8 Refinery CDU furnace: revamp case study.