ADVANCES IN WASTEWATER TREATMENT

Bryan Kumfer, Siemens Water Solutions, USA, looks at a new technology for water treatment which cleans toxic, high-strength wastewater, and even produces methane for fuel.

One of China's largest refineries on the outskirts of a city of 26 million people consistently wins the nation's top environmental awards despite the potential impacts of processing more than 20 million tpy of crude oil. Outputs include various grades of gasoline, diesel, and jet fuels, plus asphalt, polypropylene plastics, and more than 1 million tpy of ethylene.

Winning these awards took considerable effort and investment in effective water treatment technology. After all, ethylene production generates spent caustic, an extremely toxic wastewater. It consists of high dissolved solids; biorefractory, hazardous, and inhibitory reduced sulfur compounds; and a salts mass fraction of almost 10% by weight.

Using biological treatment processes on spent caustic is not practical and can even destroy the biomass used. Then there is the matter of hydrogen sulfide and mercaptans. To lower the pH of ethylene spent caustic sufficiently for biological treatment, these compounds can become volatile. Even in small concentrations, they are malodorous and hazardous to the life safety of plant personnel and surrounding communities.

Additionally, ethylene spent caustic has high levels of chemical oxygen demand (COD), from 10 000 to 50 000 mg/l. With flow rates of 5 – 20 m^3/hr, the COD load typically associated with ethylene spent caustic could surpass the combined COD load found in the refinery's water treatment facility's other waste streams.

To address this challenge, the plant's engineers chose Siemens Zimpro® wet air oxidation (WAO) technology.

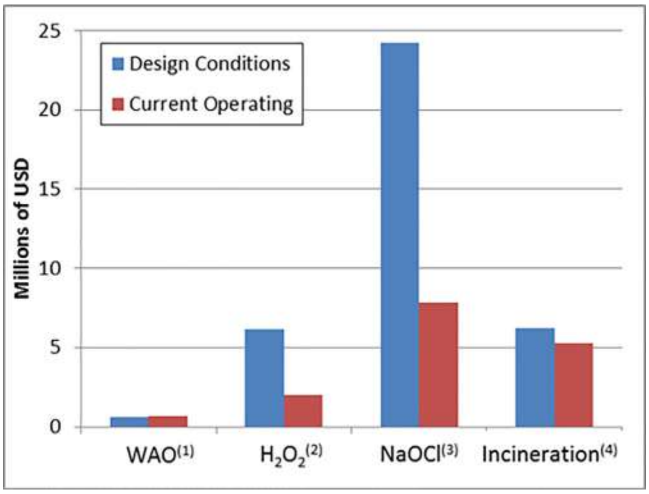

Figure 1. Comparison of annual operational expenses between WAO technology vs traditional oxidation treatment alternatives for treating ethylene spent caustic at current operating conditions and design conditions. (1) Includes electricity, steam, boiler feedwater, cooling water, and instrument air; (2) H_2O_2 only; (3) NaOCl only; (4) fuel only.

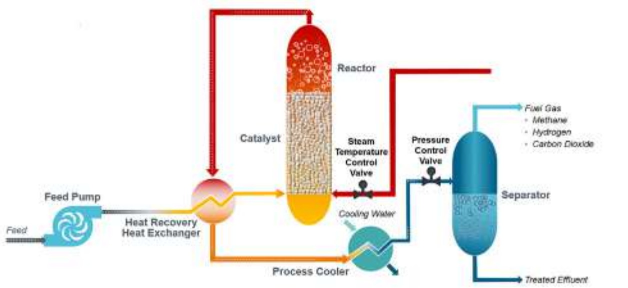

Figure 2. Catalytic gasification technology process flow diagram.

Other approaches may try to strip the sulfides out of the spent caustic – resulting in a corrosive and odorous sulfide gas – or incinerate it in a gaseous phase. But incineration is not ideal either because it is both corrosive and energy-intensive. Alternative approaches may also have high operating and maintenance costs as shown in Figure 1. Incineration needs fuel, while advanced oxidation uses expensive and hazardous liquid oxidising agents to oxidise the spent caustic.

By comparison, when WAO oxidises spent caustic, the toxic stream turns into an effluent comprising fully oxidised, non-reactive inorganic salts and carboxylic organics with a low-molecular weight. Having no noxious odours, this effluent can be safely neutralised. Also, with its COD levels significantly reduced and its organics oxidised, the result can be directed into biological treatment for final polishing prior to discharge.

Catalytic gasification

While WAO has proven itself similarly in many other oil and gas refineries and petrochemical plants worldwide for decades, today's hydrocarbon engineers will want to keep watch on the development of a derivative technology from Siemens called catalytic gasification.

This technology also makes use of principles drawn from catalytic wet air oxidation (CWAO) systems. In effect, catalytic gasification offers a new solution for addressing hard-to-treat industrial wastewaters. For example, in some cases, especially if large amounts of halogens are present, it can be difficult to find appropriate materials for cost-effectively building a WAO system.

In addition, if many of the compounds in a waste stream are biorefractory, biological treatment may not be an option. That is because, even if compounds are biodegradable, they require an extremely large dilution to reduce the salt concentrations to acceptable levels. This limits any type of water or salt recovery.

The many advantages of catalytic gasification include high COD destruction rates, which help to reduce downstream treatment costs; capital and energy savings, thanks to a process with lower temperatures; space savings; and methane fuel-gas as a by-product, which can be used to help offset operational costs.

How catalytic gasification operates

In short, catalytic gasification employs a heterogeneous catalyst to generate chemical reactions that are comparable to those that characterise steam reforming and gasification as represented by the following equations:

Steam reforming	$C_nH_m + n\,H_2O \rightleftharpoons (n + m/2)\,H_2 + n\,CO$	(1)
Methanation	$CO + 3\,H_2 \rightleftharpoons CH_4 + H_2O$	(2)
Water-gas shift	$CO + H_2O \rightleftharpoons H_2 + CO_2$	(3)

Because these reactions take place in an aqueous phase as Figure 2 illustrates, their temperatures are much lower (< 300°C) than what gas-phase gasification processes require.

In catalytic gasification, fuel gas production depends on the types of compounds treated. Below are three examples of actual methane concentrations resulting from the catalytic gasification treatment of three typical wastewater compounds: 2-propanol, 2-butoxyethanol, and acetic acid. Note the high levels of COD removal for each compound:

- Acetic acid: $C_2H_4O_2 \rightarrow CH_4 + CO_2$
  - Results: 98% COD removal, with 45% methane (CH_4) as a fuel gas by-product.
- 2-Propanol: $4\,C_3H_8O + 2\,H_2O \rightarrow 9\,CH_4 + 3\,CO_2$
  - Results: 96% COD removal, with 71% CH_4 as a fuel gas by-product.
- 2-Butoxyethanol: $5\,C_6H_{14}O_2 + 8\,H_2O \rightarrow 21\,CH_4 + 9\,CO_2$
  - Results: 93% COD removal, with 64% CH_4 as a fuel gas by-product.

Examples of catalytic gasification treatments

Catalytic gasification can achieve significant levels of COD destruction for a variety of organic compounds. For some organics, such as methanol, glycerol, and ethanol, destruction rates are as high as 99%. Catalytic gasification has also been shown to effectively treat COD levels of up to 200 000 mg/l.

A common problem with high strength wastewaters is the presence of high concentrations of chlorides and the impact that has on materials of construction. Because there is no oxygen in a catalytic gasification system, the feed waste

Table 1. Wastewater treatment results for a pharmaceutical manufacturing example

Analysis results	Reported as	Untreated wastewater	Treated effluent
Chemical oxygen demand (mg/l)	O_2	136 000	48 000
COD destruction (%)	–	–	65.0
Total organic carbon (mg/l)	C	31 700	11 200
Total chloride (mg/l)	Cl	28 500	–
Biodegradability ratio	–	–	0.63
pH	–	7.4	8.1
Off-gas data			
Hydrogen (%)	H_2	–	7.7
Carbon dioxide (%)	CO_2	–	27.0
Methane (%)	CH_4	–	61.7
Non-methane hydrocarbons (%)	CH_3CH_3	–	3.6

Table 2. Wastewater treatment results for a chemical manufacturing example

Analysis results	Reported as	Untreated wastewater	Treated effluent
Chemical oxygen demand (mg/l)	O_2	87 600	6600
COD destruction (%)	–	–	92.0
Total organic carbon (mg/l)	C	22 600	1500
Chloride (mg/l)	Cl	84 200	–
pH	–	12.8	8.0
Off-gas data			
Hydrogen (%)	H_2	–	3.0
Carbon dioxide (%)	CO_2	–	31.7
Methane (%)	CH_4	–	61.4
Non-methane hydrocarbons (%)	CH_3CH_3	–	3.8

stream can contain much higher chloride concentrations than what other oxidation treatment processes are capable of handling. This means a catalytic gasification system can treat wastewaters with up to 100 000 mg/l chloride concentrations.

For this use case, testing was done with a propylene glycol wastewater having sodium chloride salt levels of 80 000 mg/l. Although a small decrease occurred when a low concentration of salt was added, those levels remained flat as the concentration continued to increase.

When testing propylene glycol wastewater with high sodium chloride levels, catalytic gasification reduced COD levels by 99.9% – from 39 000 mg/l to less than 5 mg/l.

The catalytic gasification process works with a variety of organic compounds. And multiple catalyst types are available to meet different treatment objectives.

Two diverse use cases

Pharmaceutical wastewater

In this application, catalytic gasification was used to treat pharmaceutical wastewater. With a COD of 131 000 mg/l, this wastewater contained high concentrations of methanol and ethanol as well as 2-butanone (MEK), sodium acetate, and sodium formate.

The water also had 28 000 mg/l of chlorides. Using catalytic gasification, the COD in this wastewater was cut by 65%, which resulted in a biodegradable effluent. Approximately 28 l of fuel gas were produced per l of wastewater treated. Table 1 shows the results.

Chemical manufacturing wastewater

With a COD of 90 000 mg/l, wastewater from a chemical manufacturing plant also had a high salt concentration (> 150 000 mg/l total dissolved solids). In addition, the wastewater had high levels of methanol and propylene glycol. The customer wanted to reuse the salt rather than dispose of it, but due to the wastewater's high salt content, mostly sodium chloride, treatment methods were limited.

Current disposal required a very high dilution and then treatment by biological processes. Testing using catalytic gasification found that > 90% COD removal is possible without needing dilution. While testing is still ongoing, researchers believe this result can be further improved. Approximately 40 – 45 l of fuel gas were produced per l of wastewater treated. Table 2 shows the results.

New treatment solution

WAO and CWAO wastewater treatment technologies have proven themselves to be highly cost-effective in treating the world's dirtiest, most toxic wastewaters such as the spent caustic mentioned at the beginning of this article. In some cases, especially wastewaters with high halogen concentrations, water engineers need an alternative, which has been presented in this article.

Testing has proven that catalytic gasification technology can treat wastewaters unable to be processed economically. It uses a heterogeneous catalyst to stimulate reactions similar to those in steam reforming and gasification. But because these reactions take place in an aqueous phase, their process temperatures are much lower than what gas-phase gasification processes require. This can save energy and simplify the treatment process.

In summary, the benefits of catalytic gasification include the following:

- Produces no solids, improving effluent quality for polishing.
- Reduces COD loads substantially, helping to lower downstream treatment costs.
- Reduces energy requirements by operating at lower temperatures.
- Produces fuel gas, which can be used to offset operational costs.
- Has a compact footprint.

Currently one of the world's largest oil refiners is slated to start testing the catalytic gasification technology's efficacy at the Siemens Water Solutions treatment testing facility in Rothschild, Wisconsin, US. While results will be confidential, the interest in this new technology is growing.