

# SULFUR IN 60

# SECONDS

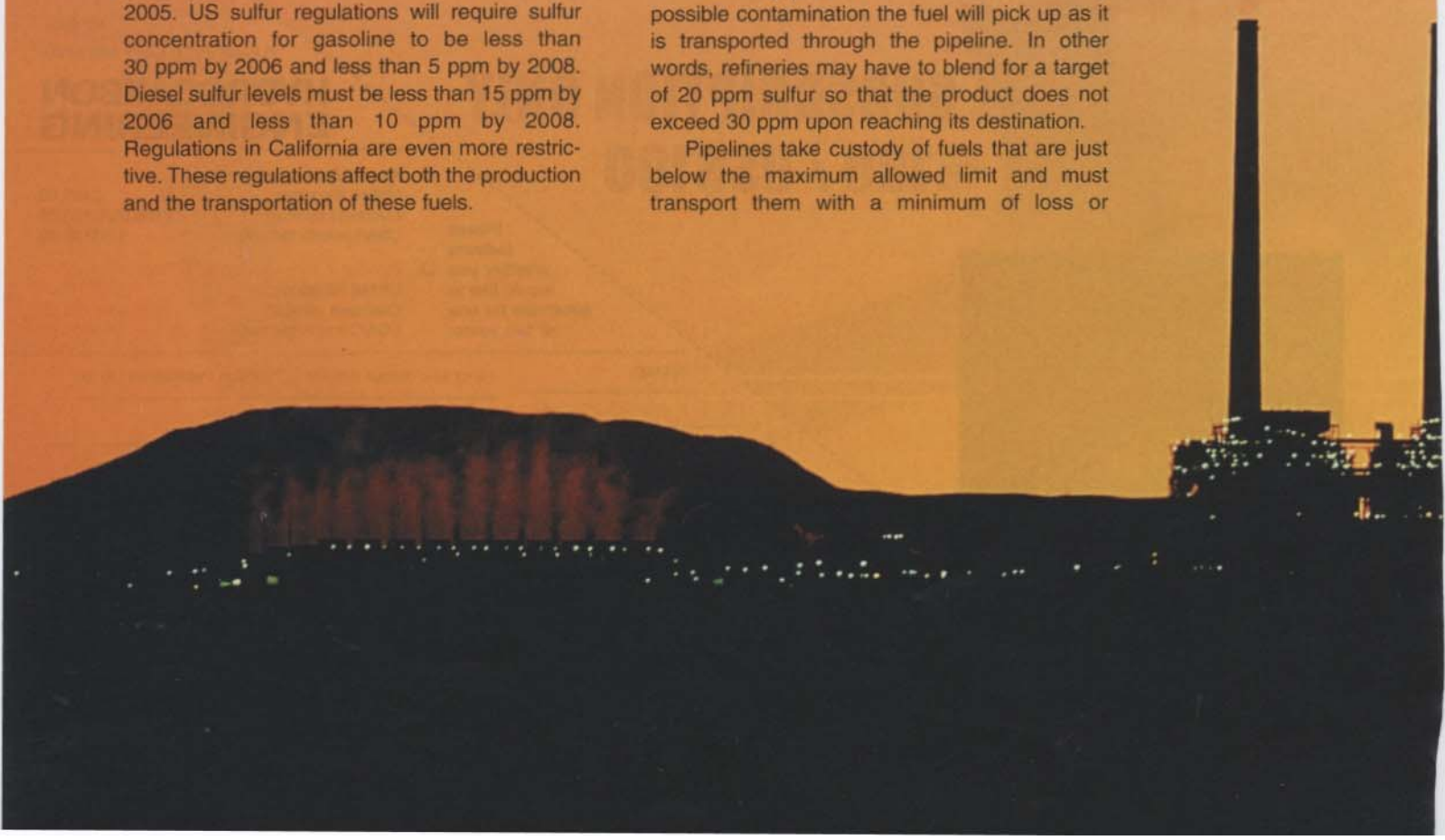
**Steve Tarkanic of PAC, USA, and Franek Olstowski, Consultant, explain a new approach for identifying products in a pipeline.**


Concerns for the environment, resulting in mandated guidelines from regulatory agencies around the world, as well as support by auto manufacturers to aid catalyst longevity, has led to a significant decrease in the allowable levels of sulfur in fuels over the last several years. The Euro 4 Directive requires that sulfur levels for both gasoline and diesel fuels sold in Europe are to be less than 10 ppm by 2005. US sulfur regulations will require sulfur concentration for gasoline to be less than 30 ppm by 2006 and less than 5 ppm by 2008. Diesel sulfur levels must be less than 15 ppm by 2006 and less than 10 ppm by 2008. Regulations in California are even more restrictive. These regulations affect both the production and the transportation of these fuels.

## **Background**

Many refineries now have the ability to produce low sulfur fuels that are cleaner than current requirements but are more expensive to produce. To minimise what is known as 'giveaway', these ultra low sulfur fuels are blended with less expensive higher sulfur fuels to produce end products as close to the legal limit as possible. The blending process takes into account any possible contamination the fuel will pick up as it is transported through the pipeline. In other words, refineries may have to blend for a target of 20 ppm sulfur so that the product does not exceed 30 ppm upon reaching its destination.

Pipelines take custody of fuels that are just below the maximum allowed limit and must transport them with a minimum of loss or





adulteration. As different products are transported through the pipeline, an interface known as the transmix region is formed where the two products mix together. Pipelines are designed to reduce this mixing effect between products but it can never be completely eliminated. Knowing that this occurs, pipeline companies try to sequence products to further minimize the impact of transmix to fuel product quality. However, scheduling situations can still arise where an ultra low sulfur fuel could be transported adjacent to other products that may have sulfur concentrations as high as 5000 ppm.

Choosing the wrong time to redirect the new product can be a costly mistake. Either some of the expensive low sulfur fuel will get sent to the wrong destination or the fuel can become contaminated and have to be re-graded. As little as 6.3 bbls of a product that has a sulfur concentration of 2000 ppm would increase the sulfur level of 2500 bbls by 5 ppm if they were allowed to completely mix. Every minute that the cut time is missed can result in degradation to a significant amount of product. This could typically be about 44 bbls every minute for an 8 in. pipeline and about 833 bbls every minute for a 40 in. pipeline. Figure 1 illustrates the amount of product that can flow through various pipeline diameters every minute between measurements.

The most frequently applied method of determining when a transition of product in the pipeline had occurred has been to use a densitometer to measure changes in API gravity. This

method was satisfactory when sulfur levels were not a major consideration. A product with high levels of sulfur can contaminate a low sulfur fuel without significantly affecting its gravity. By the time a density change is sensed, some portion of the contaminated product may have already been directed to the wrong location.

Since sulfur concentration could be the most discernable difference between the various grades of products, sulfur level becomes an obvious indicator for determining when to make the cut between products. Until now, use of sulfur concentration on which to base decisions has been difficult due to longer analysis time of the available analysers, which could allow an appreciable amount of the wrong product to pass the cut point before a change in product could be sensed. Commercially available analysers with analysis cycle times of 2.5 - 10 minutes are not fast enough for this requirement. For an 8 in. pipeline, even a 2.5 minute delay equates to about 110 bbls of product having potentially flowed past the desired cut point.

### **Current techniques**

Analysis of sulfur by pyro UV fluorescence is a well-established analytical method utilised throughout the petroleum and petrochemical industry. In online applications, samples are typically introduced by a sample injection valve and pushed through an injection tube into an oxygen rich environment contained within a pyrolysis or combustion tube. When the sample contacts

Pipe size (inches)	Barrels/hour bph	Barrels per minute bpm
40	50,000	833.33
36	37,000	616.66
16	6,000	100.00
12	4,2000	70.00
10	4,000	66.60
8	2,650	44.16

Figure 1. Comparative product volumes flowing through various pipeline diameters.

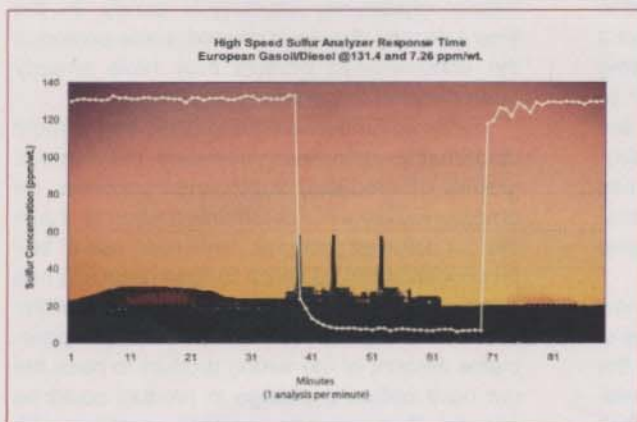


Figure 2. Response performance test of the high speed sulfur analyser demonstrating 90% response in less than one minute.

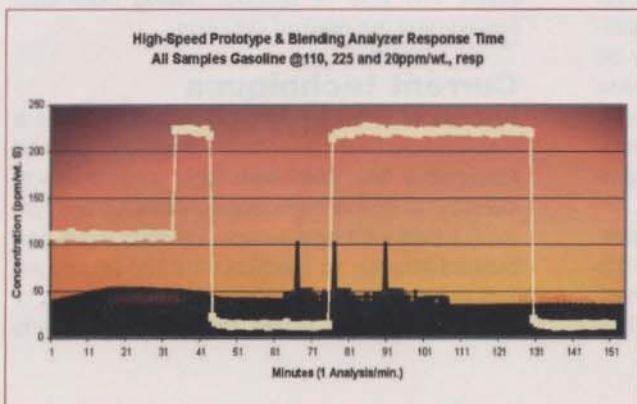


Figure 3. Response performance test of the high speed sulfur analyser with multiple gasoline products.

and mixes with the oxygen at 1000 °C all sample components are completely oxidised. The various sulfur species in the sample are converted to SO<sub>2</sub> and hydrocarbons are converted to water and carbon dioxide. Before entering the detector, the converted sample flows through a membrane dryer that removes most of the moisture produced during combustion. Once the SO<sub>2</sub> reaches the fluorescence chamber of the detector, it is exposed to short wavelength UV light. Each SO<sub>2</sub> molecule that is exposed to this UV energy is raised to an unstable higher energy state. The molecule quickly decays back to its original state by producing light of a slightly longer wave length than that of the excitation light. An optical filter allows only emission wavelengths of the excited SO<sub>2</sub> molecules to pass. A photomultiplier tube converts the fluorescence into a current that is proportional to the number of SO<sub>2</sub> molecules within the detector and thus, proportional to the concentration of sulfur in the sample. To

make the analyser produce an output that equals the sulfur concentration, a calibration must be performed with a standard of known sulfur content to establish a response factor. This response factor is then used in conjunction with the raw results of the analysis to calculate the sulfur result.

The minimum amount of time that an analysis could be completed was limited by a number of factors. First, band broadening occurs as the sample is injected and makes its way through the analytical system. When the sample is injected, some amount of the sample will wet the surfaces of the injection valve and the injection tubing that transfers the sample from the valve to the pyrolysis furnace. This portion of the sample evaporates more slowly than the initial sample thereby spreading the sample peak. As the sample is combusted with oxygen, the converted sample further diffuses in the pyrolysis tube. Then, as the converted sample reaches the membrane dryer, dead volumes in the membrane dryer and possible interactions with the membrane material cause even further spreading.

Another factor that has restricted high speed analysis in the past is the additional time required for removing water that is produced by the combustion of the hydrocarbons.

Although only trace amounts of water are produced and a membrane dryer removes most of that in the vapour phase, some amount of purge time must be allowed to remove the remaining moisture from the system. If sufficient time is not allowed, moisture will condense and accumulate in the analyser flow system. Besides the expected problems that come from having a liquid in a gas flow system, water will absorb SO<sub>2</sub> as it condenses. Once water starts condensing, the analyser loses its reproducibility and its response is decreased.

By optimising the injected sample size, using new materials with an innovative combustion tube design and an alternate approach to handling the moisture, it is now possible to produce an analysis result every minute. Some of the improvements to this method are patent pending and others remain proprietary.

## Experimental

The real test of an analyser's response time is how quickly the analyser produces an accurate result for an instantaneous step change in sulfur concentration. The response time performance of the high speed sulfur analyser was validated with both gasoline and diesel samples by rapid switching of sample flowing through the analyser's sample valve. Since the response time for diesel fuel is typically slower for online instruments utilising UV fluorescence due to sample vapourisation and combustion requirements, a European grade diesel or 'gasoil' was selected to perform the minimum anticipated speed of analyser response in the field.

The two samples selected for this test had been analysed by round robin techniques to establish accurate total sulfur content for both the high and low concentration samples, which were 131.4 ppmw and 7.26 ppmw respectively. The samples were connected to a multi-port chromatographic valve that when switched, would select alternate samples to simulate a near-instantaneous change in sample composition within a pipeline.

Each graphical point in Figure 2 indicates individual analysis values that were produced by the high speed analyser and collected at one minute intervals. The above graph represents only one product switch of several that were run to confirm test results.

To calculate the achieved analyser response time, data points from the 20 analyses just prior to stream switching for both high and low concentration samples (131.4 ppmw and 7.26 ppmw respectively) were each averaged to establish a

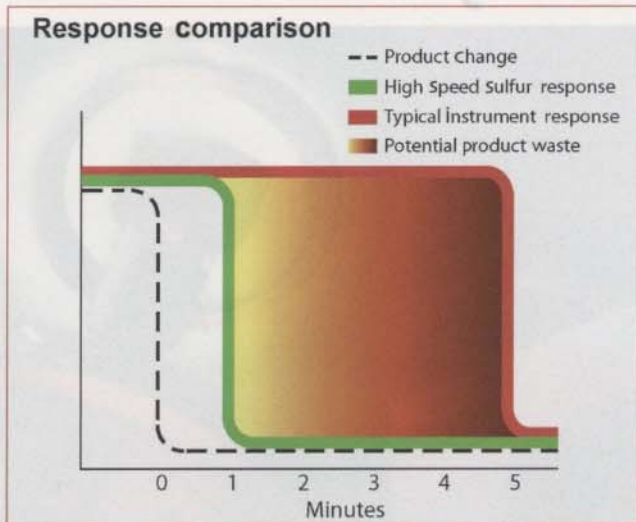


Figure 4. Potential product loss versus speed of analysis.

Table 1. Test results

Product 1 average	131.4 ppm
Product 2 average	(-) 7.0 ppm
Product delta	124.4 ppm
1st post-switch read	23.7 ppm
What it should have been	(-) 7.0 ppm
Excess product 2 reading	16.7 ppm
Relative % change	$100\% - (16.7/124.4 * 100) = 86.6\%$

stabilised reference value for comparison purposes. Next, the low concentration average was subtracted from the high concentration average to yield the expected sulfur concentration difference or 'delta' between samples.

Finally, the value obtained for the first analyser data point

after switching streams was subtracted from the difference between samples and a proportional or relative percent change was calculated.


The relative response time calculated for this sample was approximately 87% of the expected change on the first data point (one minute) after switching samples, but as previously noted, this type of sample represents a worst case scenario, as European diesel is roughly similar to a clean fuel oil. Tests, run on commercial diesels acquired in the United States, yielded a faster 90% response time and gasoline samples demonstrated better than a 95% response time within the typical one minute analysis cycle of the high speed analyser.

Figure 3 demonstrates the response performance obtained for a variety of gasoline products. The response times that were measured for all of the samples was greater than 95% of the eventual change within the first data point or analysis.



Repeatability obtained for both European diesel samples during 10 hour runs, or 600 individual samples, yielded better than 1% RSD (1-sigma) for the 131.4 ppm w sample and better than 6% RSD (1-sigma) for the 7.26 ppm sample w. A rolling average of five samples improves the precision of repeatability by approximately two fold. Figure 4 illustrates product volume that may be lost with increasing cycle time. This clearly demonstrates the correlation between increasing cycle time and potential product loss.

### Conclusion

In conclusion, pipeline transmix can influence both product quality and quantity of deliverable product. Real time high-speed analytical data allows a transmix profile to be more clearly defined and can be utilised to improve economically based cut-point decisions. These timely decisions can directly impact revenues by maximising potential cost savings. ■



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