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The hydrocracker unit of Ruhr Oel, located in Gelsenkirchen, Germany.

Photo courtesy of Ruhr Oel

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ISSN 1362-363X

Petroleum Technology Quarterly (USPS 0014-781) is published quarterly plus annual Catalysis edition by Crambeth Allen Publishing Ltd and is distributed in the USA by SPB, 75 Aberdeen Rd, Emigsville, PA 17318. Periodicals postage paid at Emigsville PA. Postmaster: send address changes to Petroleum Technology Quarterly c/o PO Box 437, Emigsville, PA 17318-0437. Back numbers available from the Publisher at \$25 per copy inc postage.



Waiting for profitability

By now, the industry has had some time to consider what to do about the low demand and oversupply of a range of refinery and petrochemical products. As discussed by the executives who participated in Outlook 2009, instability in feedstock pricing since last summer has made it difficult for downstream managers to make their business models work. It is no secret that the industry has entered a down cycle after a solid four years of strong growth. Going forward, high complexity processors will be better positioned to ride this cycle.

Although crude prices were dipping to \$50/bbl at the time of going to press, prices are expected to increase, but not above \$100/bbl any time soon. More importantly, a stable pricing environment will create stable margins for the refining sector. While the sweet spot going into 2009 will probably be \$60–80 per barrel, or even \$60–100, many refiners will be able to make their business models work in this scenario. It is when energy goes in a straight line from \$80–140, or back down again from \$140–80, that it becomes difficult for managers to plan and projects get put on hold or cancelled, which is what has been happening since last year.

Interestingly, the sharp decline in crude oil prices has not greatly affected some technology licensors and E&C contractors to date. For example, the backlog of business at Fluor is because their clients have long-term expectations of a higher price for oil instead of today's depressed price. Outside of other industries, such as nuclear, Fluor derives half of its business from both upstream and downstream oil and gas services. According to Fluor CEO Alan Boeckmann, these capital projects are based on long-term assumptions for crude to realise an average of \$50 or even \$60 per barrel. There are areas where technology, engineering and equipment suppliers will remain busy as the industry rides through the current down cycle, such as with increasing refinery distillate production, efficiency improvements and the major regulatory initiatives shaping the refining and petrochemical industry.

In the past, the petrochemical cycle, from peak-to-peak, ran for around seven to nine years, but this time the cycle had expanded to 11–12 years due to steadily rising crude oil prices up until Q3 2008 and strong Asian economies, especially China and India. China, now the world's largest petrochemical importer, began importing significant quantities of basic petrochemicals after 2004, so much so that, like other products such as cement and steel, this resulted in significant increases in global petrochemical prices. However, the petrochemical cycle began its downward cycle earlier than expected due to the financial crisis and impending worldwide economic slow-down. Meanwhile, new petrochemical production capacity will be the key item pressuring petrochemical prices. Whether or not these prices will drop as much as in past downturns is difficult to predict and seems to depend on which expert you talk to.

To be sure, this oversupply and drop in petrochemical prices will be leveraged by the cost-advantaged ethane-based steam crackers in the Middle East to support high operating rates, while producers in other regions will be forced to cut back production. This has already been happening, with certain naphtha-based steam crackers in Europe and the US Gulf Coast shutting down or scaling back since last November. The cost of ethylene production back in 2007 reached well over \$700 per tonne in Western Europe and the US (mainly due to the cost of naphtha feedstocks), while the cost for a typical gas-based producer in the Middle East remained under \$100 per tonne. To compound this challenge for naphtha-based crackers, propylene demand, increasing by as much as 5.5% per year, has begun decreasing to 4.5% or less since October 2008. Along with the capacity developments in the Middle East is acceleration in Asian capacity, primarily in China. Chinese cracker projects, developed in joint ventures with global downstream organisations such as BASF, Shell and BP, are highly integrated with refineries and exploit the advantages of lower fixed costs and proximity to market, relative to investments in the Middle East.

In summary, high complexity, lower fixed costs and market proximity will be key to riding out this down cycle. However, it is too early to tell when we will see the trough in this cycle. At the end of the day, it is up to the consumer.

René G Gonzalez



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Outlook for 2009

What are the important trends and issues affecting the downstream processing industry this new year? Executives and industry experts in the following pages forecast industry challenges and prospects that could affect profitability

Gene Davio Senior Vice President, Downstream Operations Fluor Corporation

The recent economic crisis has resulted in an outlook for 2009 that is rapidly changing and difficult to predict. While the current climate is causing many owners to consider the viability and timing of new investments, there is also a new window of opportunity opening for owners who are positioned to move their projects ahead.

The high price of transportation fuel shook consumers in the first half of 2008. Their reaction, reducing vehicle miles travelled by 3.7% from 2007 and switching from SUVs and pickups to more fuel economical cars, has caused a sudden shift in fuel demand, particularly in the US. The economic meltdown that followed has caused capital to dry up, share prices to fall and owners to move towards preserving cash flow. While some projects are being scaled back and others are seeing their completion dates extended to delay expenditures, most projects that have passed through their funding gate are continuing through the engineering and construction phases. The challenge for owners is to determine which new projects to undertake and at what pace.

We believe that owners who proactively move their projects forward through FEED and then proceed to select their EPC contractor will position themselves very well to take advantage of favourable pricing for equipment, bulk materials and construction services in 2009 and 2010. At the present time, equipment and material suppliers are experiencing strong backlog. A year ago, most would have predicted that this trend would continue for the foreseeable future, but it is apparent now that there will be a delay in new orders, reducing the impacts of escalation and resulting in reduced pricing for some equipment and materials. How long this window will be available is difficult to predict, as the long-term demand forecasts continue to suggest that the projects that have been recently delayed will be needed and when the economy again strengthens they will be reinstated.

So owners who put their projects into a position to place orders for equipment and materials during 2009 will be able to react when the market situation looks most advantageous to them. This means getting equipment clearly specified and completing engineering to a level that materials can be quantified, and ensuring execution plans for procurement, low-cost sourcing, fabrication and construction are



Davio

developed with rigour by the EPC contractor who will implement them.

Definitely, the market has changed dramatically. While the future is never certain, the project teams that work now to position themselves to react to the opportunities that have been created by these changing conditions will have the greatest level of success.

Guillermo Guariguata U President Onyx Engineering

The oil industry will always remember 2008 as the year when oil prices exceeded the \$160/bbl threshold for the first time. Fortunately, we seem to be positioned once more for fundamentals to drive the market and for product prices to again take a lead in establishing crude prices, since the refiner, as the voice of the consumer and after covering his costs and customary profits, will pass to the producer what he is willing to and can pay for the feed to the plants. This is an obvious first principle concept, yet when exogenous third-party players are present in the feedstock pricing mechanism, the market experiences what was lived in 2008, when crudes prices were totally out of sync with product prices, as confirmed by an article in the *Washington Post* that a single trading house had at one time more than 10% of all oil contracts on the regulated NYMEX. There were many others. What seemed a speculative comment at first became reality and very unlikely to repeat itself in the near term.

So 2009 will be a year of tempered spirits, a mystified consumer and an industry that will again have to retrench — something it has done successfully in the past. The year will bring memories of the combined effects of market fundamentals and unilateral actions from OPEC on petroleum prices. Are less than \$2/gal gasoline prices supporting a less than \$60/bbl average crude price with refinery margins profitable around a \$9/bbl range, depending on technology, indicative of a meltdown? Not exactly, they are familiar territory that the industry has successfully weathered in the past. This environment should return the sector to sustained profitability, postponing some expansions, yet likely keeping debottlenecking and maintenance programmes on track. This is a great opportunity to excel, improve on operational efficiencies and re-educate the public over the industry's polluting and price-gouging image, with which it has been unfairly labelled in recent years.



Guariguata U

What are the obvious risks? It is a known fact that most of the future oil reserves are in the hands of those countries that have little sympathy for the governments and the majority of the people who consume it. This has been a strong driving force to reduce the dependence on oil all together and to begin examining more seriously the possibilities of alternatives to electrical power generation and hydrocarbon-powered vehicles, while preparing the grid for more power from wind turbines and photovoltaic cells. However, despite the omen of a few, oil will continue to play an important role in transportation fuels for years to come, but less so in other areas such as heating and power generation.

The most recent US refinery data show yields in transportation fuels at 88%, of which half is motor gasoline and one-third is distillate for automotive use and heating oil. The remainder is some residual fuel, speciality products and pet coke. So it is evident that refineries are not the main source of product for electrical power generation — that honour belongs to coal and nuclear. A rapid move to wind and photovoltaic cells will take time to develop. In the interim, oil will still be relevant, and steps to reduce foreign dependency while developing alternatives energies seem to be the right path — one that has been talked about often in the past and whose time has finally arrived.

Unfortunately, alternative energy-producing technologies become less attractive when crude prices are low, so there may be a need for government incentives to provide the market drivers for projects to occur. Eventually, the consumer will foot the cost of this market intervention. The crude producers, on the other hand, will continue to manage their resources with a criterion of scarcity while the petrodollars significantly decrease. Some will become visionary about keeping their main resource viable and needed in times of anticipated irreversible structural demand change, while others will re-evaluate the merits of using energy as a political means with oil funds, now significantly diminished and most likely to remain so for the near future. In the long run, crude prices will again raise as a result of postponed projects in the critical production areas. Some even argue that they will again exceed the \$100/bbl threshold, since also the consumer, fortunately for the industry, has shown in the past collective amnesia to these cycles and returns to their habits of uncontrolled consumption when transportation fuels remain inexpensive and the cycle again comes full circle. Hopefully, not on my watch.

Charles Cameron

Marketing Director
Axens

“**M**ay you live in interesting times” is a euphemism that entered the English language circa 1936. It is an appropriate description of recent events, when the prices of crude climbed from \$50/barrel to over \$140/barrel in 18 months, only to peak in early July and fall to \$50/barrel in November.

The next 12 months are unpredictable and depend on factors outside of a company's control, in particular government stimulus packages, OPEC's reduction in production volumes and consumer sentiment. The “glass half-full” consensus is that an upturn is unlikely until the second half of 2010. Keep your eyes



Cameron

“Companies that thrive in changing markets, have cash and are patient are perfectly positioned to take advantage of the current downturn”

fixed on a handful of key indicators: the Michigan Consumer Sentiment Index (MCSI), the Chinese GDP growth rate, the price and production volumes of crude, the monthly number of new car sales, and a basket of stock market indices.

A wide spectrum market consolidation will occur over the next two years. Companies that increased debt loads for external growth will have a difficult time making it through this downturn. Those who have cash are likely to keep what they can and hunker down until visibility returns, and then acquire weak prey. Groups in the refining, petrochemical and engineering sectors have lost significant market capitalisation. The larger predators are already preparing to pounce on undervalued competitors with oil and gas reserves (oil companies) or with specific engineering competencies for the future, such as nuclear, wind or solar power (engineering contractors).

The next two years will be interesting times — a period from which the leaders of the future will emerge in politics, in finance and in the petroleum industry. We have the fortune to participate in this period of change. It is a chapter in history that will lead to a redistribution of cards and the creation of new industry kings, some of which will ride in from the east on steeds of sovereign wealth funds.

Consumers are worried about their jobs. Thus, the acquisition of major non-essential goods, such as new cars and appliances that contain plastics, will be largely foregone in 2009. Thus, a very poor petrochemical climate is expected with production turndowns, even with soft naphtha prices. Conversely, motor fuel consumption could rise compared to 2008 due to the lower fuel prices. Speculation is that crude should average around \$80/barrel next year, which would be sufficient to continue most investment plans.

Many refinery projects will be delayed either due to a lack of financing, for those without the cash, or expectations of lower project costs. Steel demand and prices are plummeting. Also, the unexpected short-term availability of contractors is stimulating operators to reopen projects for competitive bidding. Cash-rich operators will opportunistically advance new projects in the next three to six quarters to maximise project value. Catalyst vendors may see some reduced operating rates in 2009 as new capacities have come on-stream, but fuels specifications will continue to be tightened, thus the future of the business is sound.

Refined product demand will pause for several quarters, but will inevitably grow in the mid- to long term. The same challenges remain: mid-term supply tightness, gasoline-diesel imbalances, bottom-of-the-barrel upgrading needs, and fuel oil sulphur reduction. In the long term, there are many challenges surrounding greenhouse gas emission reductions: carbon capture and storage, clean coal, second-generation biofuels, the place for nuclear energy, and the implementation of a World-Wide Emissions Trading Scheme (WW ETS).

Companies that thrive in changing markets, have cash and are patient are perfectly positioned to take advantage of the current downturn. Enterprising groups that have the depth to continue to invest for future challenges are well positioned for tomorrow's growth markets.



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Lou Pucher President Shaw Energy & Chemicals Group

As we enter 2009, we find ourselves in a very different landscape than a year ago. A string of global economic upheavals throughout 2008 has culminated in one of the largest financial crises in generations. Its effects, felt most immediately on Wall Street and overseas stock markets, are rippling throughout every strata of our society: from corporate boardrooms to corner shops to the kitchen table.

From a heady high near \$150 this past summer, oil prices have tumbled to \$50 today. Early in 2008, high feedstock costs led to elevated world ethylene prices, which have since returned to typical industry averages. The story is similar for propylene production.

As economic growth continues to slow, industrial production will be affected. We see some refiners and petrochemical producers deferring plans for grass-roots facilities and reducing current production. What other key concerns do we recognise in our respective industries? Mandated environmental initiatives, such as carbon capture and storage (CCS), will be absorbing a greater share of a shrinking supply of capital, putting more pressure on the funding of traditional capital projects. The petrochemical and refining industry will have to account for higher costs associated with applying carbon capture technology to meet mandated requirements.

And what about plans to develop alternate energy sources — solar, wind and waves? Current low oil prices make these kinds of investments more difficult to justify, but we must anticipate eventual crude oil price recurrence.

Many oil company executives contend that the recent drop in oil prices will make it more challenging to sanction the projects required to meet future demand. Already projects in Canada's oil sands and other major projects in remote, difficult areas are being delayed. However, many other projects, including coal conversions, continue as planned.

The immediate approach will be to develop technologies that help us ultimately reduce our production costs. We are investigating ways to improve operating efficiency and profitability of existing plants and find lower cost routes to produce ethylene and propylene. For example, refining and petrochemical technology experts are jointly developing ways to produce olefins from catalytic cracking technologies and olefin-rich refinery off-gas recovery.

Many ethylene plants as well as FCCUs in the US and Europe are now over 30 years old. We expect to see significant technology revamp projects of these older units aimed at lowering feedstock cost, improving energy efficiency and reducing emissions. Expansion may well be an indirect benefit of these changes, but will generally not be the prime reason for the improvements in US and Europe.

Propylene production can also benefit from the application of new technology. Much of the planned steam cracker olefin capacity being built in the Middle East and Asia uses ethane as a feedstock, creating a shortfall of propylene as a by-product. Deep catalytic cracking (DCC) technology, which uses a fluidised bed process to produce high yields of propylene product, can help eliminate these shortfalls.

In uncertain times, there's a tendency for companies to focus on fundamentals to improve overall operating efficiencies. And now, more than ever, we rely on the talent of our highly skilled engineers and technologists. Additionally, the industry should look to respective government organisations to support the



Pucher

energy initiatives required to meet the growing energy demand in an environmentally responsible manner.

Yet it is also important to remember that despite the steep decline in oil prices in recent months, it will ultimately remain at historically high levels. Cyclic trends periodically reduce demand for fuels and petrochemicals, but as global population and economies grow, so will related production and our technology contributions.

Carlos A Cabrera President & CEO UOP, a Honeywell company

Today's refining industry is confronted with a very challenging and dynamic environment. It needs to be able to profitably produce a variety of products to meet growing demand, comply with ever-changing regulations and mandates, and accommodate unprecedented volatility in feedstock costs and product prices.

Some estimates suggest the world will consume 90–100 million bpd of refined products in the next decade. The diesel-to-gasoline demand ratio is poised to further increase and the demand for heavy fuel oil is expected to decline. At the same time, prevailing environmental and political forces, in general, remain hostile to the oil industry, making permitting for new facilities and expansions burdensome and virtually impossible in many regions, particularly in the US.

In some areas where expansions and upgrades can be considered, capital is becoming increasingly scarce. The question becomes how can the industry increase yields and further optimise existing operations to reduce costs? To remain competitive, refiners and petrochemical producers can focus on reducing energy consumption. Using novel processes, catalysts, adsorbents, equipment and automation technology, refiners can realise up to 25% savings in energy consumption and substantial reductions in carbon dioxide emissions.

This carbon dioxide reduction is important, because looming on the horizon is the uncertainty of when and how additional government regulations on emissions will be enacted, and at what cost to industry. Global harmonisation of sulphur, nitrogen, benzene and other contaminant content of fuels are expected to continue, bringing the need for additional investment. We have found that most of these challenges can be met through combinations of solutions, ranging from technology and catalyst enhancements to deploying new technology aided by advanced process optimisation and automation.

To face the challenges posed by this rapidly changing environment, another key area of focus is feedstock selection. As new sources of crude oil become more complex and expensive to produce and refine, we must be prepared to diversify our feed sources and modify existing facilities to process heavier and more contaminated feedstocks. Energy security will play an increasing role in determining future investments in new technology and feedstock diversification, particularly as governments become increasingly active in regulating and stimulating the energy sector. As noted earlier, the projected increase in world demand is such that all sources of transportation fuels need to be considered. However, any regulatory framework developed — while stimulating alternatives — must ensure that the oil and gas



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industry remains robust and capable of investing and marshalling the resources to meet the daunting demand challenge. This is particularly critical in the short term, as currently there is no viable economic substitute for petroleum in the transportation sector.

Biofuels will also play a role in the future. But we cannot pursue biofuels without careful thought and planning. Production of biofuels must be profitable, efficient and sustainable. Biofuel options that are fungible and compatible with conventional refinery products, and maximise the use of existing infrastructure and transportation technology, should be the preferred choice. Major challenges remain in developing the technology and the infrastructure required to enable investments of the scale required for biofuels to make significant impact on the world supply of transportation fuels. Additionally, feedstocks that displace arable land required for the production of food or require deforestation are not sustainable or environmentally desirable options.

Heavy tar sand-derived synthetic crudes are another source we must look to as we prepare to meet increased demand. Today, there are ongoing developments of technology to economically and efficiently maximise yields from these heavier, more contaminated feeds. Shale oil is another option; however, it will require considerable infusion of new technology to be competitive with existing fossil sources of transportation fuels. The attractiveness of the tar sands and shale oil is their abundant and untapped supply potential, which is comparable in magnitude to known reserves of crude oil.

It is clear that new technology is the key to our energy future, and nowhere is that more apparent than for transportation fuels. Closing this technology gap to someday replace petroleum-derived transportation fuels requires substantial invention and innovation. Well-educated and experienced scientists and engineers, in short supply today, are critical to this success. In 2009 and the years to follow, the industry will face significant challenges in securing experienced talent. As veteran workers retire in record numbers and college graduates are hired to take their places, we must place strong emphasis on training, knowledge management and optimised practices throughout the plant lifecycle. We must capture the knowledge of experts and put it to use broadly and effectively.

We have faced severe challenges before and our industry always seems to find economic, sustainable and viable solutions. It is no different this time. Government actions that allow the marketplace to determine economical and efficient solutions will, in the long run, bring the greatest societal and economic benefit. Ensuring a level playing field will determine the true winning solutions.

Karl D Bartholomew

Director
Jacobs Consultancy

Coming up with a coherent outlook for 2009, given the upheaval we are currently seeing in this last quarter of 2008, will be a challenge for any forecaster. One suggestion is to see how the industries and markets reacted to past events. At mid-year, our outlook for clients and our own management focused on capital cost issues and concerns on demand reduction due to high oil prices. Since



Bartholomew

the financial crisis began and we watched oil prices plummet and demand pull back more than expected, the number one question clients ask is how long will the pull-back in demand last? If you look at how the world reacted to the events during the Iranian crisis (1979–81) and subsequent events, global demand did not reach 1979 levels until 1987–1988.

This time the market reaction may be different. In just under 12 months, we have gone from relatively high double-digit prices for oil to triple digits, and now the question is how low oil could go in response to global demand. Some of the firms trading in oil that bet on \$150–200/bbl oil are now betting on \$20–30/bbl oil (somewhat of a self-fulfilling prophecy). How quickly will consumers resume typical driving patterns and bring back demand? Firms that were not positioned to handle sharp downturns in the 1980s are now able to quickly shed resources and position themselves better for either an extended downturn or a quick recovery. Consumer reaction over the next six months will dictate the market response for the downstream sectors.

Our outlook for 2009 focuses on two major themes:

- The hydrocarbon industry response to demand loss
- Environmentally driven issues: renewable fuels, greenhouse gas regulations.

The international refining picture for the past several years has been one of new capacity announcements, with a guessing game of which project gets funding and support to move forward. Our list of project announcements has grown over the past few years from 20 million bpd to almost 30 million bpd as companies and countries issued press releases. However, as we review each project by its sponsor, location, past history of success, the realistic numbers for capacity expansion through mid-decade has consistently fluctuated between 9–11 million bpd. With the credit crunch, our expected additions are now solidly on the lower end of the range.

The demand loss and credit crisis has also given a number of major projects the opportunity to take a time-out and put pressure on procurement and contracting for lower price tags. Several of the Saudi projects fall into this category, where bids will be delayed until mid-2009, with a major stated objective to drive down costs. This is happening in both upstream and downstream project investment.

As highlighted in prior outlooks for PTQ, a major driver for much of the large US investment has been tied to projects for processing Canadian oil sands. Motiva Port Arthur, Marathon Garyville, BP Whiting, ConocoPhillips Wood River, and Marathon Detroit fall within this group. The cost and financial issues, however, have led to several of these projects slowing down their spending and delaying project execution. Along with the slowdown on the US side of the border have been project cancellations or delays in Canadian projects. Petro-Canada Fort Hills, Total and Statoil have all delayed or deferred major capital decisions or spending due to rapidly escalating price tags for projects. Other synthetic crude oil producers such as Suncor, Syncrude and Canadian Natural Resources Limited have decided to delay later phases of projects.

The loss in demand presents as significant a challenge, if not bigger, in petrochemicals. We are already seeing substantial drops in facility utilisation, from our own survey services such as the Hodson Report for ethylene crackers as well as announcements of plants being idled (BASF, Equistar and Nova) to facilities being shut down entirely (Flint Hills Odessa). The feedstock supply chain in the Middle East and Asia is particularly sensitive to the loss in demand growth, as much of the market is export driven.

Even with the market challenges, companies continue to look at smart investment opportunities. As crude oil prices retreat to levels more in line with natural gas feedstocks, those US facilities with flexibility in feedstock selection may now have an advantage over investment spending in light feed projects. However, these facilities will still be at a competitive feedstock disadvantage to the Middle East crackers.

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The next game-changing event for the process industries will be the implementation of greenhouse gas/climate change regulations. The refining sector is focused on how the GHG regulations will tie into the Renewable Fuels Standards (RFS 2) required by the Energy Independence and Security Act of 2007 (EISA 2007). At the time this column was written, how many issues will be addressed is still unknown. We do know that including indirect land use for corn-based ethanol substantially increases its impact on the environment in a negative (not positive) manner.

The refining industry will be challenged to meet increased volumes of renewable fuels in the gasoline pool as a result of the EISA 2007 mandate as well as determine how to reconfigure their hydrocarbon fuels to offset ethanol's impact. Companies will also be learning how to develop their GHG inventories as we move from voluntary reporting to mandatory reporting. As our own firm moves through the process of ANSI (American National Standards Institute) certification for GHG auditing and verification, it is easy to see that developing a verifiable inventory will become a major learning curve for those in the industry who have not yet looked at their carbon footprints.

The lack of climate change standards is frequently cited as a major reason (along with escalating capital costs) why gasification projects are not making as much progress as once anticipated. A colleague in the project finance community has several projects unable to progress — the main reason stated is the uncertainty in how CO₂ will be handled, either by a cap and trade programme or by carbon tax.

In October 2008, the International Maritime Organization (IMO) adopted the MARPOL VI (Marine Pollution) standards for maritime ship emissions. The deadlines and effective sulphur limits are now known: by 2015, those ships moving through Sulfur Emission Control Areas (SECAs) will be required to burn the equivalent of 0.1% sulphur marine fuel. The European Union had already signed onto the MARPOL VI standards; the US has now done the same. The globally critical deadline is 2020, where all ships in waters except in SECAs will have to use the equivalent of 0.5% sulphur fuel.

Implementing MARPOL VI is not straightforward. At first, it would appear adding fuel oil conversion capacity and hydrotreating to produce lower sulphur marine distillate is the answer. Some parts of the shipping industry see this as the proper outcome. Other participants believe the price tag for marine distillates will be too high and on-board scrubbers are the right answer. The scrubbing solution for MARPOL VI has not been fully vetted with regards to the technology or the costs. A concern that we believe will come to the forefront will be how ships will handle the scrubber wastes. Putting the scrubber effluent back into the ocean will likely face strong challenges from environmental interest groups. We believe this dynamic will become clearer in the next couple of years.

George Bright
CEO

KBC Advanced Technologies

The recent financial and economic gloom has gradually created today's mood, in which it is widely accepted that we are in a recession that could develop into something worse. The oil price has been a direct casualty of the crisis. In the first half of the year, the accepted view was that global GDP and oil demand were growing satisfactorily and there were strains in oil supply.



Bright

"We are optimistic that 2010 will see a strong recovery in oil demand growth, which will be maintained for much of the following decade"

With oil prices increasing, motorists voted with their wallets. For example, in the US, sales of SUVs sank like a stone and consumption of gasoline fell by 8% versus last year. Similar declines in demand became the norm throughout the developed world. A new phrase, "demand destruction", came into being. Just as our attention switched from worrying where the supply was coming from to worrying where demand had gone, Saudi Arabia, in a masterpiece of timing, reacted to months of pressure as prices rocketed by announcing increases in oil production totalling more than half a million barrels per day.

Within 80 trading days, the price of oil fell from \$147–60/bbl. Incredibly, from looking for the price ceiling, we are now searching for the price floor. Instead of the OPEC countries producing oil at full capacity, they are now scrambling to make production cuts in an effort to shore up the price. At an October 2008 emergency meeting in Vienna, OPEC announced 1.5 million bpd of production cuts and, for the time being, this move has helped to stabilise the market.

The issue now is discovering the consequences of such a massive cut in prices; where are prices headed in the short and medium term? The consequences of \$60/bbl oil are many and varied. First, they bring relief to consumers in the developed world faced with high heating and transportation bills; second, they disrupt the best-laid budget plans of the OPEC countries; and third, they raise doubts about the viability of projects both upstream and downstream.

The first issue is critical to the economic health of the developed countries. Lower oil bills might help kick-start economic recovery; however, consumer confidence is so low that little immediate benefit will be felt. If \$60/bbl becomes the norm, there will eventually be a boost to oil demand. The second issue of OPEC's budgets is very intriguing. It is widely held that a price of \$75–95 is required to meet the cost of developing new sources of oil and the needs of social programmes of certain OPEC countries. The third factor — the viability of projects — is of profound importance for the direction of oil prices in the long term. It was widely reported that Total Petroleum requires an oil price of \$90/bbl to achieve a 12.5% internal rate of return (IRR) for its Canadian tar sands project and a \$70/bbl price to achieve the same IRR for its deepwater production project in Angola. Many other projects also carry a high cost structure and must be at risk from \$60/bbl oil. In the downstream sector, before the economic crisis engulfed us all and destroyed demand, we were faced with a wave of new refining capacity coming on-stream that exceeded oil demand growth by a factor of nearly three. Too much refining capacity facing too little demand growth spells poor refining profitability. The essential point is that investors, faced with lower crude oil prices and declining oil demand growth, are starting to defer or cancel both production and refining projects, thus storing up the prospect of future shortages of capacity when oil demand growth eventually recovers. In refining, we see marginal refining capacity being shut down in both Europe and the US and increasing pressure on margins as new capacity comes on-stream in Asia. We would expect a return to the sentiment of the 1980s and 1990s, with an absolute focus on cost minimisation.

Having laid out the possible consequences of prices at \$60/bbl, what does KBC think will actually happen to prices? In the very short term, we believe that OPEC will succeed in



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stabilising the oil price with production cuts; as a result, in 2009, the average price of Brent crude oil will be \$80/bbl. We are optimistic that 2010 will see a strong recovery in oil demand growth, which will be maintained for much of the following decade.

While this all seems perfectly logical, the problem is that inside of three months we have seen prices fall by nearly \$90/bbl. So, how on earth can we be sure the same thing will not happen again, this time in reverse? We cannot.

Steve Sonnenberg President Emerson Process Management

The high cost of doing business and a worldwide economic slowdown will pressure petroleum refiners to operate more reliably and efficiently in 2009.

While the stalled economy and erratic financial markets probably will not affect ongoing refinery expansion and modernisation projects, refiners may decide to proceed more slowly with new projects now in the conceptual phase. The crisis in the economic investment world has thrown companies a curve ball, and they are reacting to that with caution.

Today, refiners' profits are continually squeezed by a combination of reduced market demand for their products and crude price swings "on the front end" that challenge their ability to get profits "on the back end". When operating costs remain high and demand goes down, refiners must consider new ways to cut costs and avoid process slowdowns and shutdowns. The best use of technology can address these challenges by allowing companies to gain reliability and efficiency.

Wireless devices can collect data about plant processes and assets throughout the facility, including areas that were previously inaccessible. Many refiners, including one of the world's largest energy producers, have worked to test and establish numerous wireless applications. The ways wireless can be applied to cope with today's challenges and improve refining operations are limited only by the creativity of the user.

A long-time industry challenge that will continue into the new year is the shortage of adequately trained refinery operators and other skilled employees. As senior staff members retire, companies cannot hire knowledgeable, experienced personnel to take their place. For some companies, finding qualified employees is their largest expense, such as in the oil sands of Calgary, Canada, where refinery personnel are flown in regularly for each work shift from Atlantic Canada and the interior of British Columbia to the work site.

Significant world events often influence the refining industry, and it will be no different in 2009. During the last few years, government-owned oil companies, such as Petrobras in Brazil, Petroleos de Venezuela in Venezuela and Gazprom in Russia, have begun to produce enough oil to not only supply their countries' needs, but to export crude and refined products to the world market. These national oil companies, part of a group called the New Seven Sisters, sit on 80% of the world's oil reserves and wield a market force greater than the industry's original Seven Sisters (Amoco, BP Chevron, Exxon, Mobil, Shell and Texaco). This new breed of oil company will redefine the oil business for the next several decades. The



Sonnenberg

challenge for Emerson and other suppliers is to learn more about these government-owned firms and their business practices so we can help them compete globally.

In the US, the lessons learned during the 2005 hurricane season by refineries and their partners meant hurricane Ike had much less of an impact on refining in September 2008. While there was significant short-term loss in refining capability, for the most part those refineries were back on line quicker than in the past. That improved ability to respond to threats will serve the industry well in 2009 and beyond.

Don Clark Vice President, Global Industry Solutions Invensys Process Systems

The future of petroleum refineries and petrochemical plants will be significantly impacted and affected by their need to reduce carbon emissions. Refineries and plants will accomplish this primarily by reducing their energy consumption and carbon sequestration, and they will rely on advanced process automation and control technology to achieve this.

Dwindling availability of light conventional crude oil has created a growing demand for clean fuels refined from alternative crude sources. Oil sands, oil shale, coal and natural gas will become increasingly important fuel sources. While this is good for oil importing countries, it will require new capital investments to upgrade refineries so they are able to handle these liquids, or synthetic crude oils, that have significantly different chemical properties than those of conventional crude oils.

As vehicle fuel economy improves, primarily due to government mandates and consumers' desire to reduce their own CO₂ emissions, and as baby-boomers retire and the use of renewable fuels increases, demand for petroleum-based fuels will slow. As a result, petroleum refiners will be challenged, at least in the near term, to maintain profitability.

In the US, demand for diesel fuel is expected to grow steadily, somewhat offsetting the decline in gasoline demand. This forecast is predicated on changes in demographics and the composition of the vehicle fleet. Over the next decade, diesel production per barrel of crude is expected to grow to 30% from the current yield of 20%.

A slowdown in China's economic growth will put pressure on petrochemical producers, since demand for consumer goods will also slow. Emphasis will be placed not on maximising production, but on minimising operating costs. As with energy management, advanced automation and control technology has proven to be a cost-effective means of managing plant economic performance. For example, recent initiatives taken by Sasol, a South African company involved in mining, energy, chemicals and synthetic fuels, have shown that substantial reductions in variable costs can be achieved, with little to no capital investment, simply by giving operators real-time information about the economic impact of their decisions and permitting them to take action based on this information.

To better leverage technical expertise and reduce support costs, multi-site refining and petrochemical companies will increasingly centralise their operations centres, which will facilitate teamwork and collaboration by bringing operational and technical issues and problems to the experts rather than requiring the experts travel to the site. This too will rely on advanced process automation and control technology.



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Processing trends

Outside of the realm of traditional refining processes typically discussed in PTQ are developments equally important to the diversification of transportation fuels and petrochemical product sources. Market volatility and fluctuations in feedstock costs compel the industry to continuously reassess viable process scenarios in GTL and olefins processing

Converting natural gas into liquid fuels

On again, off again: when is gas-to-liquids (GTL) ever going to become competitive? Efforts continue in the development of a cheaper and cleaner way to convert natural gas into gasoline and other liquid fuels, making it economical to tap natural gas reserves that in the past have been too small or remote to develop. For example, there have been efforts at developing a process that involves fewer steps and is more efficient than the more established techniques that are based on the Fischer-Tropsch (FT) process. However, if such a process works well, it will no doubt drive up the price of natural gas as more natural gas gets used to produce liquid fuels for transportation. That will, in turn, reduce the desirability of natural gas for use in heating and electrical power generation.

A better way to convert natural gas into liquid fuels, according to some developers, is by using small chemical plants that would allow many smaller and/or remote natural fields to be tapped. For example, natural gas on the northern slope of Alaska has not yet been exploited because the costs of building a natural gas pipeline to bring it down to the lower 48 states is quite high. Therefore, if there was a way to convert the Alaskan natural gas to liquid form, this would allow the existing Alaskan oil pipeline to move the liquid south.

A start-up company in California, Gas Reaction Technologies, claims its GTL technology will work well for medium- and small-sized natural gas fields. If such technology indeed lowers the cost of GTL, then why use natural gas as a vehicle fuel when it can be converted to a far more convenient liquid form? But since the conversion itself uses energy, natural gas converted to liquid fuel represents a loss of energy that would not occur if natural gas was directly burned in cars. This is the reason for scepticism that there will ever be a big shift to natural gas for vehicle transportation, as there is apparently a trend (albeit gradual) towards more efficient and less costly GTL technology. Liquid fuels are more convenient and use up less space. Technological developments that cut costs for achieving the natural GTL conversion will provide a more convenient and therefore more valuable way to use natural gas.

However, sceptics on the other side of the argument predict that small chemical plants using non FT-based technology for capturing remote pockets of natural gas into liquid fuels will probably never be built on a commercial scale considering the current financial and credit crisis. They will be too risky to build at the scale needed to make it viable. Another important reason is that natural gas to LNG is around 90% efficient on a carbon basis compared to the claimed 50% for this proposed non-FT technology. In any event, methanol manufacture from natural gas is around 70% efficient for specifically defined circumstances (eg, world-scale size rather than small or modular scale), so if an investor wants to make liquid fuels from natural gas, methanol may be the way to go, as methanol technology is already proven at scale.

To be sure, non-FT technology developers have never claimed to have superior efficiency compared to FT technology or other concepts that have been patented. They only claim to be more efficient than FT on much smaller scale applications (ie, monetisation of remote pockets of stranded gas). So, small-scale non-FT technology would be ideal for the conversion of gas reserves that are too far from the market or

currently being flared. The liquid product is also flexible, since it can produce either diesel, 95 octane gasoline or ethylene.

One of the major deterrents to widespread development of world-scale GTL projects in the past has been the high capital costs of such ventures. However, the rapidly increasing price of a barrel of crude, touching new highs of \$100, and the emergence of new technologies to drive down costs, as well as the employment of economies of scale — such as the Pearl GTL and Oryx GTL projects — all serve to indicate that GTL projects could soon emerge at the forefront of the alternative energy and fuel markets, provided crude prices again escalate to above \$100/bbl from the \$50/bbl in December 2008.

Otherwise, as GTL trends veer towards small to mid-sized projects, there is a critical need to drive down capital costs to accommodate smaller investors. The viability of small-scale projects is being considered. For example, the proprietary Microchannel process technology developed by Velocys may have a role to play in terms of reducing the size and cost of GTL projects.

Commercialised FT technologies combined with the more traditional cost reduction strategy of catalyst recycling also help make existing FT technology more competitive with mid-sized projects. For example, Umicore AG & Co KG, one of the companies fronting catalyst recycling technology, can help add more value to FT-based processes and increase planning reliability. With certain segments of industry now using GTL-based kerosene (eg, Qatar Airways) instead of the traditional crude-derived jet fuel or kerosene, the demand and potential for the GTL-derived liquid fuel market may be set to expand.

Ethylene-based trends in North America

Ethylene, as the largest-volume petrochemical in the world, is often used as a benchmark to measure industry competitiveness. It is a particularly important petrochemical for countries such as Canada because so much of its chemical industry is ethylene based. However, the Middle East is easily the world's lowest cost producer of ethylene. It derives that advantage from very low prices for ethane feedstock and natural gas energy, but this cost advantage is beginning to erode. New Middle Eastern contracts for natural gas and ethane will not be priced as advantageously as former contracts were. The supply of incremental ethane is also becoming constrained, forcing some new cracker projects to utilise heavier feedstocks like propane, butane and naphtha.

The province of Alberta in Canada is the second lowest cost ethylene-producing region in the world. Alberta derives its competitive advantage from a number of factors, including the fact that the price of North American natural gas has been compared to crude oil. Ethylene crackers based on natural gas liquids are advantaged compared to crackers based on crude oil-derived feedstocks like naphtha. Ethane is also less expensive in Alberta than on the US Gulf Coast due to the regions' differing market dynamics. The ethane-extracting plants in Alberta are very large and offer economies of scale. Finally, the ethylene crackers are large and modern and offer additional economies of scale. Historically, Alberta producers have a cost advantage compared to the US Gulf Coast of about six cents per pound of ethylene.

Work has been under way under the auspices of the

Hydrocarbon Upgrading Task Force in Alberta for several years to promote the concept that products and off-gases from the processing and upgrading of oil sands should be utilised within the province to produce refined petroleum products and petrochemicals. The motivation is to extract maximum value added from the bitumen resource for Alberta rather than exporting raw materials. At production levels of two million bpd of bitumen, exporting raw bitumen contributes about \$25 billion per year to Canada's gross domestic product (GDP). If the bitumen is upgraded to synthetic crude oil, the GDP contribution doubles to \$50 billion. If the upgrading continues downstream to refined petroleum products and petrochemicals, the GDP jumps to \$75 billion or higher, depending on how far down the value-added spectrum you go prior to exporting a product. Achieving this vision will require significant new investments in refinery and petrochemical capacity.

Olefins market and technology trends

A recently released Nexant ChemSystems study, *Petrochemical Market Dynamics: Olefins*, provides detailed projections on the olefins market, including ethylene, propylene and butadiene. While demand for olefins such as propylene had been increasing by at least 5.5% for the past several years up until the beginning of the financial crisis last September, the next few years will see a tempering of propylene demand. Already, certain naphtha-based steam crackers, such as one on the US Gulf Coast, have shut down indefinitely due to low propylene demand. However, it is expected that long-term demand beyond 2010 will be significant. Apart from steam cracking, FCC processing (eg, deep catalytic cracking [DCC]) and traditional production techniques, propane dehydrogenation and translocation reaction mechanisms are developing, and gas hydrocarbon technology has also been considered a viable technology.

Currently, pyrolysis technology can co-produce ethylene and propylene in ratios of around 1:0.5–0.6. Since, until recently, the demand for propylene-derived products had been very strong, the traditional co-production of ethylene and propylene via refinery recovery methods would not be enough to fulfil future demand. When the demand for propylene again exceeds 4.5% per year, as it is expected to in 2010, catalytic technologies more than likely will have been improved. This includes improvements to the traditional steam pyrolysis and catalytic technologies, such as propylene production based on catalytic cracking technology (eg, DCC), along with ethylene plant support technology such as butene disproportionation technology and C_4/C_5 cracking into propylene.

Asia's propylene production capacity of 24.269 million tonnes/year makes it the largest propylene-producing region in the world, representing 32.4% of the world's total production capacity. In 2005–2010, ChemSystems projects world propylene production capacity to increase by about 18 543 million tonnes/yr. World annual propylene production capacity will reach 96 804 million tonnes in 2010 and 108 653 million tonnes in 2015.

The trend in ethylene and propylene production technology and materials is moving in the direction of diversification and the development of new technologies. Ethylene crackers now tend to use lightweight materials, and many manufacturers try to optimise the cracker unit to produce more ethylene, and this is bound to reduce the volume of propylene cogeneration in steam cracking.

2008 now seems certain to be the turning point for olefins such as propylene, with major new plants already on-stream, and the economic outlook looking decidedly weaker. Margins have been disappearing from much of the olefin value chain in 2008, as lengthening markets prevent producers from passing through rising feedstock costs.

It is against this background that the ChemSystems olefins report investigates the market and growth profile for olefins such as ethylene, propylene and butadiene, and details the expected developments in supply and trade. The report finds that 2008 will mark the end of the period of high operating rates, which now start their decline towards a trough expected in 2011–12.

Global propylene growth has averaged 5.5% over 1995–2007, and is expected to slow down to 4.5% over 2007–2015. In contrast, global consumption of ethylene and butadiene is forecast to grow at higher rates over the next ten years than has been seen in the last decade. The fundamental driver for this transformation, according to the study, will be the increased domestic consumption in developing economies.

The tight markets and high revenues for olefins producers have permitted massive investment in new cracker capacity. Oil prices have driven polymer prices to record levels and this, coupled with a more generalised economic overheating, is now having a negative effect on polymer demand. A reduction in global capacity utilisation, and thus profitability, is therefore inevitable in the coming years.

New capacity entering production over 2008–2012 is focused on the Middle East and Asia, with the former taking advantage of low-cost feedstock, and Asia exploiting proximity to market, refinery developments and fixed cost advantages. In a high oil price environment, feedstock cost is a primary driver of competitive advantage. The new plants in the Middle East had been exploiting this advantage to supply derivative markets in both Europe and Asia, and will prove a significant threat to established suppliers whose economics are based on naphtha, such as European steam crackers. It is these naphtha-based producers, who until recently enjoyed high operating rates and good export demand, that will suffer most during the trough in 2011–12.

The ChemSystems study notes that a major shift in trade



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patterns for ethylene derivatives is also anticipated. Polyethylene expansions in the Middle East are projected to exceed the import requirements in China and the wider Asian market. Regions such as North America and Western Europe will therefore have to absorb a substantial increase in net imports. Global growth of propylene consumption remained strong in 2007, reaching 73 million tonnes. Polypropylene, accounting for 62% of propylene demand, is among the fastest growing commodity polymers. A significant change in polypropylene trade positions is expected as the Middle East emerges as a major exporter of polypropylene. Operating rates among less competitive producers in western countries will be depressed, with Asian producers protected to some extent by soaring regional demand. The global butadiene markets have also been tight due to inadequate investment in new capacity, contributing to record price levels. The rapidly developing automotive manufacturing industry in Asia, particularly China, is one of the major drivers affecting butadiene globally. Major steam cracker developments in Asia will result in increased mixed C_4 s for butadiene production and a reduction in operating rates towards 2011. In the long term, the growth of ethylene production, and therefore the availability of C_4 s, will exceed demand growth for butadiene, leading to increased reprocessing of steam cracker C_4 s.

In 2007, 115 million tonnes of ethylene was consumed globally. Polyethylene accounted for around 60% of global demand. The next largest use is in the production of ethylene oxide, primarily for the production of ethylene glycol. Growth in the vinyls chain is forecast to remain high owing to the construction boom in developing regions, although the effect on ethylene demand will be diluted by the ongoing growth in supply via acetylene routes in China. Propylene demand growth has historically been above global GDP. ChemSystems projects that growth going forward will align more closely to GDP levels. Growth in a number of derivative markets such as acrylonitrile, cumene and acrylic acid has slowed significantly. Polypropylene growth has also slowed from the impressive 7.0% seen over the last ten years, projected to be ongoing at over 5.0%. Increased penetration into other polymers markets such as polyethylene and polystyrene will be supported by increased propylene availability. Butadiene prices have broken records each year since 2004, reaching over \$3000 per tonne in Asia in mid-2008. The peak follows long periods of oversupply for both butadiene and synthetic rubbers. The Asian market has been particularly attractive for butadiene producers due to the ongoing development of car and tyre production in the region.

The proportion of ethylene capacity based on advantaged feedstock will increase rapidly in the next five years after modest growth since 2000. Countries with low-cost feedstocks such as Iran and Saudi Arabia will be bringing around 20 million tonnes of capacity per year online by 2012. The sustained period of high operating rates since 2004 has masked this underlying change to regional competitiveness. The impact of these new producers will become increasingly clear as global operating rates decline.

In 2007, approximately 15 million tonnes of ethylene was produced from ethane crackers, accounting for 14% of global production. This number is forecast to nearly double by 2015, showing the strongest growth across all cracker feedstocks. The proportion of ethylene made from mixed-feed crackers is also expected to increase, driven by rapid expansion in China. In contrast, naphtha's share of global production will decrease from 43% in 2007 to 38% in 2015. While a generic naphtha cracker can produce between 0.5–0.6 tonnes of propylene per tonne of ethylene, ethane crackers yield insignificant volumes of propylene, which is usually not economically viable to recover. The average propylene yield from steam cracking is thus declining as a result of the major ethane-based investments

in the Middle East. On-purpose propylene production has therefore become increasingly important in meeting demand growth. The proportion of propylene produced from on-purpose processes is forecast to increase from 5.0% in 2007 to 12% in 2015.

In geographic terms, propylene is surplus in North America as a result of the large refinery capacity and preference for FCC units. Only 2.0% of propylene produced in the region was derived from on-purpose processing in 2007. The scarcity of propylene in Western Europe, particularly in Germany, has meanwhile seen very strong margins for the two propylene dehydrogenation (PDH) units operating in Europe and investment in a metathesis unit.

Diversification policies in the Middle East have to some extent shifted attention to propylene derivatives rather than ethylene derivatives in the region. Several new world-scale cracker complexes are now equipped with metathesis units. There has been a lot of interest in combined PDH/polypropylene units to fill the short-term supply gap for polypropylene, but less activity is expected in the longer term. Propane will instead be consumed in ethane/propane-based steam crackers.

In Asia Pacific, heavy-liquid steam crackers are a major source of propylene supply. Around 8.0% of propylene in the region was produced from on-purpose units in 2007. The availability of advantaged ethylene derivatives from the Middle East will limit the potential for ethylene capacity development in Asia Pacific, and so also limit the availability of co-product propylene. As most new refineries in Asia are opting for hydrocrackers to upgrade heavy oil fractions, FCC propylene opportunities will also be limited. On-purpose technology, particularly olefin conversion, is therefore expected to play an important role in propylene supply in Asia Pacific.



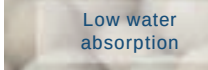


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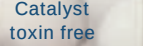
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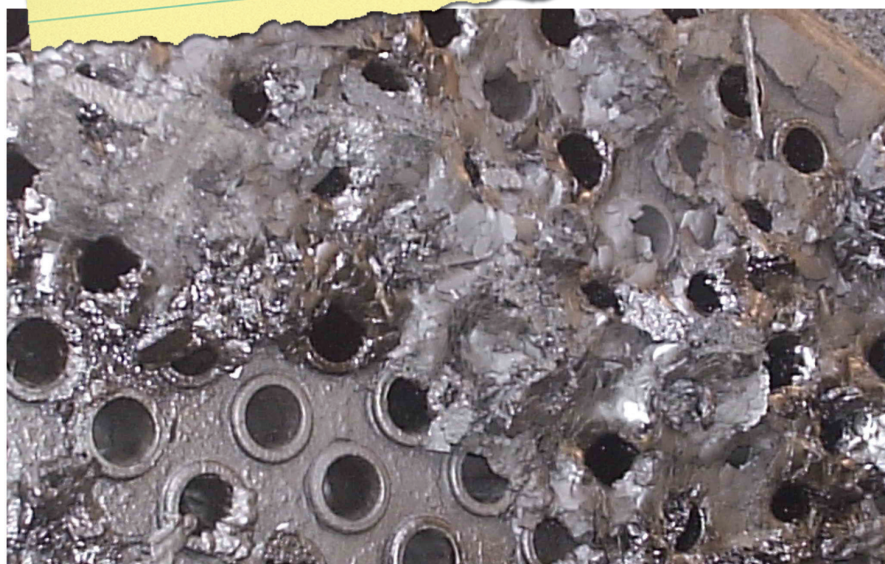


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Process Notes



Nasty Stuff

This exchanger has seen better slates.

Heavy crudes are here to stay. As long as oil prices remain high, Canadian, Venezuelan, Deep Water Gulf of Mexico, Mexican and other low API gravity crude oils will play an ever more important role in supplying world refineries. And prices promise to remain high because gainsayers notwithstanding, Hubbert was right.

A big question is how to handle best these nasty crudes? Do you revamp existing units or invest in new capacity? With refineries now running flat out, the balance might seem to favor grass roots expansion, but given the substantial cost multiplier over revamps, this could be questioned.

Whichever the case, however, an inescapable fact is that the process design of the project will prove crucial. Between the charge pump and the desalter and the units' distillation columns there are many places where miscalculations in the process design could wreck the entire project.

Can you really be sure of attaining desired crude rates? Desalting viscous crude is extremely difficult. Minimizing coking or asphaltene precipitation in the heaters demands extreme care. Can you reasonably expect high diesel and HVGO recoveries, acceptable levels of nickel, vanadium, and microcarbon residue (MCR)? Refiners who

cut deep should not be surprised when the HVGO product MCR is over 2 wt% and the vanadium content is in excess of 10 ppmw. Any one of such difficulties can result in lower revenue, unstable operation or even an inoperable unit. It is critical to understand that the inherent properties of these low API gravity crudes dictate that exact process design is of paramount importance.

The point of this litany of possible problems is to remind you not to skimp in the early phases of engineering. From the start of the LP work through the completion of front-end process engineering, actual product yield and product qualities depend on the process design.

The message is clear. Nasty crudes will continue to make up an increasing proportion of refineries' crude slates. But time is precious. The sooner we face this fact, unwelcome as it may be, the more expeditiously we can adapt.



For a more in depth review, ask for Technical Papers 173, 185 and 197.



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The following are responses to questions concerning important processing issues in the refining and petrochemical industry. Additional Q&A can be found at www.eptq.com/QandA.

PTQ wishes to thank all those respondents who have contributed both here and online

“For many crude/vacuum distillation units, up to 20–30% straight-run diesel gas oil can be found in catalytic feed and thus become downgraded in the fluid catalytic cracker. How can straight-run diesel gas oil be reduced in catalytic feed to, say, 10%?”

Alan Goelzer, Senior Consultant, Jacobs Consultancy, alan.goelzer@jacobs.com: When the heavy atmospheric gas oil, vacuum diesel, light vacuum gas oil and heavy vacuum gas oil composite within catalytic feed is analysed via GC-based simulated distillation (ASTM D6352), it is not uncommon to find more than 20 wt% of the components exhibiting normal boiling points below 662°F/350°C. FCC riser reactors, operating catalytic and hot at 977–1022°F outlet, within today’s fluid catalytic crackers will crack most of these diesel gas oil components into olefinic C₃ and C₄ LPG and FCC gasoline. The contribution from the light cycle oil (LCO) could be on the order of the diesel gas oil’s polynuclear aromatics content, and this LCO will be extremely aromatic, with low API gravity and low cetane values.

What happens to the diesel gas oil component is more complicated in FCC riser reactors operating cold at 950–968°F. If the catalytic feed assays organic hydrogen-rich and the diesel gas oil more so, it can appear that the diesel gas oil has undergone only partial cracking and boosted the API gravity and cetane values of the LCO. In any event, the LCO remains far inferior to the original diesel gas oil when ultimately making ULS 2-D on-road diesel fuels or sulphur-free Euro IV diesel gas oil.

For more and more refiners, there are an increasing number of incentives to enhance the volume percentage output of ULS 2-D on-road diesel fuels, while trimming back the output of ULS gasolines and reformulated gasoline blendstocks for oxygen blending (RBOBs). Increasing the volume percentage yield of heavy straight-run diesel gas oil off the crude atmospheric tower by lowering the 662°F boiling point components in the catalytic feed can be very helpful.

For a new crude/vacuum distillation unit, a combination of computer simulation modelling, engineering judgment and minor incremental capital costs for optional extras can maximise the volumetric partition into heavy diesel gas oil and away from the catalytic feed.

It is very important to establish the specification requirements with respect to maximum allowable values for T90(D86) or T90(D2887) or T95(D86) in finished diesel fuels, and how this translates into an operative value for T90(TBP) or T95(TBP) for heavy diesel gas oil per computer simulation modelling. The latter may require the evaluation of relative contributions of light coker gas oil, FCC LCO, SR kerosene, hydrocracked heavy diesel blendstock, and heavy diesel gas oil to 608–662°F and 662°F Simdist fractions in typical finished ULSD fuels. For new crude/vacuum distillation units, the following options are then explored via parametric computer simulation modelling to maximise the volume percentage or barrels per stream day (BPSD) output of heavy straight-run diesel gas oil within the operative constraint for T90(TBP) or T95(TBP) determined previously:

- Inclusion of separate pumparounds, draws and side steam strippers for straight-run kerosene and heavy straight-run diesel gas oil, so that the overlap of kerosene and heavy diesel gas oil is appropriate, while the kerosene flash point is enhanced (perhaps to >123°F)
- Inclusion of heavy atmospheric gas oil pumparound, draw and side steam stripper
- Parametric optimisation of stripped heavy atmospheric gas oil (HAGO) volume percentage on crude slate, not zero or too small and not too high
- Use of inlet diffuser in the atmospheric tower, plus carefully selected hardware and number for the bottoms stripping trays
- Optimisation of pounds superheated stripping steam per barrel of atmospheric tower bottoms. Superheat levels in the 700°F± range are recommended.

Within this configuration, the vacuum diesel pumparound and draw in the vacuum distillation unit are not a diesel blendstock. Rather, the VDU vacuum diesel pumparound is structured to sustain and stabilise the target “vacuum”, and vacuum diesel is the first candidate to go to the co-processing hydrocracker unit.

Within the context of revamps to existing crude/vacuum distillation units, there can be constraints and challenges that force some loss of volume percentage or BPSD out of the heavy diesel gas oil. For example, previous revamps may have shifted the crude atmospheric tower to deep-cut lift into the HAGO to unload an undersized vacuum distillation unit. This drags more diesel components into the catalytic feed pool. In other instances, the HAGO pumparound, draw and side stripper are missing, so the higher boiling fraction and the tail of the heavy diesel gas oil see the original flash, along with increased prospects for asphaltenes and metals.

“At what point does a two-stage reactor design significantly enhance HDS/HDA catalyst effectiveness (considering recent efforts to process solvent or distillate feedstock)? With current budget constraints, what factors should justify the implementation of counter-current reactor technology over conventional co-current reactor technology?”

Jesper Rødtjer, Sales Manager, Haldor Topsøe A/S, jpr@topsoe.dk: Having industrial experience in producing ultra-low aromatic diesel such as Swedish city diesel, dating back to the early 1990s, we have spent considerable time and effort on understanding catalyst effectiveness in relation to optimised process design. This continuous effort has resulted in an improved HDS/HDA technology being a cost-effective solution for upgrading heavy diesel fractions to high-quality ultra-low sulphur diesel. The development in dearomatisation catalyst has resulted in the commercialisation of catalysts with four times higher activity for the saturation of aromatics. The result is that the required catalyst volumes have been reduced to a level that makes counter-current reactors non-justifiable from an economical perspective.



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FCC reactor design: part II

In part I, reaction kinetics, cracking chemistry, pressure balance, catalyst and vapour residence times, and fluidisation were considered. In part II, feed injection technology and riser termination devices to minimise dilute-phase cracking are reviewed

Warren Letzsch, Chris Santner and Steve Tragesser
Shaw Energy & Chemicals Group

The feed injection system is the most important aspect of any fluid cracking process, since this is where the feedstock is brought into contact with the hot catalyst. In addition to vapourising the feed so catalytic cracking can proceed, the entire feed injection system must perform other essential functions, including quenching the hot catalyst coming from the regenerator as quickly as possible and contacting all of the feed with the catalyst.

Since vapourisation of the feed is essential to the process, small oil droplets must be produced to ensure rapid heat transfer. This is illustrated by the following analysis. If oil droplets and catalyst particles are assumed to be spheres of diameter D_o and D_c respectively, the weight of the catalyst and oil in the riser is:

$$\text{wt of catalyst} = N_c \cdot \frac{\pi}{6} D_c^3 \cdot \rho_c \quad (1)$$

$$\text{wt of oil} = N_o \cdot \frac{\pi}{6} D_o^3 \cdot \rho_o \quad (2)$$

where N_c , N_o are the number of catalyst and oil particles and ρ_c , ρ_o are the densities of the catalyst and oil particles. The catalyst-to-oil ratio is simply (1) divided by (2) or:

$$\text{CAT/OIL} = \frac{N_c \cdot D_c^3 \cdot \rho_c}{N_o \cdot D_o^3 \cdot \rho_o} \quad (3)$$

Substituting for the densities (56 and 90 lb/ft³ for the oil and catalyst respectively), assuming a catalyst-to-oil

ratio of 5.0 and a catalyst particle size of 70 microns into Equation 3, a single oil droplet of 280 microns must contact 199 catalyst particles, while a 70 micron oil droplet (the same size as the catalyst particles) would contact about three particles. It is highly unlikely a single droplet can contact about 200 catalyst particles. As a consequence of these hydrodynamics, the larger droplets will not be able to directly quench all of the catalyst particles. This results in a higher average reactor temperature, a higher delta coke and more dry gas in the case of large oil droplets.

A large amount of heat transfer must take place between the catalyst and oil. The smaller droplets have four times the external surface area in the previously mentioned case. The higher heat transfer rate and the smaller diameter drops greatly increase the rate of vapourisation of the oil. Table 1 by Mauleon shows the value of a small oil droplet size for intimate catalyst/oil contacting and rapid vapourisation.

Buchanan's analysis gave similar results. He also found that heat transfer between the catalyst and gas was almost instantaneous, that heat transfer by radiation is much slower than for convection and that the droplet temperature will be equal to the wet-bulb temperature based on the surface composition. The number of large droplets is important, since a few of these may comprise a relatively large percentage of the feed on a weight basis.

All of the feed nozzles used in fluid

catalytic cracking can be classified as either of two fluid nozzles: oil and steam or pressure nozzles. Pressure nozzles atomise by applying pressure to a liquid and then forcing it through an orifice. Today, all of the commercially available feed nozzles offered by FCC licensors are of the two fluid nozzle type. Nukiyama and Tanasawa found the following correlation for two fluid nozzles:

$$D_{SM} = \frac{1920}{U} d_p^{0.5} \sigma^{0.5} + 597 d_p^{0.45} \frac{\mu}{\sigma \rho_g} \frac{L}{G} \frac{\rho_g}{\rho_l} \quad (4)$$

Where:

D_{SM} = Sauter mean diameter, microns
 σ = surface tension liquid, dynes/cm
 ρ , ρ_g = liquid and gas density, gm/cm³
 μ = viscosity liquid, poise
 U = relative velocity of gas and liquid
 L/G = liquid/gas mass ratio.

This equation has two terms that contain both the fluid properties and nozzle parameters. The second term suggests the droplets will be smaller if more gas is used relative to the liquid rate, while the first term relates to how the two streams are brought into contact with each other. Higher relative velocities create more shear and smaller droplet sizes. When resid is processed, the droplet sizes tend to increase due to increases in the surface tension and viscosity of the oil. The modified Moge equation shows this relationship:

$$\frac{D_{RESID}}{D_{GASOIL}} = d_{GASOIL}^{0.5} \frac{\sigma_{RESID}}{\sigma_{GASOIL}}^{0.5} d_{MVGO}^{0.2} \frac{\mu_{MVGO}}{\mu_{PRESID}}^{0.2} \frac{\rho_{VGO}}{\rho_{PRESID}}^{0.3} \quad (5)$$

Typical numbers for gas oil and resid suggest resid would produce droplets about twice the size of gas oil feeds. Correlations of each of these fluid properties vs temperature show each increases significantly as the feed temperature is reduced from 700–350°F. The changes are largest below 450°F.

Other nozzle features that play a role in feed/catalyst contact are the spray angle, evenness of the spray (uniform flow rate) and penetration into the centre of the riser. These features control the overall distribution of the

Feed atomisation (feed nozzle exit velocity: 50 m/s)

Oil droplets size, microns	500	100	30
Relative number of droplets	1	125	4630
Catalyst particles per oil droplet	1000	9.09	0.25
Vapourisation time, m/s			
At 50% /= vapourisation	220	11	4
At 90% /= vapourisation	400	20	8

Table 1

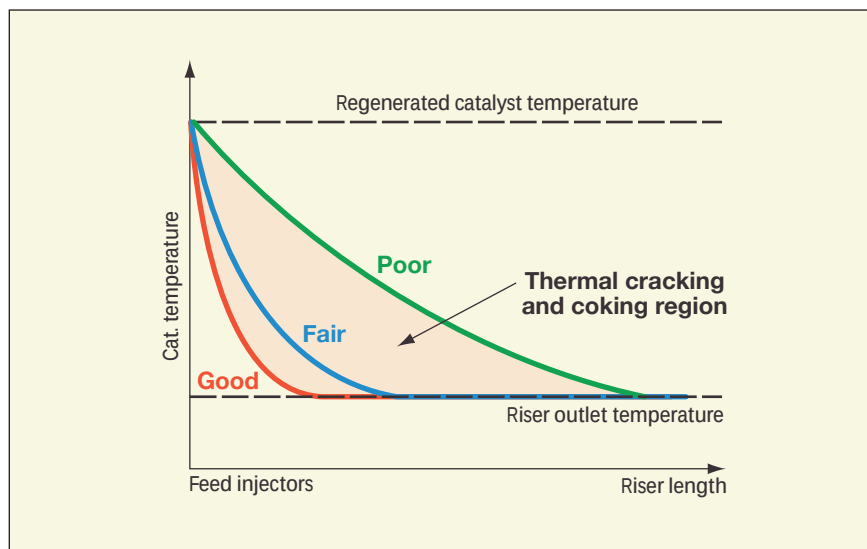


Figure 1 Influence of feed injector design on FCC reactor yields

FCC feed nozzle effect			
	Axial	Advanced radial	Delta
Feed rate	Base	1.04 Base	
Dry gas (FOE vol%)	4.44	3.1	1.34
LPG, vol%	25.51	27.05	15.54
Gasoline, vol%	55.11	61.27	6.16
LCO, vol%	22.23	17.75	-4.48
Slurry, vol%	4.23	3.94	-0.29
Coke, wt%	5.18	5.12	-0.06
Conversion, vol%	73.5	78.3	4.8
C ₃ + liquid, vol%	107.1	110	2.9
Feed preheat, °F	459	472	13
Riser temp, °F	1000	995	-5
Regenerator temp, °F	1323	1270	-53
C/O ratio	6.4	7.4	1
Delta coke, wt%	0.81	0.69	-0.12

Table 2

feed across the riser cross-section in the feed injection zone. If everything is done properly, the temperature in the riser should drop quickly and catalytic cracking will be maximised, and thermal reactions will be suppressed.

This is illustrated in Figure 1.

The improvement in yields can be quite significant, with payouts of three months or less for revamps to existing systems. As an example of this, Table 2 gives the before and after yields for one

revamp. The reduction in dry gas and delta coke frees the unit of gas and coke limits, and the increase in gasoline of 6.2 vol% is quite valuable. Research octane number may drop by 0.5–1.0 due to the lower average reactor temperatures, even though the riser outlet temperature is unchanged. However, this effect can be minimised by a change in operating conditions and catalyst.

The pressure balance around the feed injection system at the base of the riser is also important. A typical riser layout is shown in Figure 2 with four pressure locations. Point 1 is the pressure at the outlet of the regenerated catalyst slide valve, which equals the pressure at point 4, the riser base. Typically, no static head build-up is assumed from the outlet of the slide valve to the bottom of the riser. Point 2 is located at the feed injection point, and point 3 is at the riser outlet. When a modern, radial feed system replaces an axial system, the overall pressure drop across the slide valve typically drops by 0.5–1.0 psi, since the pressure drop from the slide valve to the feed nozzles increases more than the decrease in riser pressure drop due to more even contacting.

Feed nozzles are typically located as low as possible in the riser to maximise the slide valve pressure differential. Raising the feed nozzles above this decreases the active riser length and greatly reduces the slide valve pressure drop. For example, if the nozzles are located 30ft downstream of the riser, the total loss of pressure would be about 5.0 psi, assuming a catalyst density of 25lb per cubic foot. The only way to minimise this pressure loss is to add steam or lift gas to the bottom of the riser, which can reduce the catalyst density to 10–15lb per cubic foot. The table in Figure 2 illustrates this point. However, using lift steam has a detrimental effect on the main fractionator and overhead condenser. The use of lift gas also increases the load on the wet gas compressor.

Two positive features cited by some for lift gas is the lower density at the point of feed injection, allowing greater feed penetration and the passivation of contaminant metals that accumulate on the catalyst when processing heavier feeds. This passivation occurs when off-gas from the process is recycled to the base of the riser. However, sufficient time is necessary to change the oxidation state of the metals before the feed is introduced. Testing has shown that a length of 70–80ft is required to have any passivation benefit, while a short distance of 10–12ft showed no positive effect. Steam was originally used as the lift medium, but catalyst deactivation occurred due to the metals levels on the catalyst and the temperature of the catalyst coming from the regenerator.

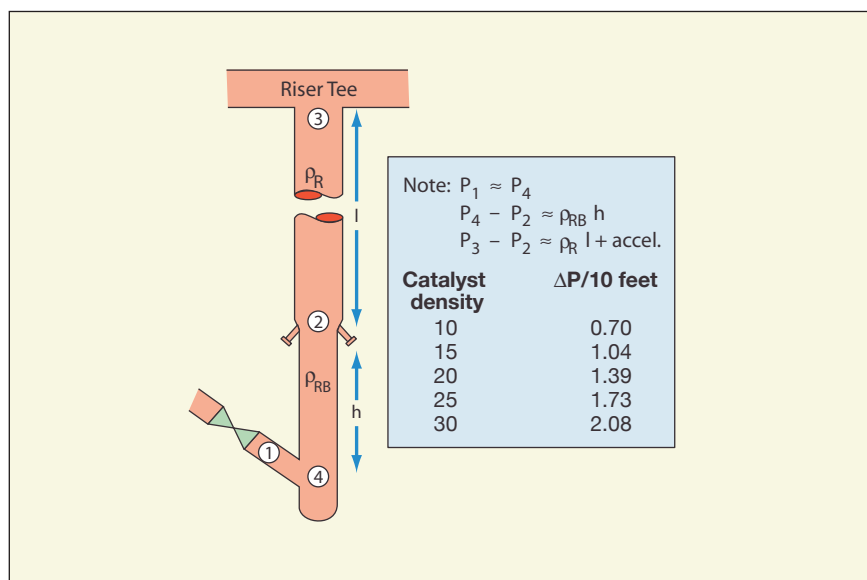


Figure 2 Typical riser layout

Steam was preferred, since it could be condensed and recovered in the overhead accumulator. However, dry gas had to be substituted to prevent the loss of catalyst activity. Contaminant metals on catalysts can be passivated with feed additives such as antimony or bismuth.

Gamma scans have been done on commercial catalytic crackers with diameters of 72in (6.0ft). Modern feed nozzles with velocities of over 200 ft/sec, penetrated the middle of the riser without a significant amount of lift gas. The density in the riser changes abruptly at the point of feed injection, which may assist with feed penetration, since the feed is not injected as a flat spray, but rather as a wedge of droplets.

The final and possibly most important consideration for the feed injection system is its mechanical reliability. If the feed nozzle erodes or fails during a run, the loss of yield performance can have a significant economic impact on the profitability of the unit. If feed nozzle steam is lost, catalyst will aspirate back into the feed nozzles, which can lead to plugging and erosion of the nozzle. Also, feed nozzles with small orifices will tend to plug and may not completely clear when steam is regained. Scale from pipes and solids in the feed can also plug small orifices on either the steam or feed side. Feed nozzle tip erosion can be a major problem. If the tip is completely lost, feed distribution and atomisation will be severely impacted. Also, coverage of the riser cross-section may be reduced from almost 90% of the cross-sectional area to about 30%, resulting in a loss of 20–50 cents per barrel of feed processed. In resid operations, coking may become severe, resulting in unplanned and costly shutdowns.

Careful design of the entire feed system is required to ensure good performance and mechanical reliability of the feed nozzles. This can include precision machining of the nozzle and hard surfacing of the feed nozzle tip to ensure integrity during operation. A properly designed feed injection system should not suffer serious damage to the feed nozzle over an entire four- to five-year run length.

Riser termination advancements

Riser termination technology has become a necessity with modern reaction systems. The high activity catalysts have essentially made riser cracking the entire reactor, and significant non-selective cracking was found to occur at the typical riser outlet temperatures employed today (520–550°C/968–1022°F) in the dilute phase of the reactor-stripper vessel. Amoco did extensive work on commercial crackers and found an Arrhenius-type relationship, where:

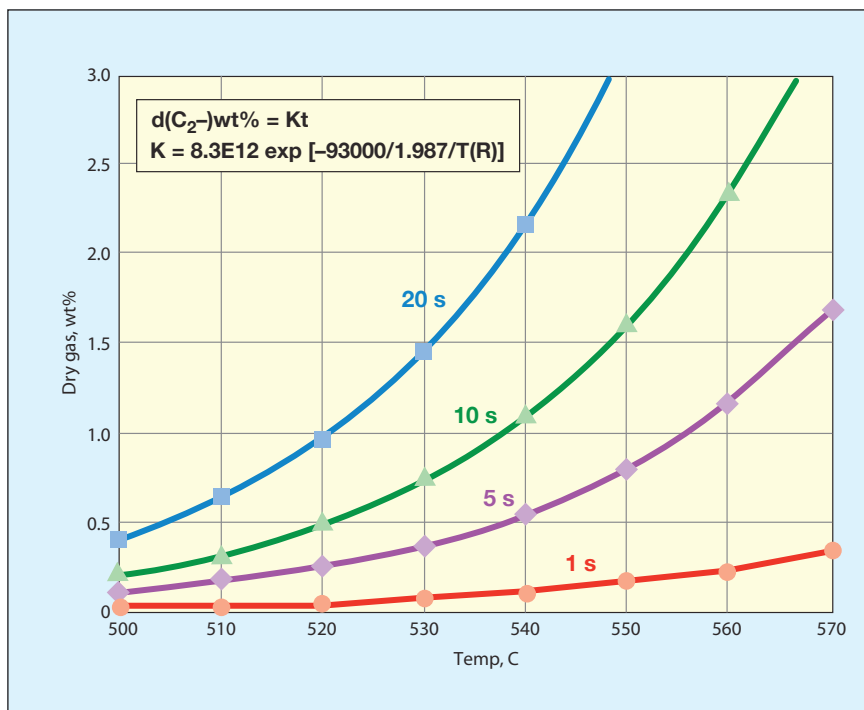


Figure 3 Dry gas production vs temperature and time

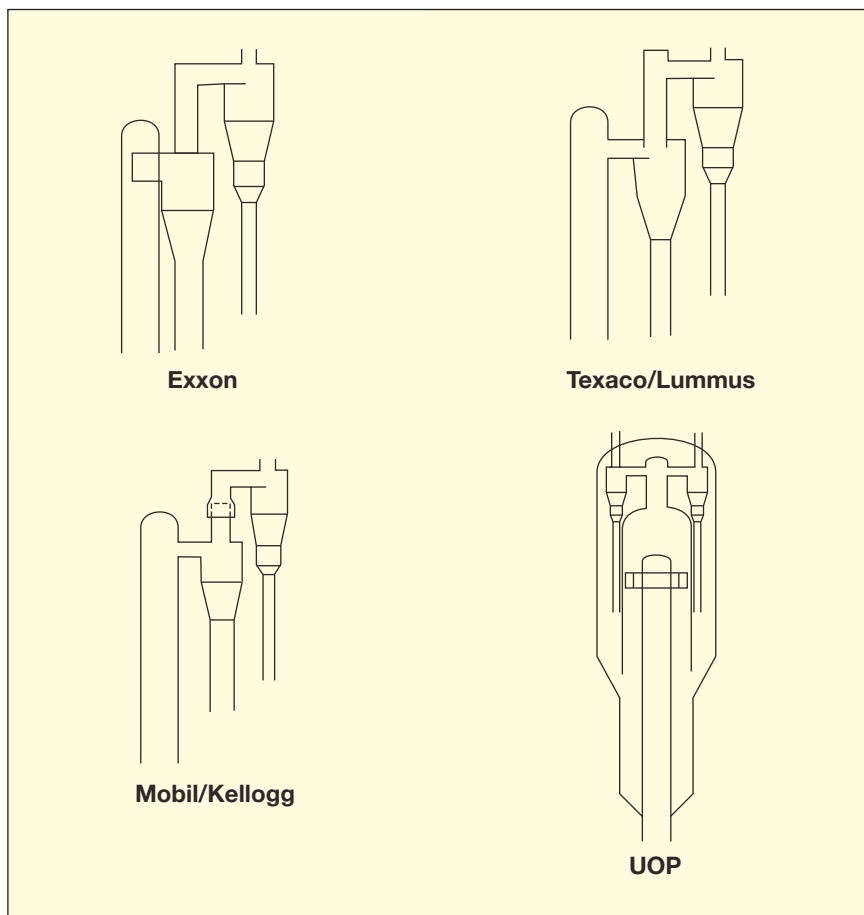


Figure 4 Closed-coupled configurations for catalyst/vapour separation

Dry gas production (SCF) = $K e^{-A/RT}$ (time) (6)

A = Activation energy; 93 000 Btu/lb-mole

K = Rate constant; SCF/Bbl-sec

R = Gas constant

T = Dilute phase Rx temp; °R

Time = seconds.

The value for the activation energy obtained from the commercial data agreed well with the laboratory value. A small number of hydrogen transfer reactions probably accounts for the difference. Figure 3 is a plot of the Amoco correlation. At low reactor temperatures, the amount of dry gas

produced in the dilute phase is small. Higher temperatures and long reaction times cause very high dry gas yields.

The vapour quench technology reduces the dry gas make by lowering the dilute-phase temperature. This is illustrated in Figure 3 by moving to the left down the appropriate residence time curve. The keys to successful quench operations are the effective separation of the spent catalyst from the riser outlet vapours prior to quenching, the use of a refractory quench material that will not crack or coke, controlling the temperature so that condensation of liquid does not occur and safeguards to ensure the quench medium is removed automatically in the event of certain unit conditions. These may include the loss of feed, when minimum reactor temperature is encountered or the loss of power to the unit.

Vapour quench has the advantage that it can be turned down or off. When fuel gas has a very high value or the refinery is short on fuel gas, it might be desirable to discontinue the use of quench. This is not possible with a short contact time riser termination device. The initial quench medium has the largest impact on reducing dry gas, since it is applied to the highest temperature.

Another benefit of lowering the dilute-phase thermal cracking is the reduction in diolefins. This includes the butadienes in the LPG stream and the pentadienes in the gasoline. Butadienes are known to increase acid consumption and to produce more acid soluble oils (ASOs) in alkylation units. Less desirable side reactions will occur as well, resulting in a higher alkylate end point. Gasoline diolefins lead to poorer stability in storage and require more chemicals to prevent colour bodies and gum formation.

Reducing the vapour residence time

will also prevent the secondary cracking reactions in the dilute phase. This is accomplished by essentially connecting the primary and secondary catalyst-vapour separation devices in the reactor. The primary separation device should be fixed to the end of the feed riser. All current licensors of FCC technology offer a close-coupled riser termination system.

The catalyst/vapour separation in the primary separator must be very high; otherwise, the reaction products are contacted with hot, spent catalyst for an extended period of time, promoting non-selective cracking and higher delta coke. Vapour containment is a secondary consideration related to the amount of underflow from the primary separator. Even three or four seconds of contact of the reaction products with spent catalyst will produce a lot of dry gas due to the high surface area presented by the catalyst and its high heat capacity that keeps the cracking temperature from dropping.

In Figure 4, three closed-coupled configurations are shown. These differ according to the location of the vent, which allows the stripper vapours to enter the cyclone system for recovery. If the vapour entry space is before the primary cyclone, the primary cyclone becomes a negative-pressure cyclone. Clearly, the pressure in the dilute phase must be greater than the pressure in the primary cyclone when the system is sealed or the gas could not leave the reactor vessel.

When the stripper vapours enter between the first- and second-stage cyclones, the pressure in the dilute phase is less than the pressure in the primary cyclone. Hence, the primary cyclone has a positive pressure.

These differences are reflected in the operation of the diplegs. In the latter case, the catalyst level is close to the reactor-bed level, while in the former

(negative-pressure cyclone) the dipleg level is above the reactor-bed level. As long as both positive- and negative-pressure cyclone diplegs are adequately sealed and the catalyst density in the diplegs is the same, the amount of vapour carried under with the catalyst will be the same. This was demonstrated by Mott, who showed that the volume of the catalyst travelling down the diplegs of the primary separator is essentially V_{gas} . This is calculated from Equations 7 and 8:

$$V_e = 1000 Q_{cat} / \rho_e \quad (7)$$

where

V_e = volume catalyst emulsion, m³/min

Q_{cat} = catalyst circulation, mt/min

ρ_e = fluidised standpipe (dipleg) density, kg/m³.

The total volume of interstitial and intraparticle gas circulated with the catalyst is:

$$V_{gas} = V_e d(1 - \frac{\rho_e}{\rho_{skel}}) n \quad (8)$$

where

V_{gas} = volume gas carried with catalyst

ρ_{skel} = skeletal density of catalyst.

Since the catalyst flow through the primary cyclones is the same for either cyclone system and essentially equal to the catalyst circulation rate, the underflow would be identical.

The size of the dipleg will influence the amount of gas underflow from the separator. Normal designs have flux rates that result in a catalyst velocity of at least 3.0 ft/sec downward that does not allow any gas to separate from the catalyst. The catalyst separation may be slightly higher under this scenario and has been a primary design consideration for catalyst/vapour separations, since this minimises catalyst carryover to the main fractionator. Normal dipleg fluxes are 80–120 lb/ft²-sec. If the flux rate is below 40 lb/ft²-sec, the gas bubbles may rise in the dipleg and leave through the gas outlet tube. This will create a higher density in the standpipe and minimise vapour underflow. Excessive underflow leads to higher dry gas make, higher delta coke, higher regenerator temperatures and lower than desired catalyst circulation rates.

Other variations of the basic two-cyclone system have been utilised. Petrobras removed the primary dipleg to prevent plugging with coke that may form during resid operations. While all of the gas leaves through the primary cyclone, the underflow is significant, since the catalyst will drag gas along with it as it leaves the primary cyclone.

A vortex separator is a closed system that has one large primary separator sealed in the stripper. All of the stripper

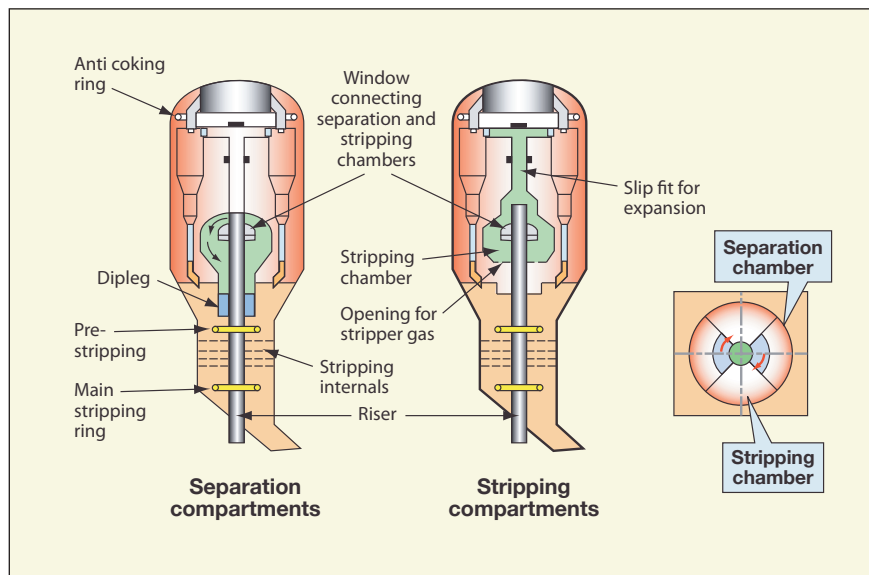


Figure 5 Axial cyclone type reactor separator-stripper coupled to conventional secondary cyclone system

Riser terminator improvements	
Feature	Effect
Separation eff. (solids/gas)	Essential to stopping secondary reactions
Separator volume	Minimise to reduce secondary reactions
Underflow of gas	Minimise to reduce dry gas and delta coke
Dipleg flux	Determines gas entrainment with catalyst
Location of stripper gas inlet to separator	Residence time of underflow and stripper gases
Operate sealed or unsealed	Versatility to optimise yields
Dilute-phase stripping	Minimise delta coke
Resistance to upsets	Avoid unscheduled shutdowns and higher maintenance costs

Table 3

vapours pass up through the primary separator and leave through the outlet tube. Vapour is kept within the system, but catalyst separation in the primary separator will be relatively low.

The reactor separator-stripper shown in Figure 5 is an axial cyclone coupled to a conventional secondary cyclone system. The stripper vapours pass through the stripper chambers and into the secondary cyclones. Catalyst separation in the primary separator is slightly lower than a cyclone due to the reduced number of turns, but the system works at any velocity unlike a cyclone and does not require additional steam usage in the riser to achieve a minimum inlet velocity for the primary separator. It also has large diplegs, which makes the separator very robust, thereby minimising the risk of catalyst carryover to the main fractionator during unit upsets. All of the two-stage riser separators achieve high overall catalyst separation and, in normal operations, catalyst carryover to the main fractionator is low.

Riser terminators have undergone continuous improvements over the years, as both licensors and users have acquired additional information on their performance and design. In addition, changes in catalyst formulation, operating conditions and feedstock components contribute to this evolution of knowledge. While eliminating dilute-phase cracking and increasing gasoline yield was the first objective, many more considerations have come to light. These are listed in Table 3.

For new units, a modern riser termination system is easy to install. For revamps, the best solution will depend on the current equipment used and how the unit is configured. Factors such as vapour residence time and the desired reactor temperatures are important, as are gas plant limitations. Frequently, a solution that might give 90% of the benefits is better than one that costs millions of dollars more to install and gives only marginal additional advantages.

While reactor design can be broken down into individual components, the entire system should be analysed and as many of the desirable features of the feed injection system, reactor configuration and the termination system should be employed to meet the current and future requirements of the job. And, as a final point, the stripper must be compatible with the new operating regime; otherwise, many of the projected benefits will be lost. This will be discussed in a future article.

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Stabilisation of asphaltenes

Asphaltenes can plug refinery equipment and can decrease or stop production. Stabilisation of asphaltene particles is an efficient and cost-effective way to avoid undesired asphaltene agglomeration or precipitation

Berthold Otzisk and Hermann Kempen
Kurita Europe

From the oil well through the refinery, fouling can interfere with production equipment. It is a common problem for oil production companies and refiners, and periodically process units have to be shut down for mechanical cleaning due to fouling, resulting in throughput losses or production shutdown. The incentives to reduce fouling are therefore significant, such as increased productivity and reduced operational costs.

The fouling phases can be coke, asphaltenes, wax, stable emulsions or inorganic solids. Refiners are currently converting more residuals into light fractions, which results in heavy fuels production that contains a higher concentration of asphaltenes. Most organic fouling is caused by insoluble asphaltenes, including coke formation. Asphaltenes are components of petroleum, and their behaviour and structure change with temperature, pressure and the composition of oil. Unwanted asphaltene precipitation can plug well bores and distillation equipment and, in many cases, decrease or stop production.

Asphaltenes and resins are responsible for adding most of the colour to crude oils. Asphaltene particles have a high affinity to associate with one another and a high tendency to adsorb resins. The wide range of size distribution indicates that asphaltenes are partly dissolved and partly in a colloidal and/or micellar form. Resins are not known to precipitate on their own, but they do deposit with asphaltenes. At a low temperature, waxy crudes containing small amounts of asphaltenes can behave differently to a clean, waxy crude containing no other heavy organics.

Asphaltene precipitation during oil production and processing is a serious problem. The economic implications are significant and can cost millions of euros. In some cases, fouling problems have been reported to be so drastic that many oil wells have been redrilled. The

fouling material, similar to that shown in Figure 1, is often transported from the well tubing to the flow lines, separator, process pumps, strainers and other downstream equipment. Asphaltenes are sensitive to shearing forces and electrostatic interactions, and crude distillation and vacuum units often are affected by asphaltene fouling. Crude preheat train and vacuum bottom heat exchangers can plug, and as a result require chemical or mechanical cleaning; otherwise, throughput has to be reduced, leading to a loss of production.

FCCUs often report fouling problems in the slurry circulation system. Asphaltenes, catalyst slurry fines, coke particles and dehydrogenated polynuclear aromatics (PNAs) can all cause fouling.

The best strategy for reducing fouling is to use basic knowledge to eliminate its formation. Asphaltenes do not melt above 300–400°C; instead, they decompose, forming carbon and volatile components. Asphaltenes contain thermally stable PNA cores, and their pendant groups are connected to the core by thermally unstable bonds. These bonds break to form free radicals above 350°C. The dispersed asphaltenes abstract hydrogen from hydro-aromatics and terminate the free radicals. The loss



Figure 1 Asphaltene precipitation

of the pendant groups results in a lower solubility of the asphaltenes. The asphaltene free radicals combine to form high molecular weight and insoluble coke.

Crude oils are a mixture of many organic compounds, and their overall properties differ from well to well. Residual oils from the Middle East and Latin America are often rich in asphaltenes. A high asphaltene content means a high Conradson carbon residue (CCR) and a high metals content (nickel and vanadium). CCR is the amount of coke produced in a standard thermal cracking test, and is a measure for potential coke formation at high temperatures.

Analytical methods

It is essential for a refiner to know the asphaltene concentration in crude oil, residue or heavy fuel. There are a number of analytical instruments and methods on the market to analyse the structure of asphaltenes, including:

- X-ray analysis
- NMR spectroscopy
- Mass spectral methods
- Elemental analysis
- Diffusion techniques.

The main diffusion techniques are:

- Fluorescence correlation spectroscopy (FCS)
- Time-resolved fluorescence depolarisation (TRFD)
- Taylor dispersion.

Asphaltenes are very complex molecules. Their structure is often described to a compact stack of many thin sheet-like layers (similar to that of a book). They are suspended by tiny colloidal particles in crude oils. The molecules are stabilised by natural resins and maintained in the oil due to its stabilisation.

The industry's knowledge of asphaltenes is still limited and little is known about their chemical properties. Asphaltenes are lyophilic with respect to aromatics, in which they form colloidal solutions. Removal of the small colloidal

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particles or resins immediately results in instability of the oil. The consequence is the formation of an agglomeration, followed by precipitation.

ASTM D2007-80 is a widely recognised standard procedure for separating asphaltenes from crude oils. The solvent n-pentane is used for asphaltene precipitation, followed by filtration. The filtered asphaltenes must be dried under a hood for several days. If the drying process is too slow, the asphaltenes can be redissolved in a minimal amount of toluene. They can then be reprecipitated with an alkane of lower molecular weight and a higher volatility. The dried filtered asphaltenes can be weighted to determine the amount of asphaltenes in the oil.

Alkane titration

Operationally, asphaltenes are defined to be insoluble in alkanes like n-heptane and soluble in aromatic solvents like toluene. ASTM D7157 is a standard test method for determining the instability of asphaltene-containing residues, heavy fuels and crude oils. There are a number of suitable automated fuel stability analysers on the market that conform to ASTM D7157.

The operating principle is based on an alkane titration and optical detection of the precipitated asphaltenes. A sample dissolved in toluene is titrated at room temperature with n-heptane. The optical probe monitors the formation of flocculated asphaltenes during the titration. Within 15–30 minutes the test result can be achieved. Depending on the optical probe system, some automated instruments are limited to products containing a minimum of 0.5% asphaltenes.

Heavy fuel instrument

One accurate method uses Turbiscan technology and conforms to ASTM D7061-04. It measures the stability reserve of heavy fuel oils upon ageing simulation (precipitation of asphaltenes in alkane). Typical applications are the control of heavy fuel oils, residues, compatibility of blends and the effect of additives. The Turbiscan MA 2000 Heavy Fuel instrument is a special development of the Turbiscan MA 2000 and combines several benefits, including

- Flexible instrument
- Easy technique
- Quick analysis
- Quantitative and qualitative analysis.

The instrument enables the accelerated detection of stabilisation tests and their documentation. By vertically scanning the sample container (Turbiscan cell), asphaltene stability can be determined. The instrument detects destabilisation phenomena 4–50 times earlier than the naked eye. The automatic result gives an

indication of the separability number and flocculation tendency:

- High stability reserve = no flocculation
- Medium stability reserve = flocculation if oil exposed to worse conditions
- Low stability reserve = easy flocculation.

The measuring technique is based on the principle of multiple light scattering. The intensity of the backscattered light is in direct correlation to the concentration and average diameter of the dispersed phase (particle, droplet and bubble). The instrument has a pulsed infrared source (850 nm) and two synchron working detector systems:

- Transmission detector for characterisation of clear products
- Backscatter detector for characterisation of opac concentrated products.

In vertical direction to the sample container, the transmission and backscattering data are taken every 40 µm (up to a maximum height of 80 mm). According to the program, the scanning is designed to give a report with multiscans. Any changes in the stability of the sample are detected, which gives an indication of the destabilisation process. ASTM D7061-04 describes the analysis in three main steps, which are:

- Dilution of heavy fuel oil (HFO) in toluene
- Precipitation of asphaltenes with n-heptane
- Measure stability using the Turbiscan.

The Turbiscan instrument is useful for determining the best antifoulant or stabilisation additive at the optimal concentration. It is a standard Kurita procedure to optimise the dosing rate of asphaltene dispersants by using Turbiscan technology. The difference between an unstabilised or stabilised sample can be detected quickly with high accuracy.

Stabilising the asphaltenes

Historically, the fraction insoluble in n-heptane has been called asphaltenes. Using modern analytical techniques, the complex structure of asphaltenes can be analysed more deeply. In general, the macrostructure of asphaltenes is composed of several sheet-like layers of condensed polycyclic aromatic compounds with porphyrin-like structures.

In 1967, the macrostructure of asphaltenes was well described by Dickie and Yen to be a composition of these 13 items:

- Crystallite and particle
- Chain bundle and single layer
- Micelle and resin
- Weak link, gap and hole



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Asphaltenes are believed to exist partly dissolved in oil and partly in a colloidal and /or micellar form. Small asphaltene particles can be dissolved in oil by using expensive aromatic washes. Relatively large asphaltene particles can flocculate and form steric colloids in the presence of excess amounts of resins and paraffin hydrocarbons. These asphaltenes are highly polar surface active compounds. Destabilised asphaltenes act as glue and mortar in hardening the deposits. The flocculation of asphaltenes in paraffinic crude oils is known to be irreversible.

It is better to avoid destabilisation of asphaltenes. Based on experimental evidence, there is a critical resin concentration below which the asphaltenes precipitate. Above the critical resin concentration, they cannot precipitate regardless of how much the oil mixture is heated, agitated or pressurised. Several investigators measured the critical micelle concentration for solutions of asphaltene in aromatic solvents. Below the critical micelle concentration, the asphaltenes in solution are in a molecular state. Above the critical micelle concentration, the formation occurs in a manner similar to that in surfactant systems. These monomers are less poly-dispersed and much more uniform in their structure.

In the presence of excess amounts of hydrocarbons, the asphaltene may self-associate, but not flocculate and form micelles. The mechanisms of asphaltene flocculation and steric colloid formation are well understood. The theories of micellar solutions of oil, surfactant or water are well known, but the phase behaviour of asphaltene micelle formation is not well characterised.

Kurita's asphaltene dispersants are substitutes for the natural resins. They work by surrounding the asphaltene molecules, similar to the natural resins. The critical resin concentration is shifted to a higher level, resulting in a more stabilised asphaltene solution. This keeps the hydrocarbons in a colloidal system and the asphaltenes in a disperse phase to prevent fouling and plugging.

Figure 2 shows the multiscan of an untreated vacuum bottom sample, taken by a Turbiscan MA 2000 Heavy Fuel. Over 15 minutes, one scan was recorded per minute. The wide range between the first and the last scan is an indication of the instability of the vacuum bottle sample. The refinery unit where the vacuum bottle sample was taken is incurring severe asphaltene problems. Without a successful antifoulant programme in place, the heat exchangers are having to be cleaned mechanically every six to eight weeks.

Figure 3 shows the multiscan of the

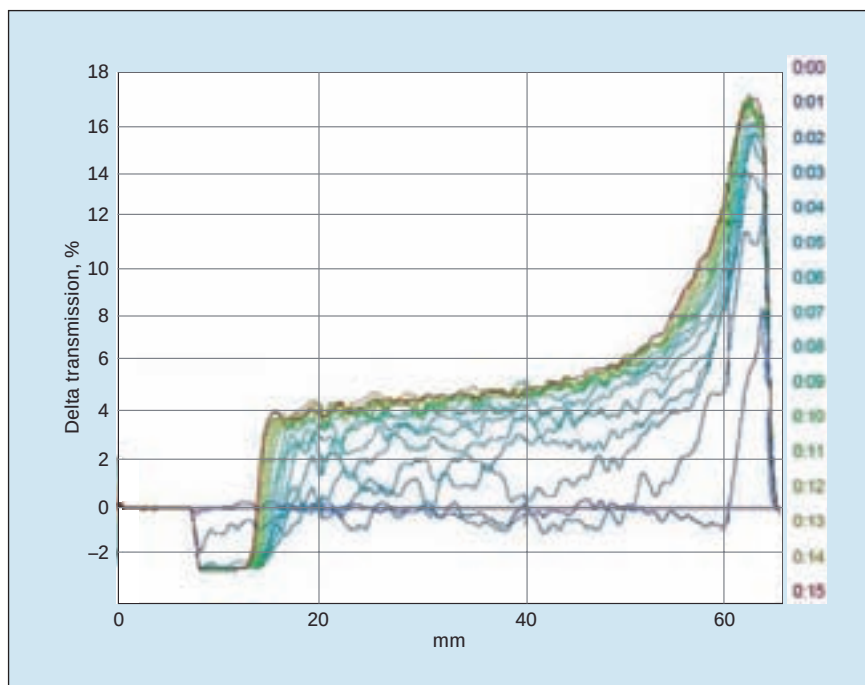


Figure 2 Untreated vacuum bottom sample

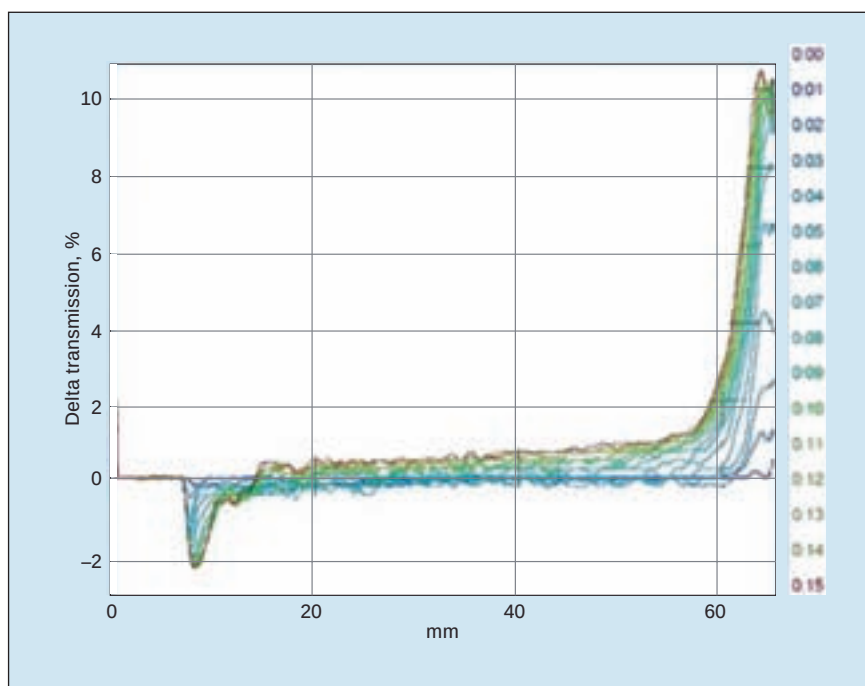


Figure 3 Stabilised vacuum bottom sample

stabilised vacuum bottom sample with a low tendency for asphaltene precipitation. The vacuum bottom sample was treated with 20 ppm of a suitable antifoulant programme. The asphaltene stability is a function of the dosing rate. A higher dosing rate of approximately 30 ppm will give a higher stability with virtually no difference between the first and last scan. Based on experience, the additive concentration required for lab tests is higher than the dosing rates needed for an operating refinery application. Thermodynamics play a big role, which cannot be simulated with most laboratory procedures and methods.

Case study

In 2000, a Western European refinery revamped its FCCU and later noticed an increased fouling in the slurry oil exchangers. Several service companies tried to solve the problem by dosing their chemical programmes, but the situation worsened and the financial losses for the unit climbed to €1 400 000 per year.

The FCC slurry system is a network of heat exchangers designed to remove heat from the cracked product. This heat is used again to preheat the FCC feed to generate steam and fractionate and recover products downstream. The cooled slurry oil is again returned to the

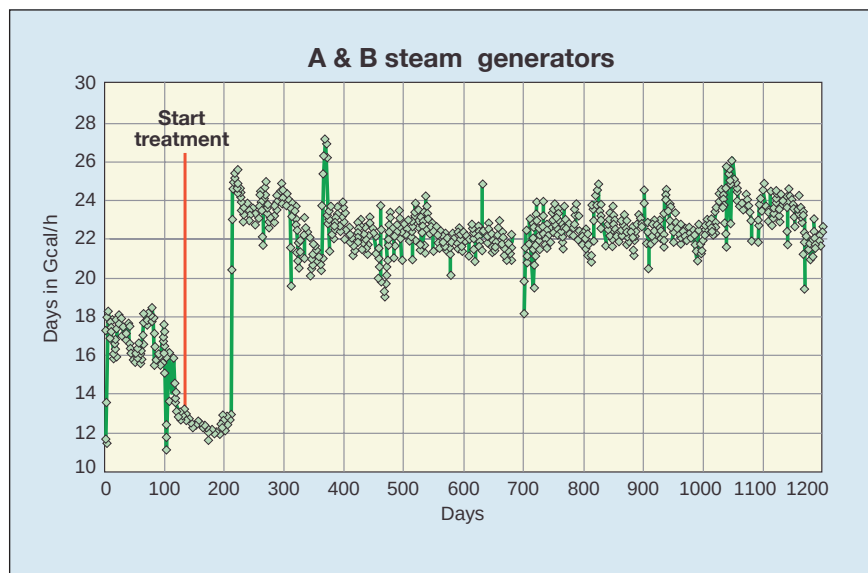


Figure 4 Duty calculation of the two steam generators

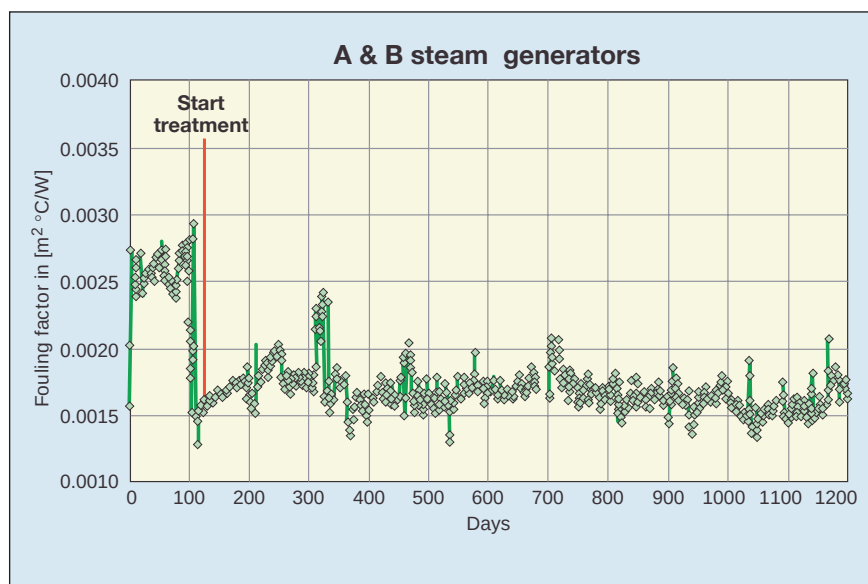


Figure 5 Fouling factor calculation of the two steam generators

main fractionator, where it acts as a quench stream. Unit throughput has to be reduced if the heat cannot be removed through exchange with other streams. Slurry circulation is integrated with the FCC product recovery system, and poor product recovery will cause significant economic losses. The slurry circuit is commonly used to reboil the debutaniser tower, which can lead to losses in C_4 olefins and potentially cause the FCC gasoline to be off-spec on vapour pressure.

Heat exchanger cleaning costs can be significant, especially if throughput must be reduced during cleaning operations. Cleaning activities in hot service can also become a safety and reliability concern.

With all these problems, the refinery was forced to either shut down the FCCU or start with another chemical programme. The current chemical antifoulant programme was terminated and Kurita was asked to reduce the

fouling as soon as possible. The FCCU was already in fouled conditions, making it more difficult to obtain the best performance. An initial survey was started in order to have a full understanding of the fouling problems in the system. This involved an intensive data collection and information exchange between the operator and Kurita.

A six-month trial was started after determination of the exact follow-up procedures. The necessary analyses and tests were defined and the dosing point for the chemical treatment programme determined. The selected product, Kurita AP-2103 D2, was dosed into the slurry oil circuit (Figures 4 and 5) and it controls the fouling caused by:

- Deposition of asphaltenes
- Catalyst slurry fines
- Coke particles
- Dehydrogenated polynuclear aromatics.

Kurita AP-2103 D2 has a high thermal

stability and dispersing power, which allows the refiner to optimise its heat recovery from the FCC main fractionator bottom stream. A higher FCC reactor outlet temperature under more stringent conditions is possible.

After optimisation of the dosing, the refiner noticed an improved heat removal, to cool the bottom of the main fractionator and achieve optimal fractions. The product recovery improved and losses of C_4 olefins were significantly reduced. No throughput limitations and reductions for cleaning and maintenance costs were reported. After positive evaluation of the test run, the refiner decided to continue the treatment and AP-2103 D2 has been continuously applied to date.

Conclusions

Asphaltene precipitation is a common problem for oil production companies and refiners. The economic implications can be significant, resulting in throughput losses or production shutdown.

Current knowledge of asphaltenes and their chemical properties remains limited. However, there are now a number of suitable analytical instruments and methods on the market. It helps to get a better understanding and indication of the asphaltene concentration and fouling potential.

Asphaltene particles have a high tendency to adsorb resins, resulting in undesired asphaltene precipitation. Powerful asphaltene dispersants are substitutes for the natural resins. By surrounding the asphaltene molecules, they keep the asphaltenes in a dispersed phase to prevent fouling and plugging.

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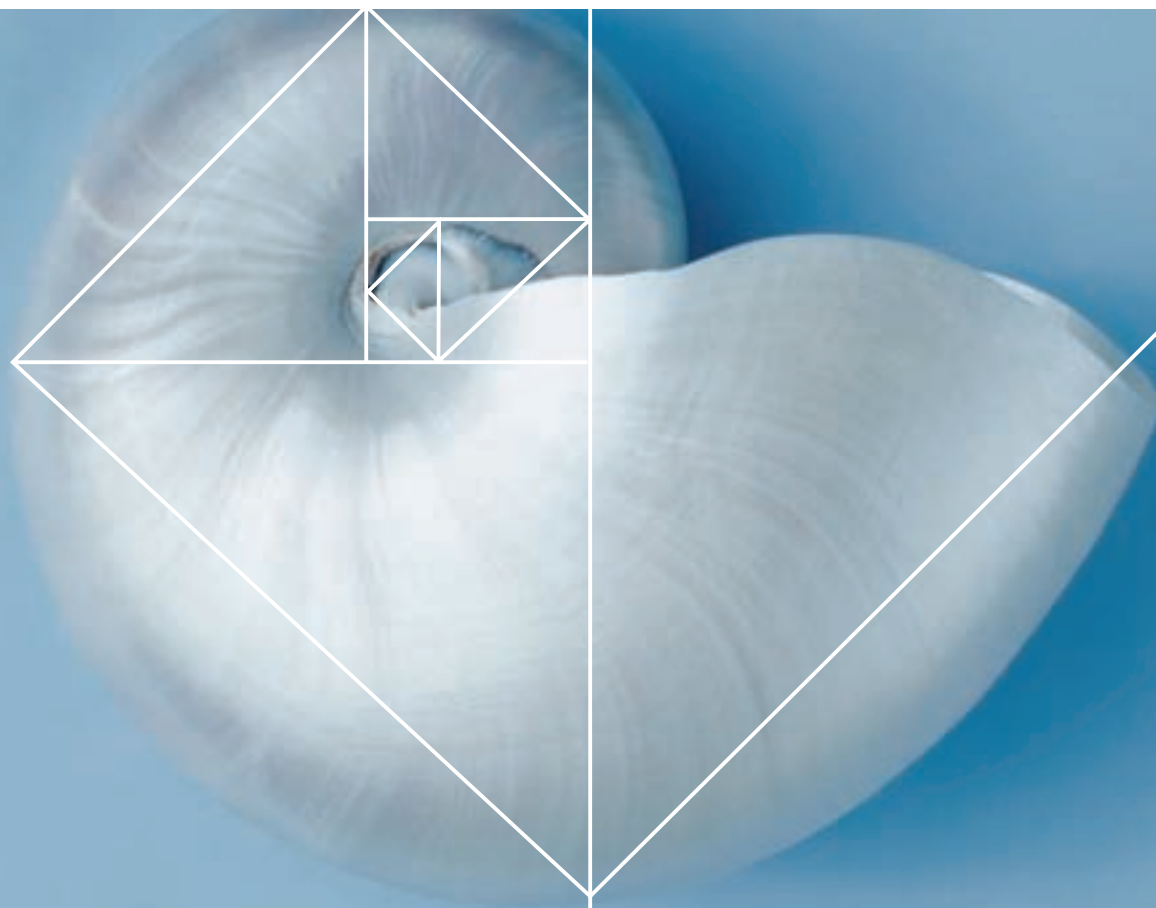
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Maximising diesel recovery from crude

The CDU/VDU process flow scheme is reviewed, including equipment design and operating fundamentals used to maximise straight-run diesel recovery. Factors important to increasing diesel yield are discussed in detail

Scott W Golden

Process Consulting Services Inc

Increased recovery of straight-run (SR) diesel from crude oil improves refinery profitability. Low crude/vacuum unit (CDU/VDU) SR diesel recovery is caused by existing unit process flow schemes, equipment designs and operating conditions. Since many FCC or hydrocracker feeds contain 25–35% or more diesel boiling-range material, there is significant opportunity to improve recovery. Low or moderate capital investments have increased refinery ULSD product yields by more than 5% on whole crude.

CDU/VDU diesel recovery

Refiners in the US have until recently targeted maximum gasoline production with little focus on CDU/VDU SR diesel recovery. Not surprisingly, few US refiners achieve good SR diesel recovery. This is because most of the existing process flow schemes and equipment were not designed to maximise the SR diesel yield from crude, nor were the operating variables associated with these flow schemes optimised for maximum SR diesel recovery. Most US refiners produce SR diesel only from their atmospheric crude columns. Even some of the new CDU/VDUs have not been designed for maximum recovery, because many major E&Cs (and some refiners) continue to believe that diesel should be produced only from the atmospheric crude column. Even though diesel margins are very strong, there are still many misunderstandings about maximising CDU/VDU diesel production.

Many non-US refiners have designed their CDU/VDU to maximise diesel recovery. Their atmospheric crude columns have 10–14 trays between the flash zone and the diesel product draws. They do not produce an atmospheric gas oil (AGO) product as FCC or hydrocracker feed. Moreover, the CDU/VDUs have been designed or revamped to produce diesel from the vacuum column's top side-draw. Conversely, many US refiners have only two to five fractionating trays between the diesel and AGO product

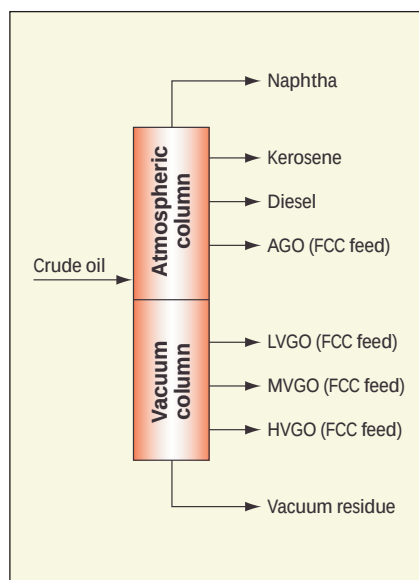


Figure 1 Atmospheric column diesel product — no diesel from vacuum column

draws, and operate with very little reflux below the diesel product draw. Furthermore, it is not unusual for a US refiner's vacuum column feeds to contain 8–10% diesel, with only a few VDUs producing a vacuum diesel product. It is also not unusual for a US refiner's top vacuum column side-draw product to contain 70–90% 650°F (343°C) minus diesel boiling-range material. In most cases, this diesel ends up in the FCCU.

Refiners can quickly determine their CDU/VDU performance by evaluating the amount of 650°F (343°C) minus diesel material in the CDU/VDU streams feeding the FCC or hydrocracker. Even though hydrocrackers may recover some of this diesel boiling-range material, it may not be the most cost-effective place to process it. A well-designed CDU/VDU produces FCC or hydrocracker feed streams containing less than 5 vol% diesel boiling-range material.

Process flow scheme

Most US refiners produce diesel product only from the atmospheric crude column (Figure 1). Changes to the CDU process

flow scheme and atmospheric column equipment design and operating changes can improve recovery. However, diesel recovery is limited by process and distillation fundamentals in the atmospheric column. It can be optimised, but it has fundamental limitations that constrain recovery. Only a few US and many non-US refiners produce both atmospheric and vacuum diesel products (Figure 2). Fractionation is inherently better in a vacuum column, therefore diesel recovery is greatly improved. Fractionation is driven by column internal efficiency and the fractionation section's liquid-to-vapour (L/V) ratio. The top section of the vacuum column has a much higher L/V ratio than the atmospheric column, hence vacuum columns fractionate better than atmospheric columns no matter how good the CDU design. Better fractionation reduces the vacuum diesel product 95% to endpoint tail compared to atmospheric column diesel. Additionally, the combined atmospheric and vacuum diesel products have better cold flow properties due to improved fractionation. The CDU/VDU process flow scheme has the largest influence on SR diesel recovery. The CDU/VDU must have a vacuum diesel product draw to maximise recovery.

It is common for US refiners to produce an AGO product (Figure 1). This stream is often combined with the vacuum gas oil (VGO) products feeding an FCC or hydrocracker. Since atmospheric crude column fractionation is inherently poor, AGO product contains 30–70% or more diesel boiling-range material. To maximise diesel recovery, no AGO product should be produced or it should be fed into the upper section of the vacuum column (Figure 3), where it can be fractionated into vacuum diesel and VGO products. Overall CDU/VDU diesel product recovery and energy consumption are improved when atmospheric column AGO is fed to the vacuum column. The amount of diesel in the AGO product will determine

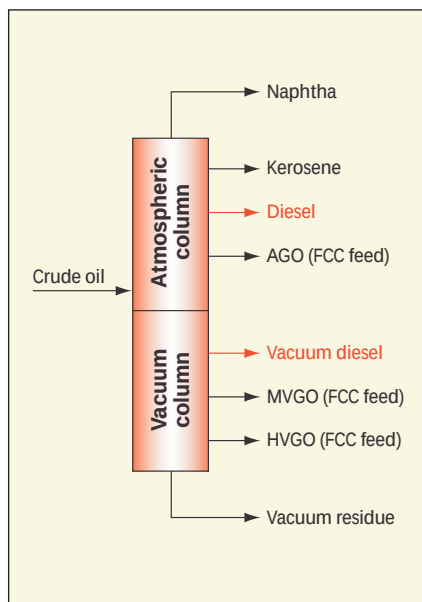


Figure 2 Atmospheric and vacuum column diesel products

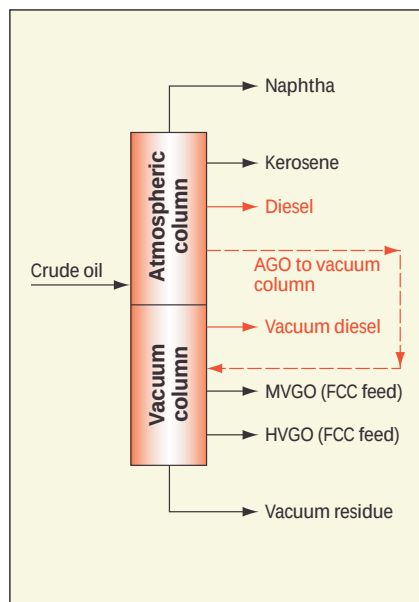


Figure 3 Atmospheric and vacuum column diesel products with AGO feeding the vacuum column

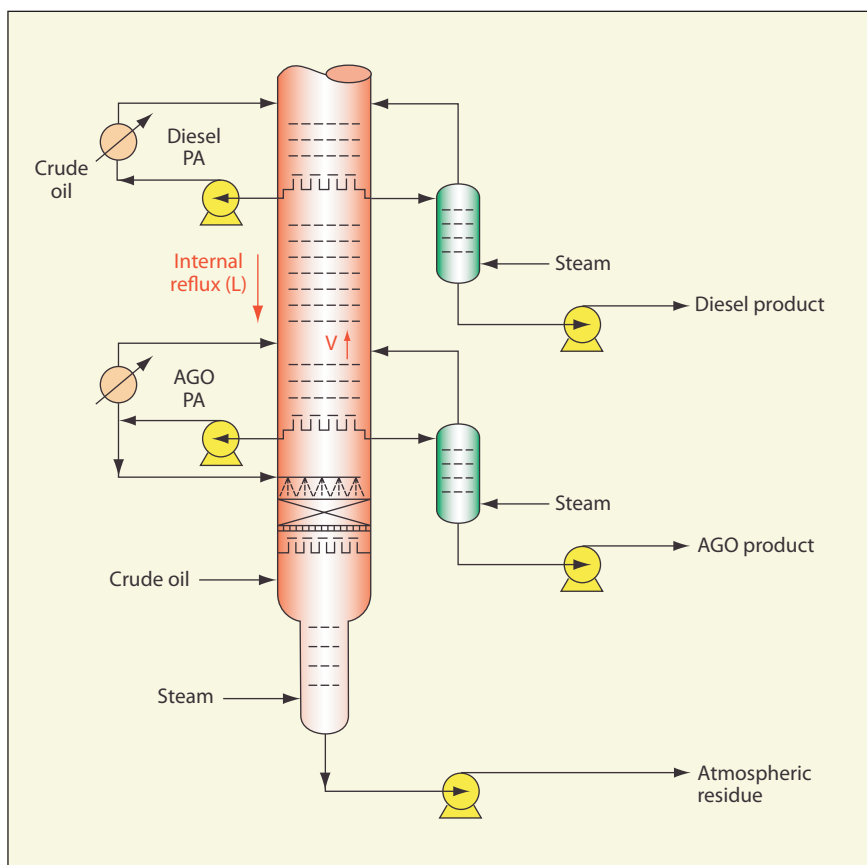


Figure 4 Atmospheric column internal reflux rate

incremental recovery from processing AGO in the vacuum column.

When revamping or designing a new CDU/VDU to improve diesel recovery, selecting the most economic process flow scheme should also consider energy efficiency and VGO product yield. Energy optimisation may set the proper amounts of diesel from the atmospheric crude and vacuum columns. Atmospheric column diesel product is withdrawn at 525–575°F (273–302°C), depending on

operating pressure and diesel product distillation. This energy can be used to preheat crude, whereas the same diesel boiling-range material produced from the vacuum column is withdrawn at only 250–300°F (121–149°C), making it impossible to cost-effectively recover the heat. Balancing diesel production between the atmospheric and vacuum columns saves energy, especially with light and moderately heavy crude oils.

Refiners processing heavy and extra-

heavy crudes like Merey or BCF 17 must balance atmospheric and vacuum column distillate yields against VDU VGO product yield objectives. Atmospheric residues from heavy crudes are so difficult to vapourise even with the best VDU design that atmospheric column distillate yields must be constrained. Increasing the amount of diesel in the atmospheric residue increases the VGO product yield. Conversely, as atmospheric residue gets heavier, VGO product decreases and vacuum residue production increases. Since maximising the VGO product yield increases the overall refinery liquid volume yield and reduces coke production, balancing atmospheric and vacuum column diesel yields is crucial when processing heavy and extra-heavy crudes.

Atmospheric crude fundamentals

Understanding atmospheric and vacuum column distillation fundamental principles is crucial to optimising CDU/VDU economics. The atmospheric column internal reflux rate below the diesel product draw and fractionation efficiency determines the diesel yield (Figure 4). The column design requires the correct number of trays or amount of packing efficiency and it also needs optimum internal reflux (L). Fractionation efficiency alone will not produce maximum diesel product. Fractionation section L/V ratio is one of the fundamental principles that determines product yield. The vapour rate into the fractionation section is set by the vapour leaving the flash zone and the column heat balance. In an atmospheric column, the vapour rate (V) is large because it consists of overhead product gas, naphtha, kerosene and diesel product, in addition to the internal reflux. Internal reflux (L) is relatively small because it consists only of overflash and AGO product. Consequently, the fractionation section L/V ratio is typically less than 0.1 on a molar basis. Atmospheric column diesel and AGO product fractionation are inherently poor. All factors influencing the internal reflux rate (L) should be considered when revamping or designing a new CDU to maximise the atmospheric column diesel yield.

Fractionation efficiency depends on equipment design. Ideally, the diesel fractionation section should have at least eight properly designed trays or a packed bed with at least five theoretical stages of efficiency. Since atmospheric crude columns are typically large diameter, the fractionating sections are designed with two- or four-pass trays to maintain a reasonable flow path length. Tray chord lengths are long, while the tray liquid rate is low. Therefore, it is not unusual to have poor tray efficiency in

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the diesel/AGO fractionation section due to very low weir loadings. Since the internal reflux (L) decreases from the tray directly below the diesel product draw to the bottom fractionating tray, it is critical to reduce the weir length (picket fencing) based on the minimum liquid rate. Maintaining weir loading of approximately 2 gpm/in of the weir on the bottom fractionation tray maintains tray efficiency at its intrinsic limit of approximately 60%. If weir loading drops below 1 gpm/in of the weir tray, efficiency drops quickly. When using packing, good distribution of the internal reflux (L) and adequate vapour distribution at the bottom of the fractionation section are key to maintaining efficiency. Proper equipment design can materially improve diesel yield or quality for a given internal reflux (L).

The atmospheric column diesel product yield depends on the internal reflux rate once a column is built. The internal reflux rate (L) is controlled by several variables, including the heater outlet temperature, column operating pressure, pumparound heat removal location, stripping section efficiency and stripping steam rate. Raising the heater outlet temperature or reducing the column operating pressure increases the amount of vapour generated in the flash zone. This allows a higher internal reflux when the column heat balance is properly controlled. Improved stripping section performance either through higher efficiency or a higher stripping steam rate also increases the amount of flash zone vapour, permitting higher internal reflux in the diesel fractionating section. For a given flash zone vapour rate, the diesel fractionating section's internal reflux is determined by heat balance.

Controlling column heat balance is essential to maintain an optimum internal reflux rate. Figure 5 shows a column with an AGO pumparound located below the diesel fractionation section. AGO PAs are used because the pumparound draw temperature is 50–100°F (28–56°C) higher than the diesel PA. Higher temperature AGO pumparound heat is easier to recover against crude. Heat recovery and fractionation compete against each other. Increasing the AGO PA duty may increase crude preheat, but it also reduces the reflux rate below the diesel product draw, which lowers the diesel product yield and increases the AGO product yield. As the AGO product yield increases, so does the amount of diesel boiling-range material in the AGO. As crudes get heavier and the flash zone vapour rate decreases, the AGO PA duty must be reduced to maintain adequate diesel fractionation section reflux. When processing extra-heavy crude oils, the

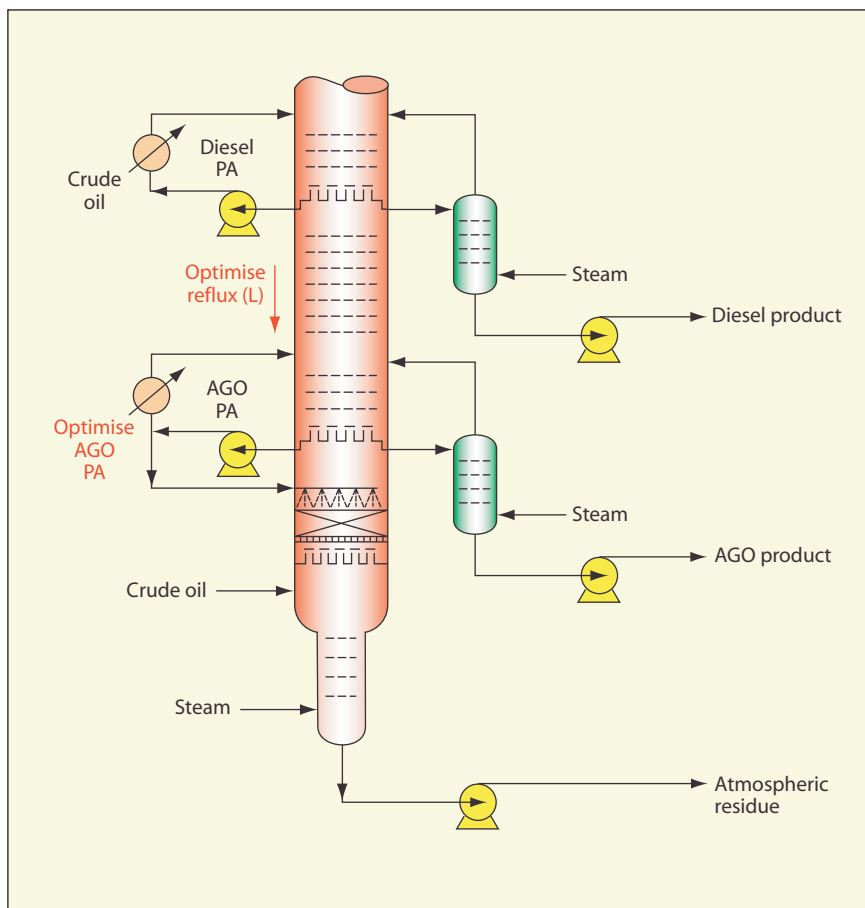


Figure 5 Optimising atmospheric column heat balance

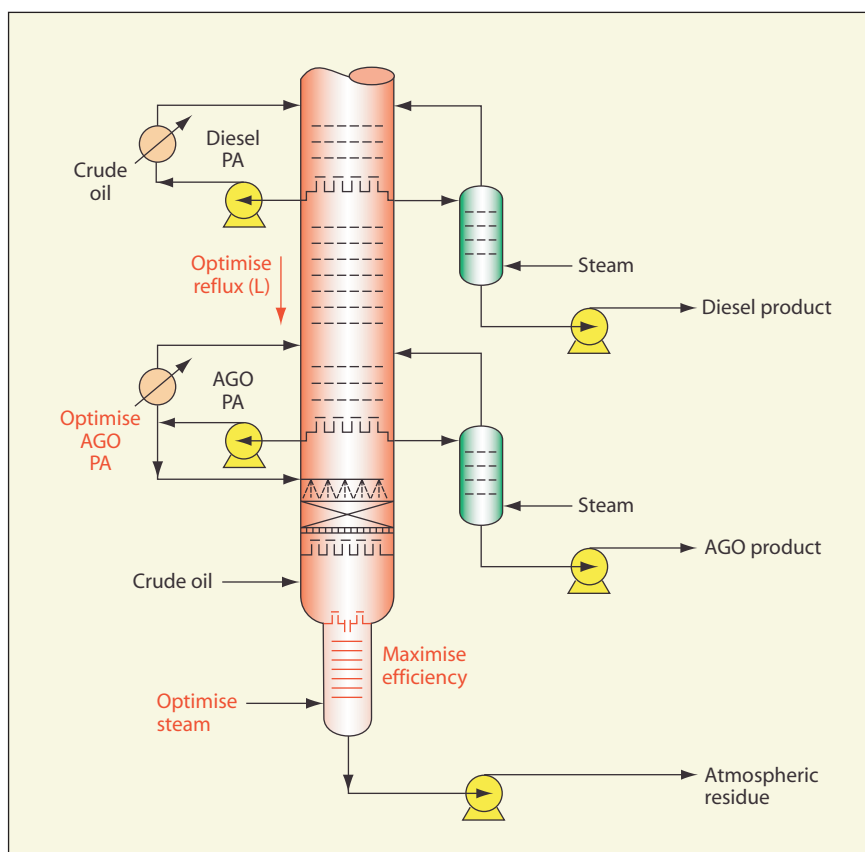


Figure 6 Atmospheric column stripping section

CDU should be designed without an AGO PA because the amount of flash zone vapour is so low it is impossible to

remove any heat below the diesel product draw and have a reasonable fractionation section internal reflux

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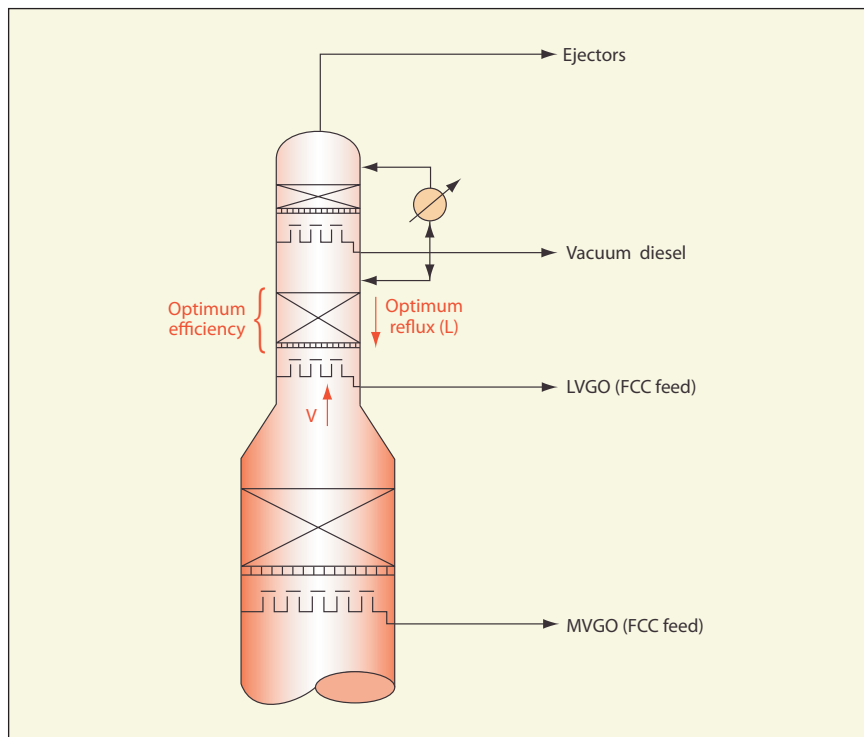


Figure 7 Vacuum column diesel products

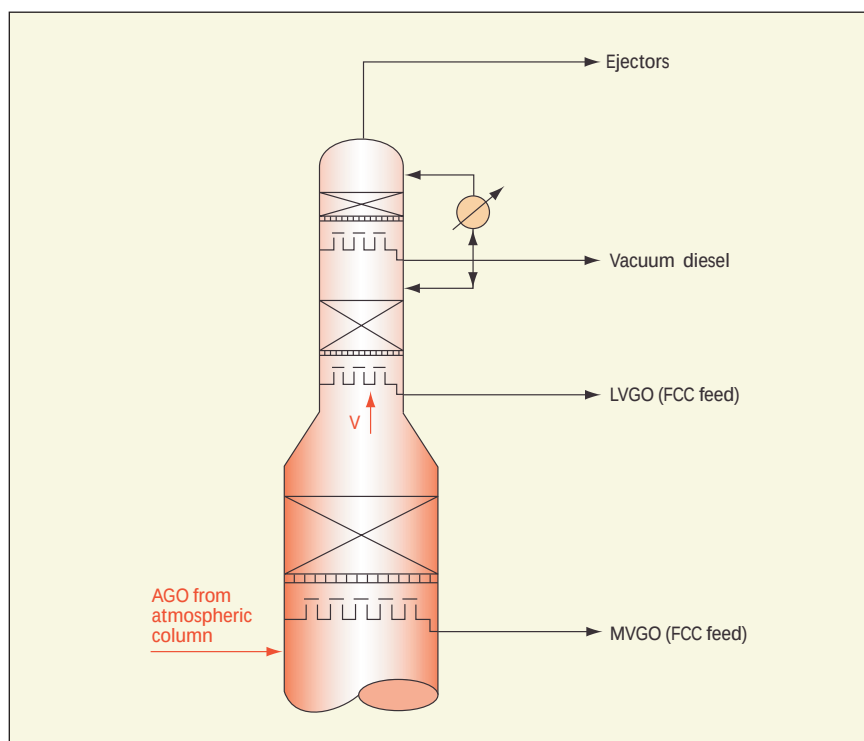


Figure 8 Maximum diesel product yield

rate. Optimising the column heat balance is critical to optimising the internal reflux and diesel product yield.

Stripping section performance is often overlooked when considering diesel product yield improvements (Figure 6). The stripping section vapourises the front end of the flash zone liquid as it flows down through the trays. Improved tray design and an increased number of trays raise efficiency, increasing the amount of flash zone vapour and reducing the amount of diesel in the

atmospheric residue. The optimum number of stripping trays is eight to ten. A customised rectangular tray designed at very high weir loadings maximises efficiency and helps prevent fouling throughout the run length. Maximum stripping section efficiency allows the diesel fractionation section reflux to be increased. The optimum stripping steam rate is 5–8 lb/barrel of atmospheric residue, depending on stripping section efficiency.

Higher CDU/VDU diesel recovery

requires yielding more atmospheric column diesel or modifying the VDU to produce vacuum diesel. Raising the atmospheric column diesel yield demands better stripping, higher flash zone temperature, lower column operating pressure, higher diesel/AGO fractionation section reflux or more fractionation efficiency. In some instances, modifying the atmospheric column may materially increase diesel recovery at a reasonable cost. Yet, in other cases, modifying the atmospheric column is very high cost, with relatively small yield improvements.

Vacuum crude fundamentals

Maximising CDU/VDU diesel recovery requires a diesel product draw on the vacuum column. Yet only a few US refiners produce a vacuum diesel product. Most still produce FCC feed from the top side-draw product, and it is not unusual for it to contain 60–80% diesel boiling-range material. Many non-US refiners already produce diesel product from the top side-draw of the vacuum column. Revamping an existing column or designing a new VDU to produce vacuum diesel requires a fractionation section (Figure 7). Fractionation is inherently better in the vacuum column because the L/V ratio is much higher than the atmospheric column. The top pumparound condenses the vacuum diesel product and reflux (L) for the fractionation section. Since the reflux flow rate is low, it must be metered and flow controlled to ensure it is maintained within the distributor limitations. Good control of the column heat balance is needed to generate sufficient fractionation section reflux.

The vacuum column diesel/LVGO fractionation section L/V ratio is high compared to the atmospheric column. The fractionation section reflux rate is typically 40–100% of the vacuum diesel product rate. Since the vapour rate leaving the top pumparound is extremely low, the vapour rate to the fractionation section is primarily vacuum diesel product and LVGO product. While in the atmospheric crude column, the vapour rate leaving the diesel pumparound contains overhead receiver gas, naphtha and kerosene, as well as the kerosene fractionation section reflux. Therefore, atmospheric column diesel fractionation section molar L/V ratio is typically 0.1 or less, whereas the vacuum column fractionation section L/V ratio is 0.3–0.5. Since the vacuum column L/V ratio is much higher than the atmospheric column, it has better fractionation.

The vacuum column pumparound heat balance determines the amount of vacuum diesel that can be produced. The top pumparound duty must be sufficient to condense the available

vacuum diesel product and the internal reflux. It is not unusual for too much heat to be removed in the lower pumparounds, resulting in low vacuum diesel product recovery even with a properly designed fractionation section. When packing efficiency is adequate (~ three theoretical stages) but the internal reflux is low, the vacuum diesel product yield will be low. Fractionation efficiency alone will not provide high vacuum diesel product recovery. Optimising the internal reflux (L) allows the maximum amount of vacuum diesel product yield.

Maximising CDU/VDU diesel product requires either no AGO product from the atmospheric column, or the AGO can be fed to the vacuum column to recover the diesel boiling-range material. When atmospheric column AGO contains a large amount of diesel, it must be fed to the vacuum column to maximise overall recovery. Since the atmospheric column operates above atmospheric pressure and vacuum below, the majority of the AGO product vapourises when it enters the vacuum column. It should be fed to the vacuum column below the fractionating bed for maximum vacuum diesel product and energy recovery (Figure 8). Selecting the proper location is critical. In a vacuum column with both an MVGO and HVGO pumparound, it should be fed below the MVGO pumparound for maximum heat recovery.

Conclusion

Atmospheric column diesel recovery is inherently difficult because the fractionation section molar L/V ratio is typically less than 0.1, whereas in the vacuum column it is 0.3–0.5. It is simply impossible to achieve high recovery without a diesel product draw on the vacuum column. Fractionation basics favour this solution. Thus, it is not surprising that the CDU/VDUs are designed differently where diesel product is the primary motor fuel and economics favour high recovery. Today that should also include US refiners.

Atmospheric and vacuum column diesel product yield should be optimised based on VDU performance and energy recovery. High atmospheric column diesel recovery makes the VDU feed heavier, reducing the VGO yield, especially with heavy and extra-heavy crudes. Heat recovery and crude preheat depend on atmospheric diesel and AGO product yield. Diesel draw temperature is much higher in the atmospheric column compared with the vacuum column. Consequently, all the heat duty needed to condense vacuum diesel and its internal reflux is lost to air and water, whereas all the condensing heat and approximately half the product cooling heat are recoverable to crude oil from the atmospheric column.

Modifying the vacuum column to produce diesel from the top section can be a relatively low- to moderate-cost revamp with a high return. Some vacuum columns can have a fractionation section added within the existing vessel dimensions, while others require the top section of the column to be replaced. Since the top section diameter is small, often no foundation changes are needed. In one case, the CDU/VDU diesel yield was increased by 40% by installing a new top section on the vacuum column with an investment of less than \$5 MM. Furthermore, by increasing diesel recovery, some refiners have been able to unload their FCC and hydrocracker, allowing higher crude charge rates without exceeding these conversion unit capacities.

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Online cleaning improves operational excellence

Online cleaning, followed by degassing and decontamination, can result in a significant reduction in downtime, increased run length, operation under cleaner conditions and potential avoidance of a turnaround, leading to an increase in production

Marcello Ferrara

ITW

Online cleaning of refinery production units has been positively proven in many severe applications such as the bottom section of visbreaker and vacuum columns with both trays and structured packing. In turnaround applications, visual inspection has confirmed positive results. An entire unit can be cleaned online in just 24–36 hours. Furthermore, online cleaning can be implemented during unit operations to recover unit performance, operate under clean conditions and improve operational excellence.

Current cleaning technologies

Today's technology for cleaning heat exchangers includes the following procedures:

- Flushing
- Isolating equipment from the process and blinding
- Removing hydrocarbons
- Steaming out for gas removal
- Scaffolding
- Unbolting
- Removing covers and distributor
- Extracting the bundle
- Transporting the bundle from plant to washing area
- Hydroblasting
- Transporting the bundle from washing area to plant
- Inserting the bundle
- Inserting new gaskets
- Installing covers and distributor
- Bolting
- Removing blinding
- Removing scaffolding
- Air removal and purging
- Performing pressure tests
- Inserting the apparatus in the process.

All of these operations have their related costs. The bidding paid costs are to be added to the customer's organisational costs in terms of:

- Awarding (bid organisation, evaluation and award)
- Planning
- Co-ordination

— Control during execution.

To these operational and organisational costs, huge production loss costs must also be added, followed by equipment downtime. Even more relevant are the costs associated with the decrease in performance during the run. Moreover, all these operations can suffer from different problems, such as:

- Long time for isolating/inserting the equipment
- Waste generation
- Hydrocarbon emissions
- Bundle damage
- Difficulties in bundle extraction
- Difficulties in unbolting
- Hazard to workers performing mechanical operations
- Hazard from scaffolding
- Hazard from spills of carcinogenic (R45) products
- Hazard to people working nearby moving equipment/vehicles
- Hazard from bundle transportation/cleaning apparatus/cranes.

Due to continuous improvements in process safety and environmental performances, these problems are now only acceptable when there really is no other choice.

Safety and environmental factors

The hydrocarbon processing industry continues to try and limit airborne emissions through technical efforts and investment. For example, consider the investments and revamps required (eg, valve substitutions, insulation of flanges, double seals on pumps and double seals on tanks) to limit volatile organic compounds (VOCs), then imagine the effects of hydroblasting on these assets.

Until recently, hydroblasting was the only effective technology for cleaning heat exchangers and process equipment. However, by performing cleaning operations in a circulation loop, online cleaning eliminates all the problems associated with hydroblasting. Moreover, sludge is converted to a fully reusable/

reprocessable product and the washing fluids are compatible with the hydrocarbon processing industry/combustion process. As a result, the equipment can be put on-stream immediately after cleaning.

Another problem encountered during turnaround is the duration of steam-out operations and their associated environmental problems, which directly impact equipment downtime.

Current operations

Mechanical cleaning is currently performed only where there is a stringent need for it. This suggests that equipment is being allowed to degrade to the minimum acceptable performance before cleaning. This situation arises from a number of peculiarities in the hydrocarbon processing industry.

First, the industry sees cleaning as a troublesome, lengthy operation that leads to a loss in production, so it is avoided. Also, the mechanical cleaning process involves at least 20 operations, each of which has an associated hazard. When the production/maintenance department faces a cleaning situation, it normally reacts in one of two ways:

- The situation is fairly typical and managed as a routine operation
- The situation is problematic and postponed until it can no longer be tolerated.

In the first case, the management team is unlikely to consider something that is not routine. Or, in the best case scenario, they will be excited about trying something new. However, unless the management team is strongly committed to the necessary testing of the new technology, there is a tendency to procrastinate.

In the second case, the management team may not be innovative enough to look for a new technology and address the problem in a brute force manner that might eventually be inefficient and costly. In both cases, process unit economics and environmental performance can suffer significantly.

Industry mindset

In view of these factors and the current industry mindset when it comes to cleaning process equipment, the cost benefits of online cleaning are significant. Budget compliance is a must in all business units, which is why divergence from a budget for long-term investment is usually not an easy decision.

The production, maintenance, environmental, investment and administrative departments all have separate budgets to which they must adhere, and each department is concerned only with their own budget. Of course, this reflects common practice when running a company, but sometimes it is better to consider the company as a whole, not as a collection of individual boxes.

Is it worthwhile increasing maintenance costs for the sake of increasing production, reducing energy costs and improving safety, reliability, environmental performance and compliance? To date, this has not been the case, as there has been no technology available for simultaneously increasing production, reducing energy costs and improving safety, reliability and environmental performance.

Advantages of online cleaning

However, an array of technologies are now available for solving problems related to equipment cleaning, including ITW's patented technology for cleaning heat exchangers and process equipment in a closed loop. Equipment can be cleaned online with this technology without having to extract the heat exchanger bundles). This is particularly beneficial in severe applications such as visbreakers and columns with structured packing internals. Crude distillation units (CDUs) and vacuum units have also

been successfully cleaned online. An entire unit can be cleaned in 24–36 hours. The advantages online cleaning has over hydroblasting include:

- Reduced downtime
- Closed loop operation, without the need for extracting the bundles
- Simultaneously cleaning of multiple units
- No waste generation
- No emissions.

The ITW cleaning method involves the injection of an oil-based chemical that transforms sludge into a fully reusable product, thereby removing any sludge and deposits from metal surfaces. The washing solution can be reutilised/reprocessed because the stabilising properties of the chemical avoid reaggregation of deposits, thereby eliminating any potential precipitation during storage and/or fouling of process equipment. Moreover, the patented chemicals used in ITW's method are compatible with hydrocarbon processing industry/combustion processes, as they:

- Do not contain any metals
- Do not contain any compounds based on P, B, S, As, Bi, Si or Pb
- Do not contain any halogen
- Do not contain any compounds that might be harmful to plant metallurgy
- Do not contain any carcinogenic compounds
- Do not contain any compound that in operating dosages might interfere with biological waste treatment processes.

After online cleaning, the heat exchangers can be immediately put back on-stream without extracting the bundle. However, if visual inspection is to be performed, a clean bundle can be extracted. The hard coke will dry if it is present, as the technology eliminates all the coke binders, and is friable and very easily removed.

Increasing revenues

The following case histories may be considered unusual by some; others may see them as typical of the hydrocarbon processing industry. Paradoxically, the industry is not energy efficient. As energy is so readily available, costs are not always taken fully into account. Another problem is that cleaning is a lengthy and unsafe operation that can lead to a loss in production, which can overwhelm the energy-saving benefits. For this reason, cleaning is usually postponed until the last minute.

Online cleaning helps to address all production, energy-saving, environmental, safety and reliability issues, as it can achieve equipment closed loop cleaning for the entire production unit in less than one day, making equipment immediately available for production.

In very difficult to solve cases, online cleaning can be performed during different periods of the run to avoid certain problems. Depending upon the magnitude of the problem and the particular application, even coke formation inside equipment (eg, columns, packings and exchangers) or delta P (ΔP) build-up can be prevented by regular online cleaning.

At current high crude oil costs and high operating margins, being able to address all these issues can lead to significant improvements in revenue. For example, by reducing the amount of fuel burned, there will be a reduction in SO_x , NO_x , CO, CO_2 and other airborne pollutants at no extra cost. When considering all the investments the hydrocarbon processing industry is implementing to reduce airborne pollutants, online cleaning can provide the following advantages:

- Reduced waste generation
- Reduced VOC emissions

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- Reduction in airborne pollutants (following energy savings and reduction in fuel burned)
- Reduced CO₂ emissions (following energy savings and reduction in fuel burned)
- Improved safety.

It is important to note that the health, safety and environment benefits are achieved without any extra investment or cost. The cost of installing spare equipment is avoided too. However, the greatest benefits of online cleaning are increased run length, operation under cleaner conditions and potential avoidance of a turnaround.

Turnaround operations improvement

A technology is also available that uses a patented chemical, added during steam-out, to significantly reduce steam-out time and hence unit downtime. The chemical also eliminates any noxious odours during steam-out, as well as any pyrophoric iron problems. The ITW patented chemical does not create any emulsion either.

By applying online cleaning followed by degassing/decontamination there is little, if any, need for mechanical cleaning, and safe entry conditions are achieved more quickly. This results in a significant reduction in downtime, which in turn leads to an increase in production.

Alternatives

There are instances where online cleaning technology was considered from the onset as an alternative to mechanical cleaning or to improve turnaround operations. This was due to the fact that the operator required visual inspection to validate the technology. As a result, online cleaning was implemented during the actual run to immediately recover unit performance, to run under cleaner conditions and increase run length. It is therefore used as a preventive tool for unit optimisation and to improve operational excellence. Achievable revenues from these optimisations depend upon unit configuration and production layout. They will certainly reach several million dollars if applied proactively.

Climate conditions and cleaning schedules

In many countries, very cold or very hot climate conditions often dictate the time for any process unit cleaning activity. As a result, refineries may be forced to tolerate inefficiencies until climate-related conditions permit. However, climate conditions only affect those mechanical cleaning techniques such as hydroblasting that are lengthy and labour and equipment intensive.



Figure 1 Visbreaker bottom exchanger



Figure 2 Visbreaker main fractionator bottom

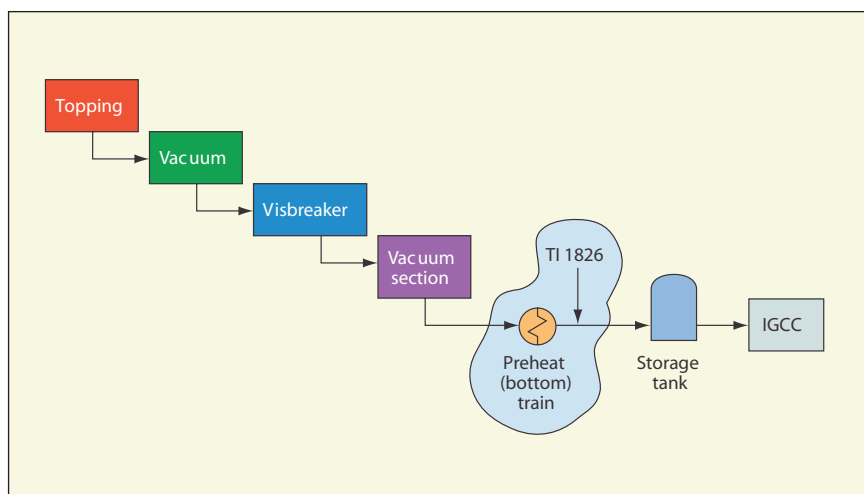


Figure 3 Online cleaning of Visbreaker vacuum bottom section: layout of refinery

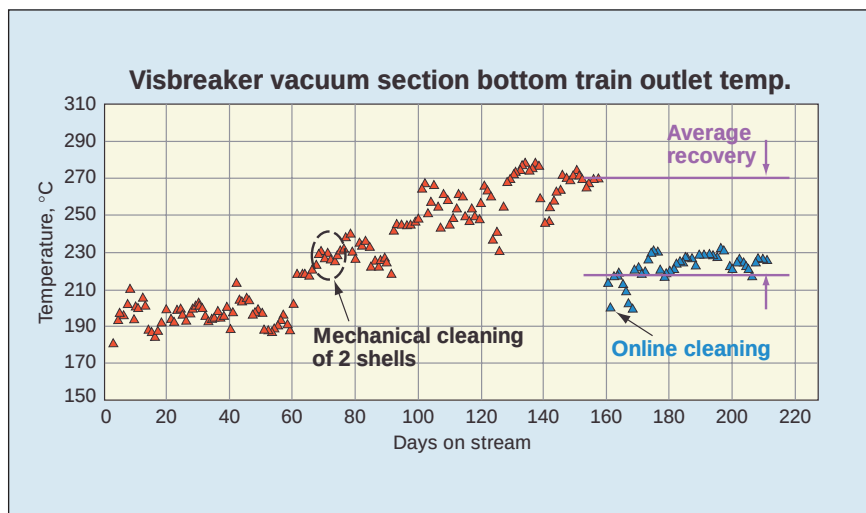


Figure 4 Online cleaning of visbreaker vacuum bottom section: recovery of outlet temperature

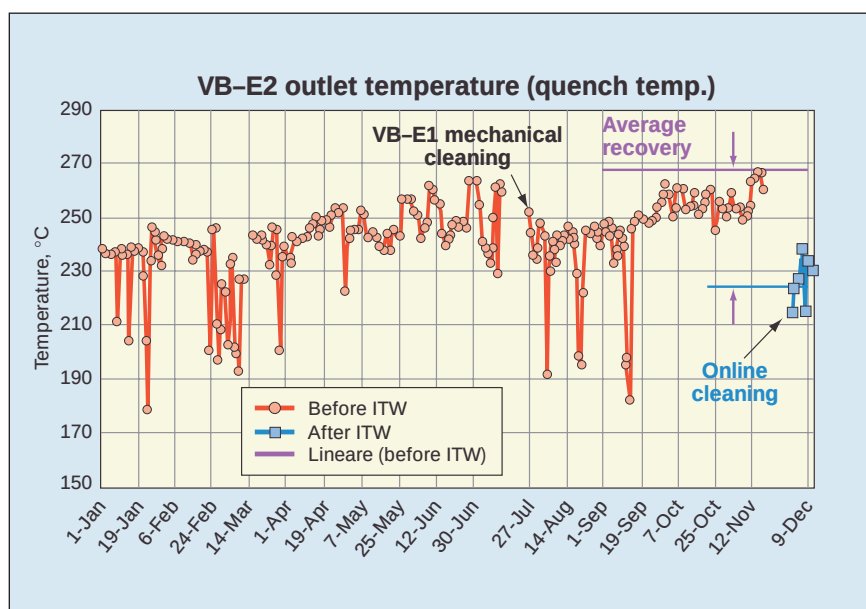


Figure 5 Simultaneous online cleaning of vacuum and visbreaker units: recovery of visbreaker quench temperature

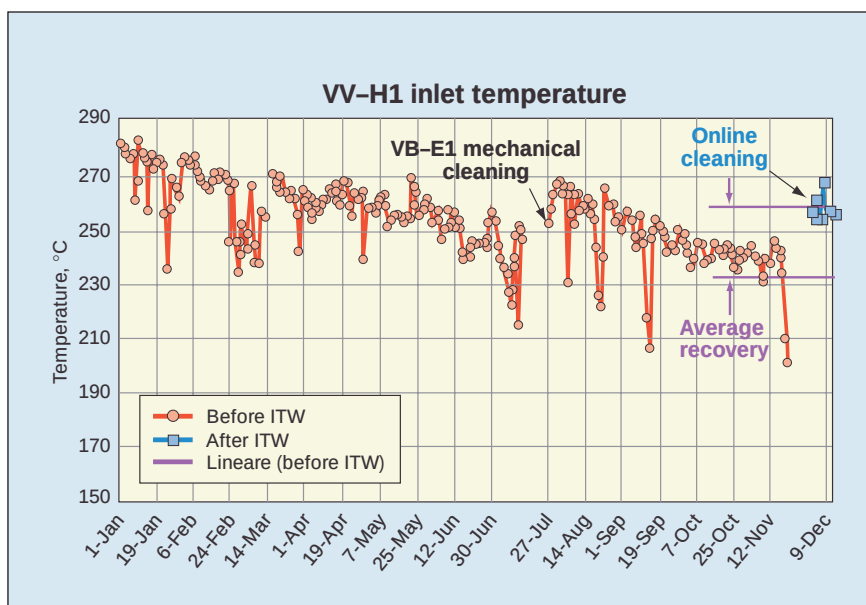


Figure 6 Simultaneous online cleaning of vacuum and visbreaker units: recovery of vacuum furnace inlet temperature

Climate-related factors do not affect online cleaning to the same degree. ITW technology only requires 24 hours on a oil-to-oil basis, normally two engineers and no heavy hardware, just the chemical and the injection pump.

The improved flexibility in solving operational problems is discussed in the following case histories.

Case study 1

Online cleaning of a visbreaker

Online cleaning was performed during a scheduled decoking of the furnaces after one year's operation of a European refinery's visbreaker unit. Cleaning of the exchangers was originally not scheduled, as the unit may bypass the critical preheat exchangers, allowing for mechanical cleaning during the run. Here is a summary of the results:

- In 36 hours, 28 bottom exchangers of a 310 tph visbreaker were cleaned
- The bottom of the main fractionator was clean (normally about 1m of sludge and coke is found)
- The bottom packing of the main fractionator was clean
- Furnace decoking time had been reduced by about 20%
- The visbreaker started up 12 hours before the scheduled time, with all the preheat, packing and lines clean (which were not in the cleaning schedule).

Visual inspection of the most severe service bottom exchanger was performed to validate the results. However, the other bottom/preheat train equipment was not opened. Figure 1 shows the visual inspection of the first bottom exchanger cleaned after one year in operation. Figure 2 shows the bottom of the main fractionator at the manway opening.

Case study 2

Online cleaning of visbreaker vacuum section bottom train

Online cleaning was applied to the vacuum section of a visbreaker. The layout of the refinery with this visbreaker is shown in Figure 3. The refinery's problem was related to an increase in the vacuum section bottom train's outlet temperature (reading TI1826). The refinery usually cleaned the exchangers when the outlet temperature approached 280°C. It had to mechanically clean two exchangers to reach the targeted run length. However, this did not recover the temperature, so the visbreaker was facing an unscheduled shutdown to mechanically clean the entire vacuum section's bottom.

To solve the problem, the vacuum section bottom was online cleaned in 48 hours. The visbreaker was then started up immediately. The temperature recovery on TI1826 was on average 45°C, which remained stable during the run (Figure 4). The unit could easily

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reach scheduled turnaround and run five more months (the full run is not reported in Figure 4).

Case study 3

Simultaneous online cleaning of a vacuum unit and a visbreaker

Online cleaning was applied to a vacuum unit integrated with a visbreaker at a European refinery. The reason for considering online cleaning was the increase in the visbreaker's quench temperature, which was limiting throughput. Mechanical cleaning of four heat exchanger shells (with the hottest at the bottom) had not helped to recover the temperature, so there was a steady increase in quench temperature.

After being cleaned online, the two units were started up in 36 hours. The recovery of the quench temperature was about 50°C (Figure 5), and as the units are integrated a recovery of 18°C on the vacuum furnace inlet temperature was also achieved (Figure 6).

Case study 4

Online cleaning of slop distillation unit

A slop distillation unit processes, on a campaign basis, all the slop collected on-site at a 280 000 bpd refinery. The facility has four topping/vacuum units, one FCCU, one residue hydrocracker and two ethylene units. After the one-to two-month campaign, the slop distillation unit is shut down for cleaning, as it suffers from very heavy fouling and coke accumulation.

To demonstrate the effectiveness of online cleaning, the unit was run as usual. It was then shut down and opened to check the fouling conditions in the main fractionator and two bottom exchangers. The unit had about 1m of coke-like sludge in the bottom of the main fractionator. Moreover, the main fractionator's trays and bottom exchangers were heavily fouled.

The online cleaning lasted 24 hours. Degassing/decontamination was then implemented to reduce steam-out time, eliminate any noxious emissions and pyrophorics ignition. The main fractionator bottom and trays were free of any deposits, and some 1–2 kg deposits were found in the bottom exchangers. Fortunately, these deposits were loose and easily removed using the unit's service water at 2–3 bar. No mechanical cleaning was carried out on the unit and it was henceforth started up. Figures 7 and 8 shows the situation before online cleaning, and Figure 9 shows the improvements afterwards.

Marcello Ferrara is the Chairman of ITW S.r.l. in Augusta, Italy. Ferrara graduated with a PhD in industrial chemistry from Messina University in Italy.



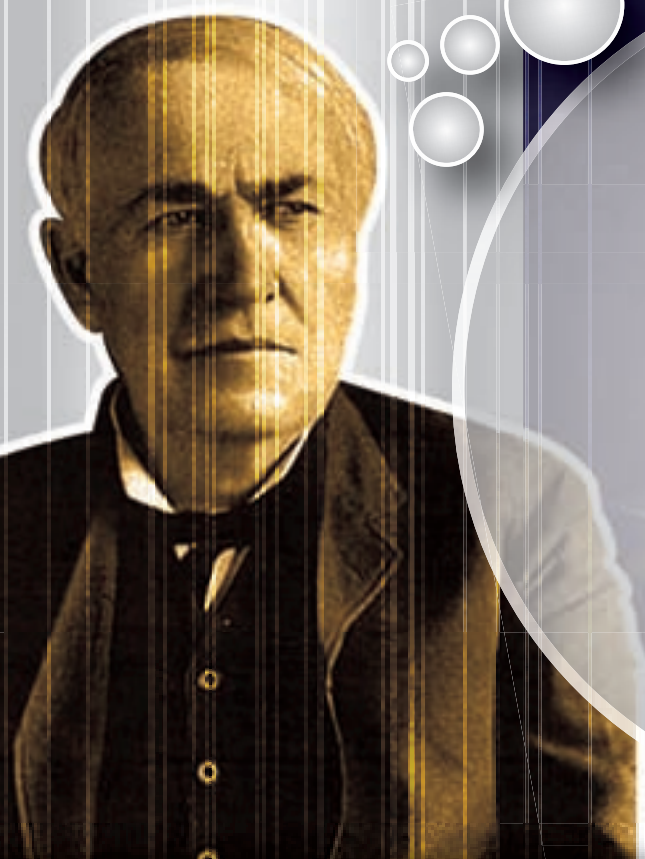
Figure 7 Online cleaning of slop distillation unit: main fractionator bottom before online cleaning



Figure 8 Online cleaning of slop distillation unit: main fractionator bottom before online cleaning



Figure 9 Online cleaning of slop distillation unit: main fractionator bottom after online cleaning



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Increasing FCC yields with oxygen enrichment

With the demand for diesel increasing faster than that for gasoline and other refined products, an increase in FCC distillate yield can provide a low-cost route to capturing margins opportunities. Oxygen enrichment can help to achieve these goals

Jack Olesen
Praxair

A relevant question posed by refiners at the recent NPRA Q&A in Orlando and the ERTC in Vienna was concerned with how to configure the FCCU towards higher distillate-to-gasoline ratios. Other related and equally important issues were concerned with ways to manage light cycle oil (LCO) production, bottoms recycling and the use of oxygen enrichment to improve FCCU profitability.

Straight-run diesel recovery

Considering the importance of major diesel-producing units in today's market, such as the hydrocracker, higher diesel yields are also possible with FCC operations. The first thing a refiner should consider is how much straight-run (SR) diesel is in the combined feed to the FCCU. It is not unusual to find up to 20% diesel-range boiling material in the FCC feed, and the target should be to get this down to 5%. SR diesel does not crack that well in the FCCU and the quality of the LCO is worse than the quality of the virgin diesel going into the unit. Then there are the obvious operational changes that can be made on the unit, such as lowering catalyst activity, increasing the matrix surface area (lower Z/M) and reducing the riser temperature.

Trade-offs: higher CSO production

The trade-offs in pursuing this route (ie, reducing severity to increase LCO production) are that the main fractionator bottoms, often referred to as slurry or clarified slurry oil (CSO), increase at a faster rate than the LCO. These increases are at the expense of gasoline and LPG. If the reduction in LPG or alkylation unit feed is a concern, the refiner should consider using a ZSM-5 additive.

In order to quantify these changes, one must first bear in mind that, as with everything in FCC operations, these changes will be unit specific. For example, Praxair recently completed a

study for a 30 000 bpd FCCU that was planning to increase LCO make. Dropping the riser temperature 40°F and lowering catalyst from 71 MAT to 63 increased LCO by 3%, but CSO also increased by 5%. This is probably not a good economic trade-off.

To provide better economic trade-offs, changing the catalyst matrix activity to compensate for a lower riser temperature and other previously noted changes has been considered. However, in this case, when making the previously discussed changes and raising the matrix surface area by 80 m²/g, LCO did indeed increase by 4%, but CSO increased even more than the LCO. The larger volume of CSO can be mitigated by taking a heavy cycle oil (HCO) draw and sending that stream to the hydrocracker, if one is available. Otherwise, the refinery should consider recycling the fractionator bottoms (ie, bottoms recycling), preferably the HCO portion if that can be drawn off separately.

Bottoms recycling

While bottoms recycling was practised in the past before high-activity zeolite catalysts were available, this option may re-emerge into a future trend. Why? If there are going to be substantial increases in LCO make, recycling HCO, or recycling HCO plus CSO (if there is no separate HCO draw), will almost always have to be considered. The recycle should be injected into the riser through separate nozzles that are preferably located above the fresh feed injection nozzles. At the same fresh feed rate, the FCCU will have to be able to handle the additional volume from the recycle and have sufficient air blower capacity to deal with the increased coke make.

Of concern is the increase in slurry at lower conversion unless the recycle stream is put into service. The recycle stream can be as high as 20% of the fresh feed rate. This volume of recycle is necessary to keep the CSO make constant relative to the higher conversion base case. Even with a coke-selective bottoms

cracking catalyst system, the type of molecules that are being cracked will increase the coke make.

Air blower constraints

If there is no additional capacity in the air blower, options to remedy this constraint include:

- Diverting some of the heavier FCCU feed to a hydrocracker
- Adding more air blower capacity
- Using oxygen enrichment to supplement the air blower.

When implementing oxygen enrichment, the refiner should first determine if there are any permitting issues related to emissions or allowed coke burning rates. Praxair has supplied oxygen enrichment systems for over 25 years and is currently supplying about 20 FCCUs. In the past, the reasons for enrichment were to increase feed rate or conversion, have the ability to process heavier feedstocks, or reduce regenerator velocity for increased time between turnarounds.

Oxygen enrichment levels

In terms of the range of possible enrichment levels, most of the FCCUs supplied by Praxair enrich to 23–28% oxygen, although levels up to the mid-30% have been reported. Praxair has no specific oxygen enrichment limit and we treat any enrichment that results in greater than 23.5% oxygen as if the system were exposed to pure oxygen. For most units, the practical enrichment limit becomes the regenerator temperature or the ability of the downstream recovery system to handle the higher charge rate and conversion. The regenerator temperature limit has often been addressed with a catalyst cooler. For situations where there is 20% recycle, oxygen enrichment is very practical. For example, in the previously discussed case, the level of enrichment required was about 23%.

Therefore, taking into account all of the previously noted issues surrounding bottoms recycling and LCO production,

a certain level of LCO increase can be expected. Referring again to the previously discussed case that Praxair studied in detail, the change in LCO was from a base case of about 10% to about 18%, while keeping the CSO constant. However, Praxair did not model the use of ZSM-5 to keep LPG make constant.

Implementation

While the increase in LCO at constant CSO and 23% oxygen enrichment is very attractive, refiners may nonetheless be concerned with the amount of time required to implement oxygen enrichment. This depends on whether the refiner is close to an oxygen pipeline or not. Where pipeline oxygen is

available, it would realistically take about nine months to implement. There are the usual permitting and HAZOP processes that need to be handled first. The equipment involved is relatively simple and consists of an oxygen metering skid, an oxygen flow controller tied into the control room instrumentation to control and monitor the process effectively and safely, and the injection quill that goes in downstream from the main air blower (MAB). If there is no oxygen pipeline, the refiner would have to consider a liquid oxygen system or an on-site air separation plant. Timing for liquid oxygen would be similar to the pipeline case. In addition, there would need to be

a site for installation of liquid oxygen tanks and a vapouriser. The timing to build an air separation unit is currently about 24 months. Praxair builds, owns, operates and maintains the unit and then sells the oxygen directly to the refiner. The oxygen cost is competitive with the cost of pipeline oxygen.

There is concern with regard to an expected octane drop in the FCC gasoline at reduced unit severity, which is another reason to consider ZSM-5 to maintain FCCU gasoline octane and keep the alkylation unit full.

Impact on emissions

It is well understood that NO_x reacts with CO to produce N_2 and CO_2 . With oxygen enrichment, there is less inert nitrogen in the regenerator and hence the CO partial pressure is higher, leading to reduced NO_x . As for SO_x , if the refiner is using a SO_x additive, the performance should increase. This is because the SO_x additive captures the SO_3 and the higher oxygen partial pressure drives the SO_2 to SO_3 .

With regards to future CO_2 limits and carbon capture and sequestration (CCS) requirements, the development of "green FCCUs" may become a possibility. Praxair is looking into this topic in cooperation with FCC licensors, since we have a lot of history with CO_2 handling due to the acquisition of Liquid Carbonic several years ago. To be sure, while the equipment we are accustomed to may be similar, the operation might be dramatically different.

Petrochemical interface

Oxygen enrichment does not only apply to FCCs, but also to sulphur plants for capacity expansion or backup purposes and process heaters for improvements in efficiency and throughput. In addition to oxygen, hydrogen is supplied either by pipeline or by on-site steam methane reformers (SMRs).

More recently, a process for reducing NO_x and or CO coming out of the regenerator is in development. This process would have application in meeting emission requirements for full-burn or partial-burn units. In the petrochemicals arena, hydrogen is being recovered and purified, which might otherwise be burned as fuel. In the next issue of PTQ, a detailed article on energy and hydrogen utilisation audits will be featured.

Jack Olesen is Senior Business Development Manager for Praxair in the US Gulf Coast region. He has over 30 years' experience in the industry. Olesen earned a BS degree at University of California Irvine, and MS and PhD degrees in chemistry at University of Colorado. Email: jack_olesen@praxair.com

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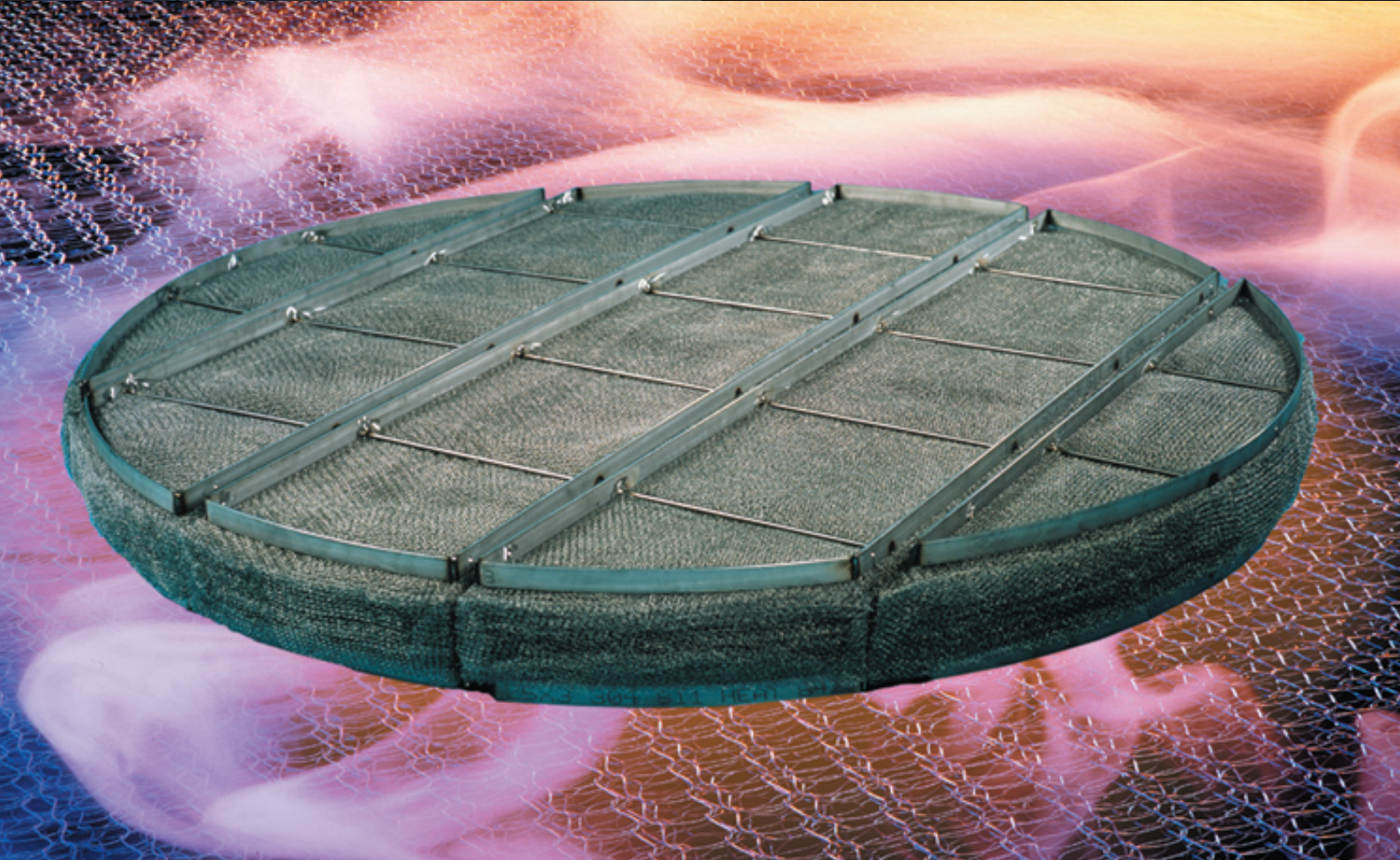


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Attention all FCCU operators

The FCCU in transition

How refiners can benefit from an unprecedented opportunity

Pre-eminent FCC expert, Warren Letzsch, and PTQ's editor, Rene Gonzalez, have co-authored an important new study with the single objective of informing refiners how they can make their FCC unit operations more profitable. Topics covered include:

- How recent projects have generated major financial advantages by converting HVGO from the latest generation deep cut vacuum distillation units (See section 6.1 of the Study)
 - How to provide a balanced output of clean burning gasolines and ULSD gas oils while optimising chemical hydrogen consumption and minimising outputs of lower value (See section 6.1)
 - How larger refineries can explore parallel conversion opportunities for heavy distillate conversion (See section 6.1)
 - How modifications to major refinery assets, such as the vacuum unit, delayed coker and MHC will directly benefit FCC operations (See section 6.6)
 - How refiners who have successfully increased diesel and/or propylene production from their FCC unit are succeeding in obtaining better separations from their FCC main fractionators (See section 8.1)
 - How best to benefit from changes in heat and energy balances resulting from an increase in the size and complexity of regenerator units (See sections 2.3, 4.1, 6.3 and 6.5)
 - How proposed legislation for carbon capture and sequestration mandates will affect FCC design, including details of CO₂ capture from conventional SMR plants and polygeneration gasification plants, allowing the regenerator to operate on ambient air w/o CO₂ capture (See section 6.5)
 - How full-burn units are performing at higher severities processing opportunity feeds but still meeting current and future emissions targets (See sections 2.3 and 7.3)
 - How to get the greatest productivity out of FCC/RFCC and associated gas plants, particularly when linked to:
 - Mild hydrocracking unit (MHC)
 - Butylene alkylation unit
 - Two-stage desulphurisation unit
 - High purity propylene plant
 - Separate draws within main fractionators
 - Integrated slurry oil filtration unit
 - Third-stage separator with underflow filtration (See section 8.2)
- PLUS**
- Assessment of FCC catalyst formulations for processing hydrotreated cat feeds and non-hydrotreated cat feeds (See sections 6.7 and 9)
 - A survey and refinery wish list of selected FCC unit components including feed nozzle injectors, cyclones and steam strippers (See sections 12.4, 12.5 and 12.6)
 - Survey of rotating equipment developments for improving reliability of new and refurbished WGCs and MABs (See section 11)
 - Process flow diagrams showing FCC units configured for specific product objectives (export-based refineries, refineries targeting WCS feedstocks, FCCUs with turboexpander/cogeneration capacity) (See figures 1.1, 5.1, 7.1 and 7.2)
 - Survey of future long-term trends affecting FCCU process design and operations, including market and regulatory trends such as higher fractions of heavier feeds, synthetic blends and biomass processed through the FCC. (See sections 13, 14.1 and 15)



For further details of the contents of this study and how to purchase it, go to www.eptq.com/studies

New roles for FCCU: carbon capture unit and coke gasifier

Environmental and energy security concerns may evoke new roles for the FCCU in addition to the production of liquid fuels and light olefins. Gasification and carbon capture are two such possibilities

Erich J Mace, Adrienne M Blume and Thomas W Yeung
Hydrocarbon Publishing Company

Fluid catalytic cracking has been evolving since the first unit was commissioned at Esso's Baton Rouge refinery in 1942.¹ Today, it continues to be a unit in transformation, adapting to increasingly heavier feeds, strict transportation fuel specifications, product demand changes and unit emissions standards.

The FCCU is traditionally configured to produce gasoline for maximum yield, maximum octane or maximum octane barrels as needed, but its role is changing. For example, gasoline demand, although still growing worldwide, is on shakier ground due to biofuels mandates that require certain percentages of gasoline to be replaced with ethanol and the recent economic turmoil that has dampened consumption. Refiners are finding value in other FCC products, such as propylene and LCO, and units running on lower-quality feeds, such as resid, are becoming increasingly common. Environmental regulations have also shaped the current state-of-the-art, with flue gas systems and catalyst additives now standard to mitigate NO_x, SO_x, PM and CO emissions and meet reformulated gasoline requirements.

The aforementioned impetuses are certainly enough to continue to foster technological development in fluid catalytic cracking. However, the current geopolitical climate suggests a new wave of FCC developments is on the horizon, potentially transforming the unit into a polygen operation including fuels production, petrochemical production, syngas production, power generation, and carbon capture. Figure 1 compares the current roles of the FCCU to its future roles.

Impending legislation

In the US, President Barack Obama's environmental platform seeks to cut CO₂ emissions to 1990 levels by 2020, curb emissions to 80% below 1990 levels by 2050, and require fuel producers to decrease the carbon content of their fuels by 10% by 2020.

Obama has repeatedly warned, "Global warming is not a 'someday' problem — it is now," and supports a carbon cap-and-trade scheme that would require greenhouse gas (GHG) emitters to either buy pollution permits or reduce emissions directly from their operations. Refiners will initially spend their extra capital on emissions permits rather than plant expansions, but as CO₂ credit prices rise they will need to consider making energy efficiency improvements and capturing CO₂ from major emissions point sources. Analysts assert that the introduction of a US cap-and-trade scheme would foster the development of such low-carbon technologies. Outside the US, Canada's Conservative government expressed interest in Q4 2008 in forming a climate change pact with the US and, in the EU, 2008 saw the adoption of a plan to implement CO₂ permit auctions starting in 2013. EU refiners will begin purchasing 20% of their permits by auction, transitioning to 100% by 2020.² Such moves by Western nations may also put pressure on countries like China and India to invest in similar technologies.

According to the US Energy Information Administration (EIA), the US emits approximately 6.0 billion mt/y of CO₂. The manufacturing sector produces 1.4 billion mt/y of that total,

of which petroleum refining claims 19.8% (277.6MM mt/y in 2002) of the emissions. Excluding the combustion of refinery fuel, the FCCU is the largest emitter of CO₂ in the refinery.³ Regenerator flue gas is almost exclusively the source and can comprise anywhere from 15–50% of refinery CO₂ emissions.⁴ Since it is the largest non-fuel-derived source in the refinery, it is in refiners' interest to investigate FCCU CO₂ reduction methods. A study released by Petrobras in 2003, shown in Figure 2, details the distribution of refinery CO₂ emissions.⁵

As the coked FCC catalyst is regenerated via combustion, the following important model reactions occur (reactions 1–10). Coke and CO combustion (reactions 3 and 6) are the chief contributors to flue gas CO₂. Thus, if the combustion of catalyst coke can be reduced (and carbon leakage within the refinery does not occur), refiners can decrease CO₂ emissions. Also, notice that the standard heats of reaction for reactions 1, 3 and 6 are large and exothermic, supplying the bulk of the heat for the FCCU:

1. $2C + O_2 \rightarrow 2CO$, $\Delta H_{rxn}^0 = -221.1 \text{ kJ/mol}$
2. $C + CO_2 \rightarrow 2CO$, $\Delta H_{rxn}^0 = 172.4 \text{ kJ/mol}$ (reverse Boudouard reaction or CO₂ reforming)
3. $C + O_2 \rightarrow CO_2$, $\Delta H_{rxn}^0 = -393.5 \text{ kJ/mol}$

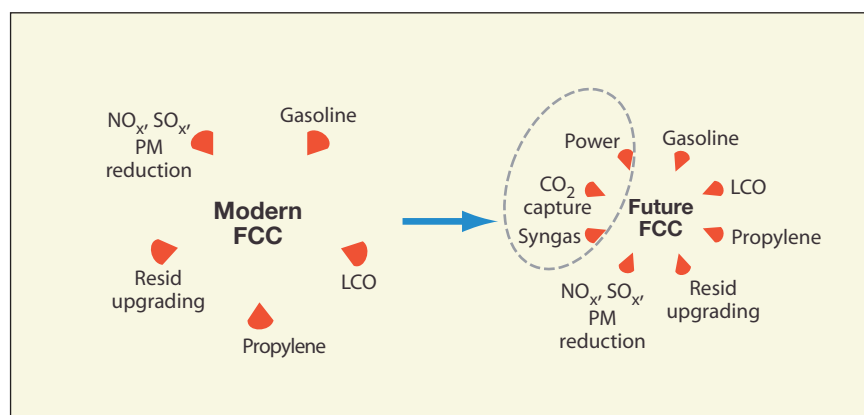


Figure 1 Future roles of fluid catalytic cracking

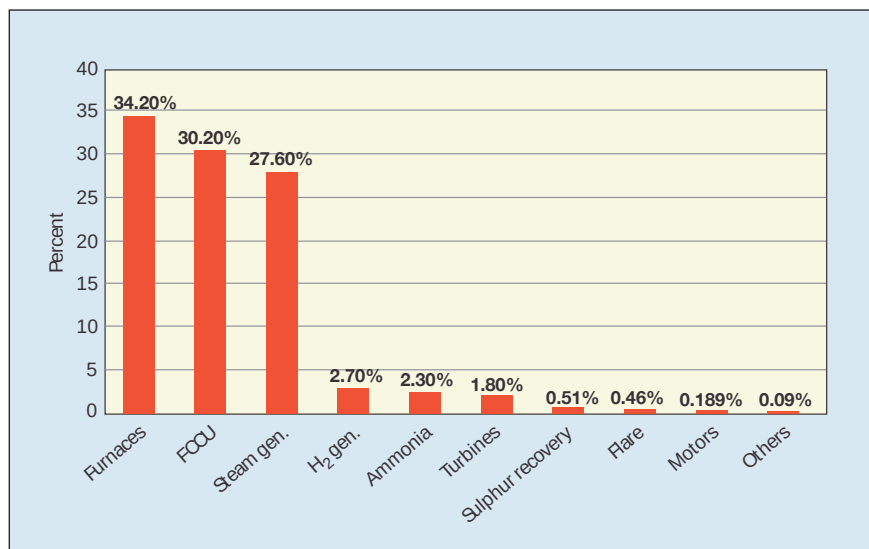


Figure 2 Refinery CO₂ emissions

4. $C + H_2O \rightarrow CO + H_2$, $\Delta H^\circ_{rxn} = 131.3$ kJ/mol
5. $C + 2H_2O \rightarrow CO_2 + 2H_2$, $\Delta H^\circ_{rxn} = 90.2$ kJ/mol
6. $CO + 1/2O_2 \rightarrow CO_2$, $\Delta H^\circ_{rxn} = -283.0$ kJ/mol
7. $2H_2 + O_2 \rightarrow 2H_2O$, $\Delta H^\circ_{rxn} = -483.7$ kJ/mol
8. $S + O_2 \rightarrow SO_2$, $\Delta H^\circ_{rxn} = -296.8$ kJ/mol
9. $2SO_2 + O_2 \rightarrow 2SO_3$, $\Delta H^\circ_{rxn} = -197.7$ kJ/mol
10. $N + xO \rightarrow NO_x$, ΔH°_{rxn} (dependent on x and minor in unit heat balance calculations)

Gasification of FCC catalyst coke

Several efforts, including work by BP and UOP, suggest that one method to shift selectivity away from combustion reactions is to operate the regenerator in gasification mode.^{6,7,8,9,10} Operating conditions for an FCCU regenerator are typically 1250–1500°F (675–815°C), with pressures near atmospheric pressure. For comparison, coal

gasification typically requires temperatures ranging from 1400–2800°F (760–1537°C) at pressures anywhere from atmospheric up to 1000 psig (7 MPa).¹¹ The defining difference between gasification and combustion is that significantly less air/oxygen is supplied during gasification. Thus, a reduction in oxygen concentration along with pressure and temperature modifications can shift an FCCU regenerator from a combustor into a gasifier, producing syngas (CO and H₂) instead of CO₂ and H₂O. One way to achieve gasification conditions is to reduce oxygen content by increasing the CO₂/O₂ ratio or the H₂O/O₂ ratio in the regenerator air feed. This action improves the rates of the two key gasification reactions: the water-gas reaction (reaction 11) and the reverse Boudouard reaction (reaction 2). A heat supply is also required to shift the thermodynamic equilibrium of these endothermic reactions to products. Typically, this heat is supplied when the exothermic

combustion and partial combustion reactions also occur. The following reactions, along with reactions 1, 2, 3, and 6, are those central to gasification:¹²

11. $C + H_2O \rightarrow H_2 + CO$, $\Delta H^\circ_{rxn} = 131.3$ kJ/mol (water-gas reaction)
12. $C + 2H_2 \rightarrow CH_4$, $\Delta H^\circ_{rxn} = -74.9$ kJ/mol
13. $CO + 3H_2 \rightarrow CH_4 + H_2O$, $\Delta H^\circ_{rxn} = -206.2$ kJ/mol
14. $CO + H_2O \rightarrow CO_2 + H_2$, $\Delta H^\circ_{rxn} = -41.1$ kJ/mol (water-gas shift)
15. $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$, $\Delta H^\circ_{rxn} = -165.0$ kJ/mol (methanation)

As seen in Figure 3, the resulting syngas evolving chiefly from reactions 2 and 11 can then undergo Fischer-Tropsch (F-T) synthesis or water gas shift (WGS). If the syngas undergoes WGS, H₂ and CO₂ are produced, and the CO₂ can be sequestered and/or recycled back to the regenerator to improve the rate of the reverse Boudouard reaction. The additional production of hydrogen has obvious benefits for energy and hydroprocessing needs. A dry gasification — ie, gasification that operates on a high CO₂/O₂ ratio vs a high H₂O/O₂ ratio — would be advantageous for CO₂ capture. If F-T products are produced from the syngas, both the liquids and the wax can conceivably be fed back into the FCCU for upgrading. Or, as has been proven by companies such as Sasol and Shell, diesel, gasoline, wax and high-quality olefins are obtainable for direct use, depending on F-T catalyst choice and process conditions. Alternatively, the syngas can be used as a combustion fuel for a gas turbine, as is the case with integrated gasification combined cycle (IGCC) applications.

The reverse Boudouard reaction is particularly advantageous because it consumes CO₂. It can be achieved at normal FCC regenerator temperatures with the addition of particular metals to the FCC catalyst. Li and Na have been observed to be most active in increasing the rate of the reverse Boudouard reaction, where a 1 wt% addition of the two metals in an undisclosed proportion yielded approximately 60% coke conversion at 1400°C. Equilibrium FCC catalyst, containing metals deposited during FCC operation, has also been cited as having high activity for the reverse Boudouard reaction.¹⁰ The endothermic reverse Boudouard reaction may be particularly useful for RFCC units, where higher Conradson carbon feeds produce a surplus of heat in the regenerator. Typically, this heat is removed by catalyst coolers or other heat removal equipment.

Maintaining unit heat balance

As was previously mentioned, the full and partial combustion of catalyst coke

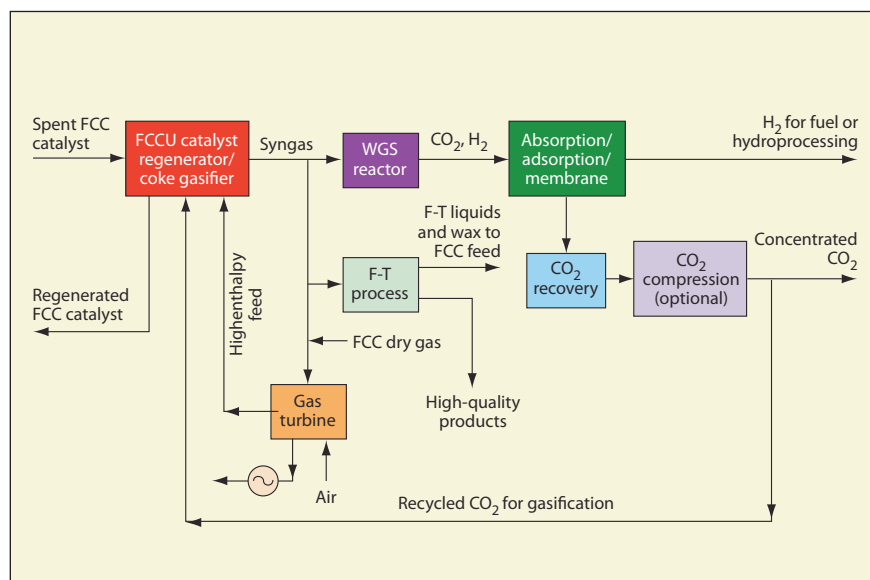


Figure 3 FCC gasification overview



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supplies the majority of heat for the FCCU. If coke is gasified instead of combusted, the heat balance will be disrupted. A potential scheme to maintain the heat balance would be to remove part of the coke by traditional oxidative methods, as well as a certain percentage via gasification. The catalyst could enter a first regeneration stage, where it is contacted with a higher CO_2/O_2 feed to undergo gasification, subsequently entering a second stage where oxidation can fully regenerate the catalyst and provide ample heat for the unit. The CO_2 created by the oxidative stage can then be recycled to the gasification stage. This concept could be extended to several regeneration stages of varying CO_2/O_2 ratios. More stages would give operators more control over the unit heat balance and the extent to which the catalyst is regenerated. Alternatively, lower-carbon heat sources might be used to close the unit heat balance if less coke is combusted. For example, dry gas from the FCCU could be used to heat the gas feed to the regenerator, thus supplying a high-enthalpy stream to heat the unit and provide heat for the endothermic gasification reactions. This option would be a significant departure from current FCC methodology, since the coke yield is not fixed by the unit's heat balance.

Gasification also requires water, and

the effect of water on FCC catalyst at elevated temperatures and pressures may cause more extensive hydrothermal deactivation of FCC catalyst. In this case, the fresh catalyst makeup might increase. If multiple regenerator stages are necessary to control the unit heat balance and fully regenerate catalyst, refiners may find the capital cost too high. Should WGS be employed, a separation system to remove CO_2 from the product stream will be needed. Capital costs and plot space will also come into play here. Some additional unanswered questions are summarised below:

— Will FCC catalyst be satisfactorily regenerated?

— Will afterburning become more or less of an issue due to high CO concentrations but lower O_2 concentrations?

— Is it possible to catalyse the reverse Boudouard reaction without poisoning the FCC catalyst?

— Can catalytic material such as Li be incorporated into the FCC catalyst matrix, or will particles need to be added into the cracking catalyst circulation, thus diluting base catalyst; or are Ecat metals sufficient catalysts?

— What sort of H_2O and CO_2 partial pressures in the regenerator are advantageous, and will CO_2 separation and compression become hurdles?

— For RFCC applications, can gasification consume enough heat to avoid the need for catalyst coolers?

— In a multiple-stage scheme of varying CO_2/O_2 ratios, can the unit maintain a heat balance or will additional heat be needed (eg, gas turbine effluent or heat exchanger)?

Additional feeds

If the FCCU can become a profitable syngas producer, other feeds may also be fed directly to the regenerator to increase syngas production. For example, residuum, coal, pitch or biomass-derived feeds could be fed into the dilute-phase transport line of the regenerator vessel to be gasified. Biomass-derived material can play another role in gasification. Instead of a traditional air-fed FCC regenerator, current research has suggested that oxygenates fed over coked FCC catalyst may be sufficient to produce syngas and regenerate catalyst in a multi-stage process, minimising the addition of air.¹⁴ This process may allow refiners to meet biofuels mandates via a new avenue. Specifically, biomass-derived oxygenates could offer a clean oxygen source, avoiding the disadvantages of N_2 inherent in air combustion to produce syngas as a valuable byproduct.

Future contributions from the FCCU

The refining industry is very likely headed toward a necessary retooling of how it conducts business in light of environmental legislation, demand shifts and crude oil volatility. The FCCU has been remarkable in fostering ingenuity among engineers and scientists for seven decades and, in light of the present situation, the stage is set for new developments to emerge. The unit may now be viewed as a potential polygen operation, producing fuels, syngas and perhaps power, while also performing CO_2 capture. Syngas can be used to synthesise F-T products for sale or for further upgrading in the FCCU. Alternatively, it can be converted to methanol and subsequently to gasoline via a methanol-to-gasoline (MTG) process. Under certain conditions, syngas can also be shifted to create a concentrated CO_2 stream, although what to do with this CO_2 stream is still under debate. Ideally, geologic storage is to be avoided, since this method permanently removes potentially useful carbon, although it is better than expelling CO_2 into the atmosphere and can be useful for enhanced oil recovery. Using CO_2 to synthesise profitable materials is perhaps a better long-term option, albeit an extremely challenging one, since CO_2 is already in a very favourable thermodynamic state.

Despite this hurdle, progress in utilising CO_2 has been made in the areas of polymers (BASF and Novomer),

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methanol production (Princeton University) and algal systems to produce fuels (Shell and Chevron).^{15,16} Perhaps it would even be profitable to produce CH₄ via CO₂ methanation if the prices for H₂ and CH₄ were right along with other economic conditions. Finally, the FCCU can potentially provide power to units other than itself through the installation of a gas turbine on the regenerator feed, not to mention the power recovery opportunities available on regenerator flue gas and steam letdown streams. If syngas is used to power the gas turbine, the FCCU could become a sort of IGCC unit. It is already known that the FCCU is a complex unit, but it has the potential for even greater complexity. In providing more functions to maximise the utility of each carbon atom that enters the unit, it can enable refiners to better position themselves for long-term success.

This article is based on selected material from Hydrocarbon Publishing Company's latest multi-client strategic report entitled, *Future roles of FCC and hydroprocessing in modern refineries*.

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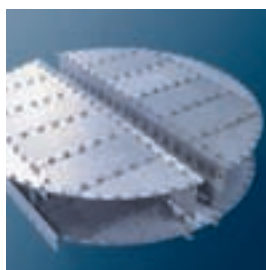
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Oil sands industry status

The steady progress made in the oil sands industry up to Q3 2008 will eventually resume. For now, an examination of the favourable market conditions and upgrading scenarios that are required for future profitability are presented

Tony Pavone
SRI Consulting

As of year-end 2008, global crude oil supply and demand were in tight balance, resulting in the rapid increases in crude oil prices and price volatility between 2007 and 2008. As marker crude West Texas Intermediate (WTI) exceeded \$145/bbl in mid-2008, the world began to see a moderation of demand growth caused by high prices. Crude oil demand actually decreased in the US, Western Europe and Southeast Asia, while demand growth moderated in the fast economic growth BRIC (Brazil, Russia, India and China) countries. Global crude oil demand growth of 2% per year, which had characterised 2000–2006, was cut nearly in half by 2008 by the cumulative impacts of higher petroleum prices, lower global GDP, and mandated production and use of biofuels. According to the US Department of Energy (DOE): “The combination of rising global demand, fairly normal seasonal inventory patterns, slow gains in non-OPEC supply, and low levels of available surplus production capacity is providing firm support for prices.”

Note that claims in some quarters that high oil prices were being driven by futures market speculation (dry barrel participants), profiteering by oil companies and the withholding of supply by OPEC are conspicuously absent from this government assessment. During the 2007–2008 period, geopolitical concerns over some major oil supplier output (Nigeria, Iraq and Venezuela) have contributed to oil price volatility.

Over the longer term, primary global energy demand is expected to increase by 50–60% by the year 2030, driven primarily by population growth and the desire for better living standards. The US National Petroleum Council, an organisation of US oil companies reporting to the US president, acknowledges that conventional oil and gas alone are unlikely to satisfy this demand growth in its seminal 2007 report, and called on the development of supplemental energy sources such as

clean coal, biofuels, alternative renewal energy, nuclear, and non-conventional fossil fuels.

Global crude oil producers

Russia, Saudi Arabia and the US are the largest producers of crude oil in 2008. The greatest concentration of production (both oil and gas) is in the Middle East. Shown in Figure 1 are the top ten producer countries.

Global proven crude oil reserves

Since the discovery of crude oil in the late 19th century, the world has consumed approximately 1.0 trillion barrels of crude oil. There are sufficient quantities (1.0 trillion barrels) of proven conventional crude oil reserves (determined by drilling) to meet today's global demand for another 25 years. There are expected to be another 2–3 trillion barrels of unproven conventional crude oil reserves, such as the heavy Venezuelan and Canadian crudes, and shale oil, which are together much more

costly to produce than conventional oil. So although the world may not be approaching “peak oil”, it is much more likely to be approaching “peak cheap oil”.

Canadian tar sands, Venezuelan tar sands, oil shale, deep offshore oil, sub-salt oil, GTL (gas to liquid fuels), BTL (biomass to liquid fuels) and CTL (coal to liquid fuels) chemistry are expected to represent cumulatively at least 3.0 trillion barrels of higher cost crude oil resources.

What the world seems to be running out of is light, sweet crude oil that can be produced at both low costs and at low business risk. Much of the conventional crude resource oil is located in politically unstable countries (Russia, Middle East and West Africa), which adds a price premium to the cost of production. Figure 2 presents the conventional proven crude oil base of the major producers by country of origin.

In this crude oil supply constrained environment, producing oil from

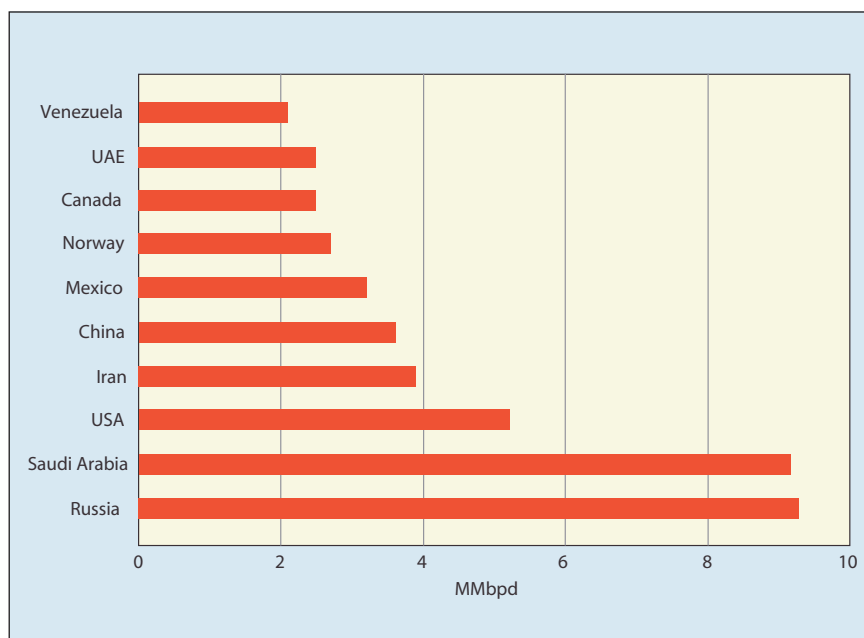


Figure 1 Top ten global crude oil-producing countries

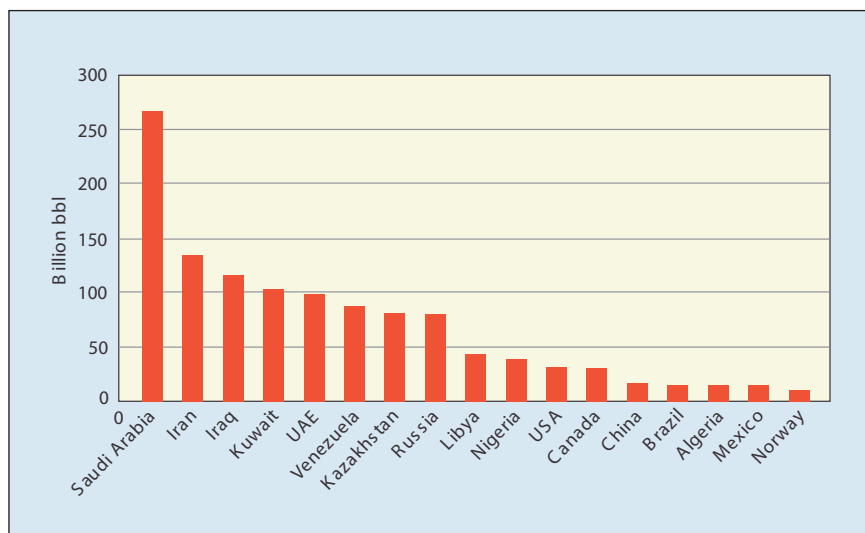


Figure 2 Crude oil reserves by country

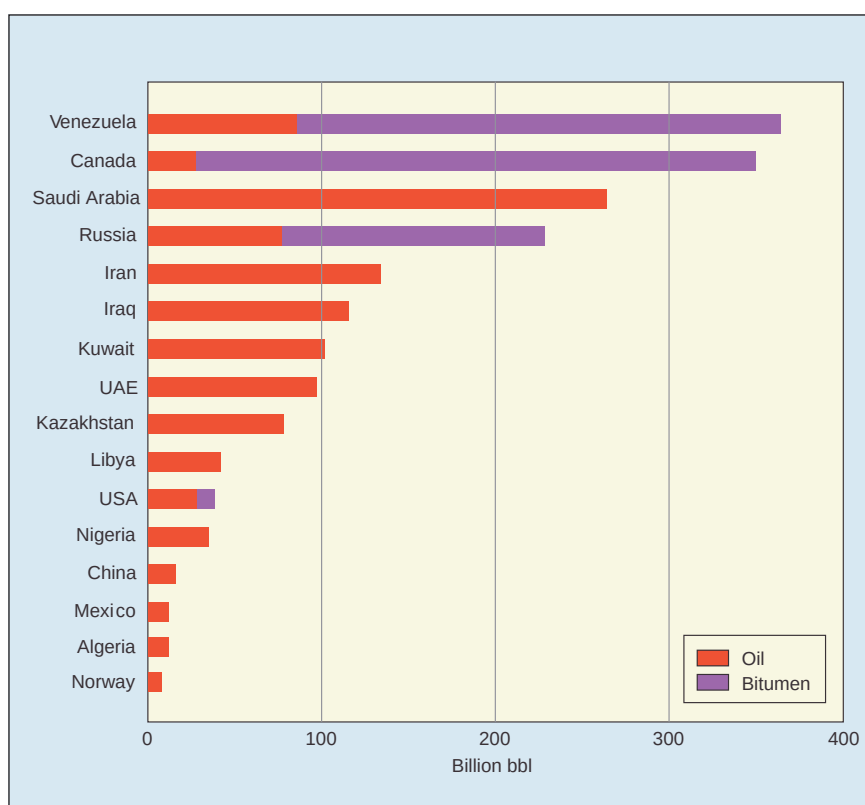


Figure 3 Distribution of conventional vs bitumen resources

Canadian tar sands is one of several sources of the world's next-generation energy supply base, especially for transportation fuels. Canadian tar sands have approximately 175 billion barrels of proven oil reserves (estimated via drilling) and 1.5–2.5 trillion barrels of unproven reserves (estimated via computer modelling).

Heavy vs light crude oil

The distribution of conventional crude oil versus the bitumen contained in Canadian tar sands for major oil-producing countries is shown in Figure 3. Most of the crude oil found in the Middle East and Western Hemisphere is conventional, while most of the

bitumen is concentrated in Russia, Canada and Venezuela.

The DOE has prepared a segmented forecast of global petroleum production from non-conventional liquid fuels, as shown in Table 1.

Of these non-conventional petroleum sources, Canadian oil sands are forecast to have the greatest volume impact, with a forecast production rate of 2.9 MM bbl/d in 2030 under modest oil price assumptions, or 4.9 MM bbl/d under a high oil price scenario. Looking at other sources of non-conventional oil (synthetic and renewable fuels), none has the potential impact of oil sands on substantially increasing the world's supply of fuel.

Forms of unconventional oil resources

Synthetic crude oils
Canadian tar sands
Extra heavy oil (Venezuela)
Shale oil (mostly western US)
Synthetic fuels
Coal to liquids (CTL)
Gas to liquids (GTL)
Biomass to liquids (BTL)
Renewable fuels
Biodiesel/green diesel
Bio-based ethanol/cellulosic ethanol

Table 1

Current Alberta tar sands capacity

According to the Canadian Association of Petroleum Producers, actual production in 2007 for tar sands-derived crude oil had increased to 1.1 MM bpd. Besides this producer organisation, Alberta's Energy Resources Conservation Board has produced its own assessment of provincial tar sands current and forecast capacity. Their claim is that 2007 production of 1.32 MM bpd will more than double by 2017 to 3.23 MM bpd.

Due to the increasing capital cost to develop tar sands projects, a number of projects have attracted additional equity participation by firms not currently involved in Canadian tar sands. Occidental Petroleum has bought a 15% interest in Total's Joslyn project.

Over the period between 1999 and 2006, it is interesting to note that most of the growth in tar sands capacity has been in steam injection as opposed to surface mining. Once bitumen is produced, it has to be pipelined to market. Since bitumen is too thick and viscous to be pipelined, it can either be diluted with lighter material (naphtha, kerosene or middle distillates) or upgraded. Upgrading involves chemically converting bitumen into pumpable synthetic crude oil via either carbon rejection (coking) or hydrogen addition (hydrocracking).

Between 1999 and 2006, oil sands upgrading capacity in Canada more than doubled and is nearly 1.0 MM bbl/d. This upgrading capacity can be compared with conventional oil refining capacity in Alberta, which is half that capacity.

The economic incentive to develop Canadian tar sands production is shown in Figure 4, which presents estimated industry expenditures for tar sands. This information was prepared by the Canadian Association of Petroleum Producers. Annual capital expenditures topped C\$10 billion in 2005 and



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Process Notes



Oil Sands Crude – Profits and Problems?

Canadian bitumen production currently runs about 1 MMbpd, with some being sold as Synbit and Dilbit. Over the next 10-12 years output is expected to increase to 3.5 MMbpd and more refiners will begin investing to process it and come to depend on the Synbit and Dilbit for a significant part of their supply. Few today, however, have ever processed these feeds at high blend ratios, and are unaware that conventional process and equipment designs are not up to the job. Canadian oil sands

feedstocks are extremely hard to desalt, difficult to vaporize, thermally unstable, corrosive, and produce high di-olefin product from the coker. If you intend to lock into a long-term supply, therefore, it is imperative that you consider reliability and run length from a particular design.

Too low tube velocity in the vacuum heater tubes will lead to precipitation of asphaltenes. Too fast a flow rate will erode the tube bends. If coil layout, burner configuration and steam rate are not correct, run length will be measured in months, not years. Diluent recovery unit designs must take into account possible

upsets from water slugs and other unpredictable situations that have damaged internals, resulting in diluent losses and high vacuum unit overhead condensable oil. Diluent is neither cheap nor plentiful, and high vacuum column operating pressure will reduce overall liquid volume yields. And if the design of the delayed coker fractionator is based on today's experience with conventional heavy feedstocks you will be lucky to run six months.

What all this means is that special process and equipment designs are needed to satisfy the special demands of processing oil sands crudes. Such processes are not generated by computer based designers who have little or no experience and never leave the office. They are developed only by engineers with know-how who have real experience wearing Nomex® suits and measuring true unit performance in Northern Alberta. Shouldn't this be kept in mind by those considering long term supply agreements?



For a discussion of factors involved in designing refinery units to process difficult oil sands feedstocks, ask for Technical Papers #234 and 238.



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increased almost 50% the following year.

Although the rising price of crude oil, such as we saw in the first half of 2008, increases the economic incentive to produce Canadian tar sands, the capital costs for developing tar sands projects have also increased substantially, doubling from 2001 to 2008.

Upgrading tar sands

Most upgraders use delayed coking as their primary mode of carbon rejection. Coking is the high temperature, ambient pressure cracking of carbon-carbon chemical bonds in a non-catalyst reaction (thermal cracking) to form two primary products: solid delayed coke that is nearly hydrogen free, plus gas oil that has the desired carbon-to-hydrogen ratio. Gas oil is further hydrocracked to produce a diesel-rich product stream, then mildly hydroprocessed for sulphur removal. Some upgraders substitute fluid catalytic cracking for hydrocracking, resulting in a product stream that is gasoline rich rather than diesel rich.

Proposed tar sands projects

The Canadian Association of Petroleum Producers anticipates the addition of significant tar sands capacity between 2008 and 2020, with just over 1.0 MM bbl/d in 2008 to nearly 3.5 MM bbl/d in 2020. Its forecast includes significant additions to capacity from both surface mining and drilling (in-situ) production using injected steam. Of the alternative methods, in-situ production is expected to grow at a much faster pace than conventional mining methods. Details of specific tar sands production and upgrading projects follow, as of year-end 2008:

- North West Upgrading will install an upgrader in Sturgeon County, Canada, capable of upgrading 77 000 bbl/d of bitumen. The upgrader will use delayed coke gasifiers provided by Lurgi, and a hydrocracking unit utilising LC-Finer (Lummus Chevron) technology
- Besides western Canada and Venezuela, commercial heavy oil developments have been considered (or are occurring) in Iran (Soroosh-Nowruz fields), Oman (Mukhaizna field) and Brazil (Marlim Sul and Jubarte)
- Occidental Petroleum has taken a 15% share of Total's Joslyn project for \$500 MM, replacing co-owner Enerplus Resources.

Issues impacting Canadian tar sands development

Several issues will impact the pace of development of tar sands production capacity in Alberta, Canada. At some point, these same issues are likely to impact heavy oil and non-conventional crude oil development elsewhere. The primary issues are:

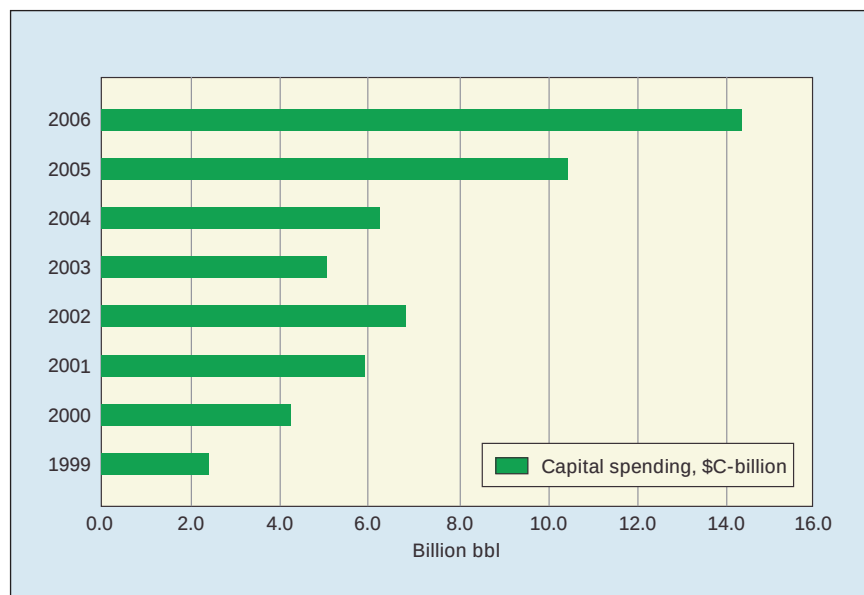


Figure 4 Estimated capital expenditures for Canadian tar sands

- Crude oil price as it affects tar sands project economic viability
- Hydrogen and utility cost inputs to tar sands production
- The capital cost of production and processing facilities
- Environmental impacts of tar sands development:
 - Surface disturbance
 - Disposition of tailings
 - Greenhouse gas emissions
 - Water consumption
 - Potential aquifer contamination
- Logistical and infrastructure requirements
- Producing tar sands below natural gas reservoirs
- Long-term storage of by-product sulphur
- Socio-economic impacts on native communities.

Crude oil price

Producing Canadian tar sands is significantly more costly than producing conventional crude oil from a simple model of cost to extract. However, tax and royalty conditions in some jurisdictions often result in an economic environment for an operating company where its actual cost becomes far higher than simple production cost (because of these taxes). As a result, Canadian tar sands economics, when compared to other tax and royalty environments, can be more desirable. Unfortunately, below a certain nominal price of oil, Canadian tar sands are not economically viable even if there are no royalty considerations. For existing tar sand producers with depreciated assets that were built when the cost of construction was far lower than it is today, that breakeven point is thought to be somewhere around \$25/bbl. For new, grass-roots projects, the breakeven point may be closer to \$100/bbl.

The feverish activity in Canadian tar sands interest since 2004 is tied directly with the quadrupling of nominal crude oil prices since 2004. As the crude oil product price increases, the economic incentive to upgrade tar sands increases even faster.

Whether tar sands economics can be viable at prices well below \$100/bbl for new capacity is not known, and will not be known until the current slate of projects are completed and their as built economics known. One developer (Total) has indicated a breakeven price of about \$90/bbl for projects under consideration in 2008.

Business risk

Compared to other crude oil-producing regions in the world, it should be reinforced that Alberta tar sands development does not present some of the major political and socio-economic issues that surround crude oil producing elsewhere. Such factors are difficult to quantify as business risk compared to better understood technical and economic risk. The benefits of producing crude oil in Canada include:

- Canada does not present the cultural, security and terrorism issues rampant in the Middle East
- Canada does not present the political stability issues associated with West African producers such as Nigeria and Angola
- Canada does not present the ethnic cleaning and social issues prevalent in countries like the Sudan and hot spots such as Darfur
- Canadian democratic institutions are not threatened by oil money influence as in Russia and some of its former republics
- Most Canadian tar sands are likely to be shipped by pipeline, which is inherently safer than oil tanker

transport: Exxon Valdez (Alaska), Prestige (Galacia), Amoco Cadiz (Brittany)

— Canadian tar sands do not present the safety and environmental risks associated with offshore oil production: Piper Alpha (North Sea), Ixtoc-1 (Mexico)

— Tar sands development has less environmental and social impact on endangered species, migratory herds and the lives of indigenous peoples compared to competing forms of the world's energy supply.

Tax environment

Prior to the current activity, tar sands development had virtually stopped after the first two large projects (Suncor and Syncrude) became operational. There was some development work by Exxon/Imperial (Cold Lake) and Shell (Peace River), but little additional commercial production.

The original tax environment was a 1% tax on production revenues until the capital investment had been paid back, and then 25% of net profits after payout. In 1997, the province created an Alberta Royalty Review Panel to recommend changes. Their recommendations, which were modified by the government, resulted in maintaining the 1% fee prior to payout, and a percentage of revenues after

payout that was indexed to price rather than profitability.

The problems that all governmental agencies have in levying royalty regimes to reflect fair economics is that specific project economics are only one component of the decision-making process by the proponent. Although the economics of a specific project can be reasonably estimated by third parties, the decision of a particular proponent to pursue a particular development project depends on the attractiveness of a special project (its return on investment) and on how those economics compare to other global opportunities available to a proponent. If developing project opportunities in the Middle East or West Africa represent a better business deal, then that is where development money will flow.

Unfortunately, estimating the economics of other projects in other regions is speculative at best. As a result, governments pursue a specific royalty regime and observe the outcome. Higher royalties in the North Sea have caused its operators to go elsewhere to pursue better opportunities. At the extreme, nationalisation in Venezuela and Bolivia has stopped outside development altogether. In Alberta, StatoilHydro (S-H) has already delayed a decision on building an upgrader based upon the

uncertainty of Alberta's royalty position. S-H will proceed with its bitumen-producing facility, but avoid upgrading until the business risks with royalty rates are resolved. Oil consultant Wood MacKenzie has also evaluated the impact of increasing royalty revenue and predicted a \$26 billion reduction in tar sands investment.

Another approach by the government in Alberta is to avoid royalty cash payments from tar sands, and instead accept its share of royalty in the form of in-kind bitumen. The provincial government has advertised for offers to upgrade a portion of its bitumen to higher valued products, such as synthetic crude oil or petrochemicals.

Capital cost escalation

As the price of crude oil has dramatically increased, so have other basic commodities used to produce oil and gas. These include structural steel, heavy wall (high pressure) fabricated steel vessels, corrosion-resistant alloys, other base (copper, nickel, zinc) and precious (platinum, palladium, rhodium) metals, concrete and wood. This has resulted in global construction costs doubling between 2001 and 2008, and higher levels in Alberta, where shortages of skilled labour, construction equipment and infrastructure have exacerbated the situation. As a result,

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some proposed tar sand projects have been deferred and will have their economic viability tested later.

Current and potential environmental impacts

Tar sands that have been produced via surface strip mining are required to have the surface area restored to near-original state at the completion of each project. The first certificate for land reclamation was issued to Syncrude Canada for a 104 hectare parcel known as Gateway Hill approximately 35 km north of Fort McMurray. When mined, producing one barrel of bitumen consumes approximately two metric tonnes of tar sands.

Permits for surface mining of Canadian tar sands require that disturbed areas be reclaimed after the bitumen has been removed. While the industry claims it conducts a continuous process of mine reclamation, environmental activists such as the Environmental Integrity Project claim the tailings ponds represent: "Twenty square miles of non-reclaimable toxic lakes of mining waste, making them some of the largest manmade structures on the planet."

The debate on whether the surface above the tailings ponds can or cannot be restored to its natural state can only be settled by deeds rather than words. There is also a concern that migrating birds that land on active tailings ponds are likely to be poisoned and die. The operating companies will have to address the issue of near-term impact, as well as surface reclamation long-term impact.

While Syncrude claims to have reclaimed 22% of its mining area by 2006, it is now seeking formal recognition by the province for its Gateway Hill recovery efforts. A reclamation issue without a clear answer is how to manage the environmental trade-offs in purposeful reclamation. One environmental side wishes a restoration effort that maximises biological diversity, while another wishes restoration to near-original conditions, while a third would prefer a restoration plan designed to maximise natural carbon capture through the planting of high growth vegetation. These three alternative environmental objectives are mutually exclusive.

Tailings disposal

The tar sands processed for bitumen recovery use primarily hot alkaline water and/or steam to displace the hydrocarbon from the surrounding inorganic material. Since the inorganic material tends to be rich in clays, it swells upon grinding and wetting to form a semi-solid material that is difficult to de-water. The current approach is to create bottom-sealed tailings ponds to receive the tailings. Over an extended period of time (up to

"The most obvious opportunity for CO₂ mitigation (beyond better process technology) is to recompress and re-inject CO₂ back into hydrocarbon-bearing subsurface layers"

two years), some of the contained water will separate into an upper layer that can be decanted and recycled to the process. Once de-watered, the remaining tailings will stabilise over time, and can then be covered with muskeg and replanted. However, during the period that the tailings ponds are exposed at their surface, wildlife (especially birds) will sometimes be attracted to and land on the ponds, causing high levels of mortality. One of the challenges is therefore to manage active tailings ponds while minimising impact to wildlife.

A related problem is mature fine tailings, representing a decanted water layer that is rich in stable (caused by ionic charge) clay particles that form suspensions that are extremely difficult to separate. Surfactant treatment to reduce charge and agglomerate mean particle size can help, but advanced technology is needed to adequately separate the clay from the water.

Another environmental concern over replanted tailings ponds is how the final surface is graded and what is used for replanting vegetation. Since most of the stripped original surface is boreal forest on sloped terrain, the desire by some for restoration to its original state provides a technical and economic challenge. Since the stability of de-water tailings ponds may not allow steep terrain to be created on restored mining areas, some government guidance will be needed to establish the desired end condition and the means to accomplish it.

Greenhouse gas emissions

The production and processing of tar sands generates significantly more CO₂ than conventional oil production due to the higher energy intensity required for steam injection of in-situ deposits and mining of surface and near-surface deposits. Since all heavy crude oils are hydrogen deficient, hydroprocessing requires additional energy consumption for converting natural gas to hydrogen, or alternatively producing hydrogen via coal or coke gasification. According to estimates made by the Pembina Institute, tar sands production in ten years is likely to generate 67 MM tpy of CO₂.

This represents 0.19% of global energy CO₂ emissions, while supplying 3% of global energy supply. This ratio is due to the much higher CO₂ intensity of coal-based energy production and use. Greenhouse gas emissions (GHGs) from tar sands development are three to four times higher than from conventional wells, but conventional oil wells pose other environmental issues that have been raised by the eco-activist community.

The most obvious opportunity for CO₂ mitigation (beyond better process technology) is to recompress and re-inject CO₂ back into hydrocarbon-bearing subsurface layers (either tar sands or conventional reservoirs). CO₂ has been historically used by the crude oil industry in tertiary oil recovery (also known as enhanced oil recovery [EOR]). CO₂ re-injected into subsurface reservoirs reduces the viscosity and density of the hydrocarbon liquids, lowers their adhesion (surface tension) to the surrounding sedimentary rock, and increases the oil flow rate to the well. Within western Canada, the Weyburn demonstration project in Saskatchewan is examining the performance and predictability of design parameters used for CO₂ enhanced oil recovery.

Water consumption

Approximately two to three barrels of water are needed to produce one barrel of bitumen. This compares favourably with the consumption of 100 bbls of water to produce one barrel of fuel-grade ethanol. Although surface water supply in Alberta is limited, large amounts of produced water accompany in-situ oil production, while mined tar sands contain 10% water by weight. In the future, water supply for tar sands recovery may be developed from subaquifer brine layers. Tar sand operators have undertaken efforts to recycle nearly 100% of the water consumed, minimise unit consumption of water and utilise (when economically justified) air-fin heat exchangers rather than cooling water towers for process heat removal.

Cogeneration

Due to the high costs of producing and processing tar sands, the potential exists for using some of the tar sands or their processing derivatives (tar and delayed coke) as fuel sources to provide both electricity and process steam. Since solids-based cogeneration requires relatively new and capital-intensive technologies (gasifiers, particulate filters, acid gas extraction, steam and combustion turbines, and boilers), the scale for individual tar sands facilities may not be large enough to be economically competitive. However, to some extent, these liabilities are counter-

balanced by the continuous demand load for both process steam and power.

Synthetic crude oil composition

The synthetic crude oil produced from Canadian tar sands can be one of two basic compositions. The most easy to produce is a bitumen-rich mixture diluted with conventional refinery blend stocks (LPG, naphtha, kerosene or gas oil). Alternatively, the synthetic crude oil can be a fuel in which the bitumen has been chemically altered (via carbon rejection and/or hydrogen addition) to more closely resemble light, sweet crude oil. A number of

environmental organisations (most prominently the Pembina Institute and the Environmental Integrity Project) have reported that oil refineries planning on processing Canadian syncrude are likely to emit more pollutants (SO_x , NO_x , particulates and heavy metals) than if they were to process more conventional light and sweeter crude oils. Since refineries are required to adopt best available technology for pollution abatement, it is likely that environmental activists will file lawsuits to prevent conventional refineries from making the modifications necessary to process Canadian syncrudes. If an existing refinery

requires extensive modifications to process Canadian syncrudes, it may be subject to other environmental provisions defining these changes as constituting a new source of pollution. Again, environmental activists are likely to file lawsuits claiming that the processing of Canadian syncrude violates legal provisions designed to minimise pollutant emissions.

If these challenges are perceived by tar sand operators to be serious challenges to the use of their product, the likely outcome is for the operators to expand the severity of their upgraders to incorporate severe hydrocracking that would remove most of the troublesome pollutants at the upgrader rather than at the oil refinery.

Long-term storage of by-product sulphur

Since tar sands contain a high concentration of sulphur (3–5 wt%), upgraders first convert the sulphur bound to carbon atoms in the bitumen to hydrogen sulphide (H_2S), then convert the H_2S to high purity sulphur in solid yellow form (usually pills or flakes). Given the low market price of sulphur (<\$100/mt), there is little economic incentive to ship it from Alberta to markets. Instead, producers cast molten liquid sulphur into large solid blocks, then store the blocks in bulk earthen containers. The design life for this form of storage is approximately 25 years, after which regular monitoring is used to detect degradation. If observed, the blocks are physically sealed (usually in plastic) and stored indefinitely.

The concern by some people is that these sites may be abandoned after the economic life of the tar sands project is over, with the potential for subsequent degradation that will result in releases to the environment. The Alberta Energy Resources Conservation Board (ERCB) has several standards for the management of sulphur blocks in long-term storage.

An alternative approach is to eliminate the Claus/Stretford processing of H_2S to solid sulphur and instead inject the H_2S (plus the CO_2 acid gas that often accompanies it) into deep subsurface reservoirs, where it is unlikely to cause contamination of ground water supplies. If a particular operator wishes to capture the exothermic heat of combustion of H_2S , he can alternatively burn the H_2S to SO_2 in a heat recovery steam generator, then inject the SO_2 into the subsurface reservoir.

Lastly, some effort is being made to find new commercial market outlets for sulphur. Shell Oil is developing both sulphur-containing concrete and sulphur-containing roadway asphalt. Both dispositions provide a large potential sink for excess sulphur, if the

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Availability of natural gas feedstock

Due to the high consumption of energy to produce tar sands, the availability of natural gas fuel at competitive prices would substantially improve the overall economics for producing synthetic crude oil. Natural gas is used both as a fuel and as a feedstock in tar sands production. In fuel mode, natural gas is used to produce the steam required for in-situ production of tar sands and to heat the hot water required to separate the hydrocarbon from the surrounding sandstone material. Natural gas is also used in fuel mode to generate the electricity required to drive reciprocating equipment (pumps, compressors and centrifuges). In-situ injection steam is used to release the hydrocarbons (tar sand) from the surrounding rock and sand formations, as well as to heat the tar sands warm enough to reduce their viscosity to a level that can flow easily into recovery wells.

As a feedstock, natural gas is chemically reformed (steam methane reforming) to produce the hydrogen that is required in upgraders for hydrocracking and for desulphurisation via hydroprocessing. As a feedstock, natural gas is the most energy-efficient way to produce the hydrogen (H_2) that is necessary to both crack open heavy molecules and remove the sulphur contained in those heavy molecules. The cracking process consumes H_2 by saturating carbon-carbon chemical double bonds. The sulphur in heavy bitumen is converted to H_2S by reaction with H_2 . The H_2S is then oxidised to pure molten sulphur end product, with its H_2 converted to water (H_2O). If natural gas for reforming is not available, or not available at competitive prices, H_2 must then be produced by cracking open water molecules via gasification (partial oxidation), which is highly energy intensive.

As a H_2 -deficient fuel, tar sand bitumen can be converted to a pumpable liquid fuel by either rejecting carbon (by coking) or by adding H_2 (hydrocracking). The preferred option currently is delayed coking. However, as catalyst technology improves the economies for H_2 addition, this option may become the dominant technology, requiring additional amounts of H_2 feed that normally is sourced from natural gas through reforming.

Supplying the energy required for tar sands recovery results in enormous production of GHGs. If a low enough cost fuel is available, such as coal or delayed coke, operators may select this option despite its GHG implications. However, if a relatively low-cost source

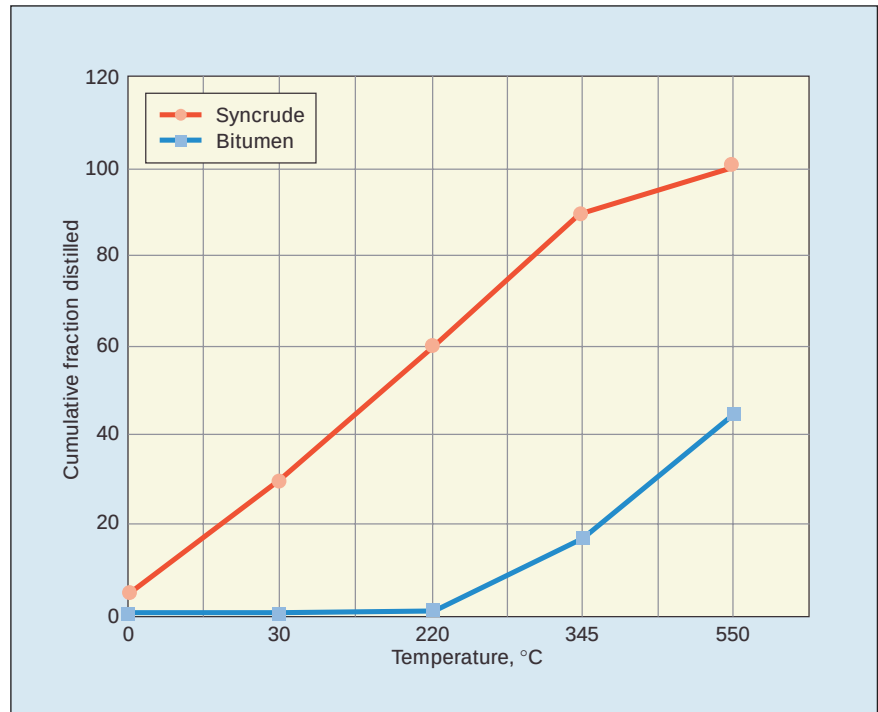


Figure 5 Distillation curve of bitumen vs synthetic crude oil

of natural gas is available, producing H_2 from natural gas becomes both the economically and environmentally preferred option. Compared to using natural gas as a fuel and feedstock, using coal or coke produces nearly twice as much GHG emissions for a specified amount of hydrogen produced, or steam and/or power raised.

The excess amount of natural gas produced in Alberta that was formerly pipelined to foreign markets in the US is no longer in excess and no longer available at low cost. As a result, tar sands producers in Canada are either buying high-priced natural gas or using some of the tar sands product as a substitute for natural gas.

There are market indications that the natural gas availability situation in Alberta may change with time. Enormous quantities of natural gas are known to exist on the Alaska North Slope and along the McKenzie Valley in Canada's Northwest Territories. Recovering gas from both sources would require very long pipelines. Projects announced thus far to transport natural

gas from these sources to market have been stymied by economic and social issues. However, if either or both natural gas pipeline systems are built, it is likely that both proposed pipeline systems will pass close enough to Alberta's tar sands deposits to provide a new source of natural gas at attractive prices. If market prices for the gas are set in the US Midwest (Chicago), netback prices of the natural gas to Alberta should be considerably lower.

Market pricing of tar sands

Synthetic crude oils derived from tar sands and other heavy hydrocarbons are priced at a significant discount to benchmark crude oils that are both lighter (lower viscosity) and sweeter (lower sulphur content). In order to upgrade synthetic crude oils from tar sands to the same yield of clean refined fuels (gasoline, kerosene and diesel), significantly more refinery processing is required. Refinery heating oil has similar physical properties as kerosene and diesel, and is used as a proxy for kerosene and diesel in the options marketplace.

A simple distillation yield comparison (Figure 5) of tar sand-derived synthetic crude oils vs bitumen shows that approximately one-quarter of synthetic crude oils is composed of heavy molecules that boil above $400^{\circ}C$, while almost 60% of bitumen boils above that temperature.

Nearly half of tar sand-derived crude oils are composed of heavy molecules boiling above $400^{\circ}C$. Since more capital cost and more operating cost is required to convert tar sands-derived crude oils into acceptable clean refined fuels, the

"As a H_2 -deficient fuel, tar sand bitumen can be converted to a pumpable liquid fuel by either rejecting carbon (by coking) or by adding H_2 (hydrocracking)"

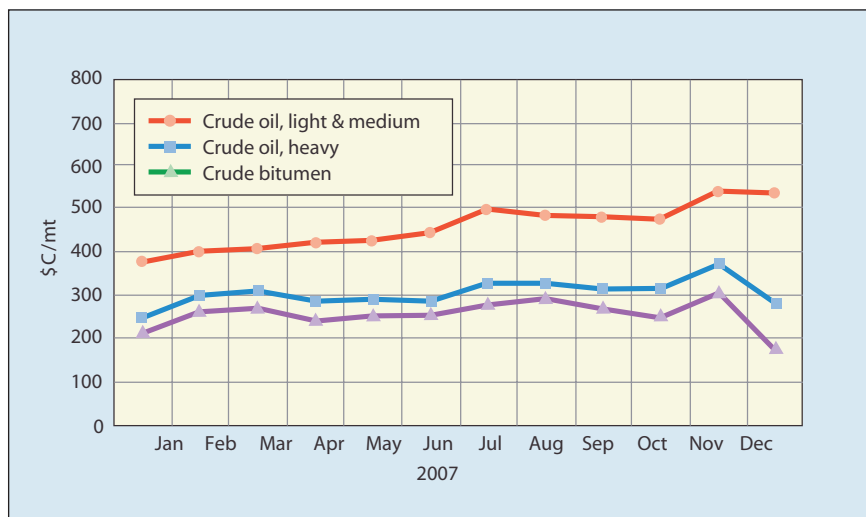


Figure 6 Historic pricing of Canadian crude oil

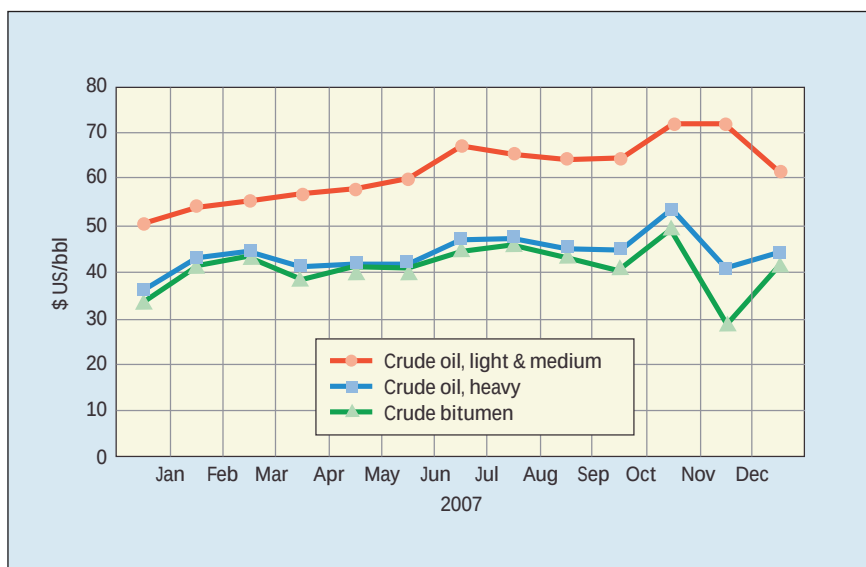


Figure 7 Historic pricing of Canadian crude oil

source crude oil is not nearly as valuable as benchmark crude oil.

Whether a refiner can be profitable or not processing tar sand-derived crude oil can be measured quantitatively using an industry standard called refinery crack spread. Although different organisations define the crack spread in similar but different ways, we present here refinery crack spread as defined by the New York Mercantile Exchange (NYME), which publishes this data on a daily basis. The NYME calculates the refinery crack spread as the difference between the sales price of a unit of refined fuels gasoline (unleaded regular gasoline) and heating oil (low sulphur heating oil) compared to the purchase price of the amount of light and sweet crude oil (benchmark crude oil) required to produce the refined fuels.

The NYME assumes in its calculation that one barrel of crude oil produces one barrel of refined fuel. Although this is not precisely true, it serves as an easy means for calculating refinery crack spread. Different organisations use

different ratios of feedstock to calculate crack spread. Several of the more prominent ratios are:

- One barrel of crude oil producing one barrel of gasoline
- Three barrels of crude oil producing two barrels of gasoline plus one barrel of heating oil
- Five barrels of crude oil producing three barrels of gasoline plus two barrels of heating oil.

The calculated refinery crack spread is used by options traders to buy (call options or long call) or sell (put option or short call) dry barrel contracts to

Densities of canadian crude oils

	Bbl/mt
Heavy Canadian crude oil	6.9
Light/Medium Canadian crude oil	7.3
Canadian bitumen	6.2

Using these conversion factors, Table 2 has been regraphed, as shown in Figure 7.

Table 2

reduce the business risk of operating a refinery. What started out as business risk insurance for refiners in the futures market has changed radically to one in which most of the participants today have no relationship to oil refinery operators and instead trade refinery crack spread options to make money. The dry barrel options market trades approximately ten barrels each day to one barrel of wet barrels (actual oil) produced by the refining business. When traded (contract to buy or sell), the refinery crack spread price becomes the exercise or strike price used to buy or sell the options contract.

Petrochemical potential for tar sands

Approximately 10% of the petroleum produced worldwide is converted to petrochemicals, with most of the balance used for transportation fuels. A small amount is used in power production. The fundamental feedstocks used to produce petrochemicals from crude oil are refinery by-products LPG and naphtha, and a smaller quantity of natural gas production by-product natural gas liquids (NGLs). NGLs are primarily composed of ethane, propane, butane, pentane and some hexane.

These fundamental petrochemical feedstocks are converted primarily to olefins (ethylene, propylene, butadiene and butylene) and aromatics (benzene, toluene and xylenes) through the processes of steam cracking and catalytic naphtha reforming to produce petrochemical derivatives (monomers and polymers).

Canadian tar sands also provide the potential for contributing some by-products that could be used as petrochemical feedstocks. The process of extracting bitumen from tar sands produces small quantities of light gases (methane, ethane and propane) and light liquids (butane, pentane and naphtha). The methane, if produced in sufficient quantity, could be steam reformed to produce ammonia, methanol, carbon monoxide, hydrogen and their derivatives. The C_2 - C_6 fraction could be steam cracked to produce olefins. The C_6 + material could be catalytically reformed to produce aromatics.

Bitumen upgrading processes (delayed coking, gasification, hydrocracking and hydroprocessing) produce the same starting materials for producing petrochemicals. Syngas produced from gasification could also produce hydrogen, ammonia, methanol, oxo-alcohols, Fischer-Tropsch liquids and their derivatives.

An indirect source of petrochemicals feedstock could also be provided by expanded Canadian tar sands production. Tar sands upgrading

Syncrude's 2007 cost of tar sands production	
Bitumen mining costs	
Overburden removal	2.14
Bitumen production	9.90
Purchased energy	2.33
Sum bitumen production	14.37
Upgrading costs	
Processing costs	3.63
Turnaround & catalyst costs	0.45
Purchased energy	2.77
Other & research	2.54
Sum upgrading	9.39
Total cost of synthetic crude oil	23.76
Net sales price	82.07
Net operating costs	23.76
Royalty payments	12.81
Net profit	45.50
Mining costs	14.37
Upgrading costs	9.39
Royalty payments	12.81
Net profit	45.50
Net sales price	82.07

Table 3

requires H₂, which is most often provided via the steam methane reforming of natural gas. Hence, Alberta upgraders will attract natural gas pipeline supplies if the offering price is attractive compared to their alternative source (gasification of delayed coke). Raw natural gas in Alberta as well as other potential supply sources (proposed MacKenzie Valley pipeline) is generally rich in NGLs, which could economically be extracted from wet natural gas to produce additional quantities of petrochemicals.

Market pricing of tar sands

ERCB maintains a history of prices for Canadian crude oils. These can be used to compare heavy and light conventional crude oil prices with the corresponding prices for bitumen on a consistent basis. Figure 6 shows ERCB published monthly prices for Canadian crude oils for 2007.

These values have been converted to US dollars on the basis of published currency translation prices (*Wall Street Journal*, 24 July 2008) at 0.987 US\$/C\$. The mass quantity has also been converted from metric tonnes to barrels using the density factors for Canadian crude oils shown in Table 2.

What Figure 7 shows is that all of the crude oils move directionally with global prices. Bitumen is priced at a slight discount to Canadian heavy crude oil (less than \$1/bbl discount), while Canadian heavy crude oil is priced on average at a \$10/bbl discount to a mixture of conventional Canadian light and medium crude oils.

Tar sands industry profitability

The Alberta tar sands industry has experienced extended periods of low or no profitability and recent periods of considerable profitability. The tar sands production business is primarily a fixed-cost business. A certain threshold crude oil price provides adequate return on investment, and prices above the threshold provide considerable profit. However, below the threshold price level, profits evaporate.

The early Suncor and Syncrude commercial projects were driven by active Canadian government involvement, as were the high-risk offshore production programmes off eastern Canada (Hibernia and White Rose). After the initial Suncor and Syncrude capital investments were made, the tar sands industry remained dormant for nearly 20 years.

Those production facilities that have been fully depreciated were making considerable profits, as are those that were built prior to the 2005-plus run-up in process industry capital costs. Whether current announced capacity will be built on schedule, deferred or cancelled is a function primarily of the market price of crude oil and the capital costs to build the plants.

The fragile nature of tar sands profitability was summarised in a *Financial Times* article of 12 September 2008 during a period of rapidly falling crude oil price declines: "Total's extra heavy oil sands project in Canada (Joslyn) requires an oil price of just below \$90 a barrel to achieve a 12.5% internal rate of return, while Total's developments in the deep waters off Angola need about \$70 a barrel, the company revealed in a mid-year presentation."

PTQ reported that the cost of producing bitumen from Canadian tar sands is \$13.21/bbl, while the cost to upgrade the bitumen to light, sweet synthetic crude oil is \$15/bbl. According to ENI Chairman Paolo Scaroni: "Personally, I expect oil prices will go further down. The limit is the cost of the most expensive barrel of oil, which is the Canadian tar sands, which cost \$65–\$70 a barrel. This seems to me the bottom. Otherwise, those supplies will not be coming."

Oil Sands Review magazine quarterly summarises the economics of existing tar sands production units in Canada. Table 3 summarises the major cost components for mining costs of Syncrude Canada during Q4 2007. The cost for bitumen production was C\$14.37/bbl, and the cost to upgrade the bitumen to synthetic crude oil was C\$9.39/bbl, for a total production cost of C\$23.76/bbl. During Q4 2007, Syncrude was able to realise a netback

In-situ 2007 cost of tar sands production	
Cash costs of production	9.95
Natural gas purchases	9.95
Depreciation & SGA costs	6.80
Sum bitumen production	26.70
Husky upgrading costs	
Operating costs	8.95
Sum upgrading	8.95
Total cost of synthetic crude oil	35.65
Net sales price	65.79
Net operating costs	35.65
Transportation & selling (EnCana)	2.75
Royalty payments	5.83
Net profit	21.56
In-situ bitumen production costs	26.70
Upgrading costs	8.95
Transportation & selling (EnCana)	2.75
Royalty payments	5.83
Net profit	21.56
Net sales price	65.79

Table 4

price for selling its crude at an average price of C\$82.07. After subtracting the previously described operating cost and its royalty payments of C\$12.81/bbl, Syncrude was able to realise a net profit of C\$45.50/bbl. This level of margin describes in full the enormous emphasis in producing Canadian tar sands in the current crude oil economic environment.

A similar economic environment was experienced by in-situ (mostly steam-assisted gravity drainage and cyclic steam stimulation) producers of Canadian tar sands. To develop reasonably representative economics, production cost data were combined from three separate in-situ producers (Suncor, Husky and EnCana). The results are presented in Table 4. Data for Suncor's Firebag SAGD bitumen production costs for Q4 2007 were C\$26.70/bbl. During the same period, Husky Oil reported average upgrader costs at its Lloyminster facility of C\$8.95/bbl. The sum of these is an averaged in-situ synthetic crude oil cost of C\$35.65/bbl. When transportation and selling costs (averaging C\$2.75/bbl for EnCana) are added to representative royalty payments of C\$.83/bbl, a net profit of C\$21.56/bbl was realised when an average netback sales price of C\$65.70 was attained.

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Beyond turnaround planning

Utilising process- and unit-specific knowledge transfer to improve turnaround execution. A better approach is needed to ensure the transfer of critical event information to an experience- and discipline-diverse workforce

Brian Cormier *Resource Development Company*

Charles F Gillard *C F Gillard and Associates*

How often is a plant's year spoiled by poor performance on a maintenance turnaround? Excellent safety and environmental performance, outstanding cost management and near perfect reliability — all hard earned through great effort — can be destroyed by poor performance during a single turnaround. Turnarounds are almost always well planned. The problem lies in executing that well-crafted plan.

Successful execution is dependent on communication and information transfer from the planners to the doers. Moving from a traditional informal and unstructured approach to a knowledge engineered communication and information exchange programme greatly decreases the risks, cost and duration of turnarounds. A structured approach and detailed agenda for turnaround information exchange that ensures success are imperative.

Maintenance turnarounds and process unit revamps are arguably the greatest points of exposure for refineries in terms of safety incidents, production delays and lost profits. These events require a tremendous amount of planning, awareness and motivation to ensure a safe and successful execution.

Turnarounds are a time when the unit is in a constant state of flux through shutdown, de-inventory, clearing and cleaning, mechanical work-over, inventory and startup. The number of personnel supporting these activities rises and falls in a typical bell curve-like fashion.

Planning and scheduling activities begin months or even years in advance. Plans and contingencies are revised again and again with the help of operations and maintenance staff, tenured personnel, outside supporting vendors and refining peers. Much time and effort is spent planning every conceivable detail, with the single-minded goal of performing the work safely and on schedule. The product of this effort is often a thick binder containing marked-

up P&IDs, blind lists, expandable Gantt charts and pages of procedure check-off sheets. Now what?

Executable knowledge transfer

Herein lies the fundamental problem. Unfortunately, the same zeal applied to planning and scheduling is too often not paid to transferring those critical details to the minds of the personnel actually executing the work. Many work groups (including operations, technicians, contractors and vendors) are given a one- or two-day overview of big picture concepts such as critical path, a shutdown/de-inventory strategy and a general timeline of execution. This type of training is usually given in a group classroom setting about four to six weeks prior to oil out, but regrettably provides no verification that the necessary knowledge has been successfully transferred and can be applied when executing the work list tasks.

While the variability and lack of detail provided in such traditional training sessions have long been a concern, the skilled workforce attrition that the industry faces today magnifies the risks, increases the need for best practices and calls for a new paradigm: process- and unit-specific knowledge transfer.

Skilled workforce attrition

Senior plant operators are retiring in unprecedented numbers, and with them goes invaluable best practices, process knowledge and expertise. They are being replaced with new hires, each with a unique background and varying degrees of expertise and knowledge. Many have never been through a unit turnaround before. Detailed process- and unit-specific knowledge transfer is needed to close the knowledge gap and reduce risk.

Operations staff are becoming leaner because of this demographic change, and time is often not available to operators for training activities outside of their daily operating tasks. Maintenance resources are stretched too

thin to take time away from repairing process equipment. Event-specific training and awareness for contractors, who will be brought in by the hundreds to support the field work, is often limited to general refinery safety training and tailgate job safety analyses (JSAs) during shift change.

Yet, the probability of safely meeting the turnaround event's goals and objectives so heavily depends on these groups working closely and effectively together. How can your refinery ensure this complex co-ordination has the best chance of happening and certify that everyone has the knowledge they require, both by craft and individual, to work safely and productively to meet your turnaround schedule?

Communication is key

The success of any turnaround can be greatly improved, while reducing the associated risks, simply by implementing a rigorous, well-structured knowledge transfer system that communicates the proper process- and unit-specific information, specifications and procedures to all those involved. This means that all of the tasks, schedules, priorities, contingencies and perceived risks that should or might occur to a group of workers, who range widely in terms of craft, experience and responsibility, need to be documented, structured and delivered to the appropriate audience through a validated process.

Conversely, miscommunication and misinformation typically lead to poor decision-making, which creates misdirection and ultimately results in confusion and potentially hazardous situations. That confusion becomes contagious as shift changes take place across all disciplines and can easily cause a schedule delay of one or two days before everyone can realign as a team and regain momentum.

The other vital part of a successful turnaround is the agreement on common goals and objectives by all the

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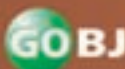
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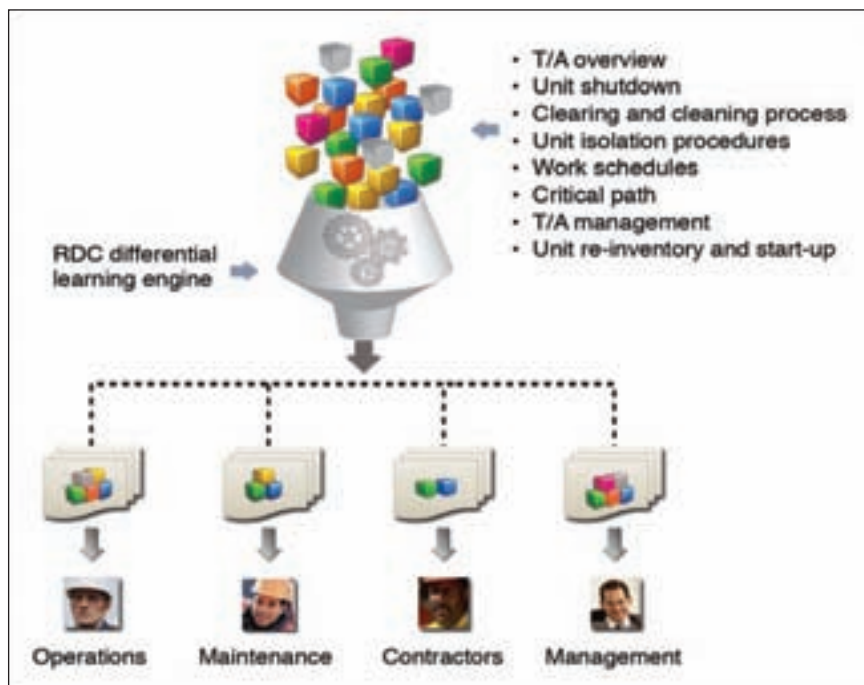


Figure 1 The RDC personalised learning path is part of the knowledge engineering solution, enabling cost-effective transfer of job-, site-, and process-specific skills based on the individual employee's role and existing skill set

departments involved. Nothing will kill a turnaround faster than departments working independently toward their own objectives. It takes many disciplines working as a team to achieve a successful turnaround, and only one group or department from the usual sectors of management, process engineers, maintenance, operators, turnaround coordinators and contractors with misaligned priorities can cause large amounts of discourse, delays and costly setbacks. For this reason, everyone must agree on the primary target and process of the turnaround to improve the chances of success and reduce risks. This can also best be achieved by transferring and certifying the understanding of the goals, assignments and work details in order to create a cohesive, efficient and unidirectional team. Communication is the key. But with so many diverse groups and talents, dissemination of information must be done in a way that is efficient and effective.

Refining companies would be prudent to take a much closer look at how they are effectively transferring that valuable knowledge across this spectrum of workers. Successful companies will ensure that a well-engineered, formal knowledge transfer process is in place that certifies critical turnaround information is documented, organised and communicated in the right quantity, to the right individual and craft, and in the context that is relevant to their role and responsibility.

Consistency

Without a rigorous process and system for knowledge transfer, there is no best

practice and each turnaround will differ based on the backgrounds, expertise and biases of the key players. More often than not, planning styles will vary from one planner to another and from one turnaround to the next; formal communication of the plan to all parties involved tends to relax as the event draws closer; and training is general in nature, casual in format and varies based upon the experience of the trainer. So, you may have a good turnaround if you have the right people in leadership positions, or you may have a disastrous turnaround without an established knowledge transfer process in place.

In order to be effective, a turnaround training knowledge base should cover the major strategic initiatives, from which a consistent set of learning objectives can be created and assigned. It should be dynamic in design, with the capability to deliver a personalised learning path, tailoring the knowledge transferred based upon the individual's role as a contractor, new hire operator or experienced maintenance craftsman. In other words, you need to get the right information to the right people — not all of the information to all of the people — and then you need to deliver the knowledge in a consistent and efficient process that certifies full knowledge transfer to 100% proficiency.

Structuring the knowledge base in a modular fashion offers flexibility in delivery of the information. The following are the recommended key modules and associated learning objectives:

1. Turnaround basics:

— General overview of a turnaround:

key objectives are duration and typical scope

— Training on turnaround management tools: this is training on the tools used for managing the turnaround. For example, training on how the blind list is provided and how to use it

— Information on the specific upcoming turnaround:

– Work schedule

– Organisational structure, such as how the turnaround is going to be staffed, work schedules and work assignments

– Turnaround activities, such as critical path and heavy lifts.

2. Project task tracking — critical path schedule:

— Use of typical project task tracking with the inclusion of anticipation of discoveries and changes that may be necessary during the actual shutdown.

3. Shutdown of the unit:

— General step-wise overview of how this unit is shut down

— More detailed procedure review of unit shutdown by process system (ie, preheat train and pumparounds)

4. De-inventory and cleaning of process piping/vessels:

De-inventory:

— Understanding the difference in clearing process liquids vs gases

— What utilities are available to facilitate the clearing process (ie, flare and oil recovery system) and what are their operating capacities?

— How dead legs and trapped liquids should be handled. What lessons have been learned from previous turnarounds?

— Lessons learned might include:

– A little bit of liquid hydrocarbon left in a low spot can really slow down a turnaround while shift after shift is spent trying to pass the explosivity or hydrocarbon content test on a vent

– Drain and purge lines are usually small compared to normal process lines. It is frequently difficult to get enough flow through the gas purge inlet and outlet piping to carry liquid down a line and impossible to carry liquid up a vertical pipe run

– Installation and use of big-bore steam lines at the discharge of product draw and pumparound pumps can help to significantly reduce de-inventory times of those circuits and have the two-fold effect of enhancing the cleaning process.

Cleaning:

— Use of the best-in-class cleaning technology. Liquid circulation can be costly in terms of waste effluent processing and the equipment and real estate to facilitate the process. Vapour-phase technology is proving to be more

efficiency



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effective in terms of cleanliness and can be coupled with the unit steam-out process

— Illustration and proper documentation of isolation, blinding and cleaning of specific vessels and equipment.

5. Safety, work permits, tagging and blinding:

— Appropriate training for employees and contractors of permitting process

— Review of hot work and vessel entry permits

— Review of tagging and blinding system.

6. Work list execution:

— Proper material, crafts and access to complete specific turnaround tasks

— Teams for inspection, verification and sign-off of completion of each task

— Documentation and tracking system to ensure managers know of work status and can quickly update any critical path assessments based upon discovery work.

7. Unit start-up:

— Review of overall start-up process

— Step-wise review of start-up by process system.

8. MOC process:

— Proper orientation of management of change (MOC) process for change and approval of work plan, documentation and equipment repairs

— Beneficial for documenting actual turnaround events and updating information for use after turnaround.

Keep best practices evergreen

The adage that, if we do not learn from the past, history is bound to repeat itself rings especially true for turnarounds given the typical five- to seven-year interval between events and the continued loss of experienced refining personnel to retirement.

Any turnaround training knowledge base must be kept evergreen. Most refineries conduct post-event reviews to identify and document lessons learnt and areas for improvement. Those enhancements are often made to the planning book, only to be shelved for the next turnaround and forgotten or overlooked in the next turnaround cycle. That valuable information came at a significant price, be it sweat equity or otherwise, so make the effort to build it into additional learning objectives.

Knowledge engineering solution

The good news is that refineries do not want for information. Volumes of P&IDs, procedures, Gantt charts and blind lists reside in binders created for previous turnarounds. On the surface, it seems an almost impossible task to take this

enormous pile of relevant data and organise it into a useful knowledge base.

A well-structured turnaround knowledgebase template is now available that is modularised in the format previously referenced and through a proprietary Knowledge Engineering process, made site-, unit- and event-specific for each unique plant. Throughout the instructional design process, RDC works in partnership with refining companies to blend information from existing turnaround plans into this learning tool. In addition, interviews are conducted with the most experienced planners, operators and maintenance personnel to gather best practices information that can be cultivated into knowledge, tied to learning objectives and overlaid in a craft- and unit-specific manner.

It is important to clarify that the instructional design focus should be on adult learning and conveying technical process knowledge. As adults, we absorb knowledge differently than we did in our younger years. Adults require participation throughout the learning process and the information that is being presented must be relevant to the learner's specific job responsibilities and, to a greater extent, be information that fills gaps in their knowledge. One-size-fits-all training in a classroom setting largely has proved ineffective at efficiently transferring such detailed technical knowledge.

Differential learning

Crafting a complete and customised knowledge base is only half of the total solution. Automated delivery of this information to the learner and an assessment process that validates the learner has absorbed and comprehends the information completes the closed-loop solution.

The learning environment is capable of handling the flux of hundreds of workers that will support a given turnaround event. Access to the turnaround knowledge base content is personalised, based on the role(s) an individual is assigned. The scope and depth of a curriculum assigned to a contractor supporting the turnaround will differ from that of a unit operator, because the learning environment personalises each individual's learning path, based upon their role and the prior level of knowledge they exhibit. Training on the unit's permitting process, as well as who is qualified to sign a work permit, can easily be applied to the learner's knowledge requirements by assigning a permit-qualified role to a maintenance contractor, cleaning vendor or operator.

Knowledge gaps = risk

Accidents and safety impacts associated with turnarounds in recent years have

heightened awareness and culpability, dictating that refining companies can no longer continue to use a broad-stroke approach to training and knowledge certification. Group training in a classroom setting for contractors, especially when they are talked through the training, watch a video or two and then complete a paper test, can leave a refinery exposed in the wake of a deadly accident or explosion.

Workers must be remediated and certified to prove 100% competency across all knowledge requirements to perform a job safely. The technology is available to pre-assess a worker's existing knowledge gaps with respect to a group of learning objectives, automatically deliver a personalised learning path, and post-assess and validate proficiency until all knowledge gaps are remediated.

Conclusion

Successful and lower risk turnarounds can be achieved by establishing a best practice for documenting, organising and disseminating information. Skilled workforce attrition is a subject that is tirelessly discussed in the energy industry, as well as much of manufacturing. Every refining company invests a hefty sum in the professional development of its workforce. An operator, through training efforts and on-the-job experience, develops a wealth of best practices knowledge over a 25-year career.

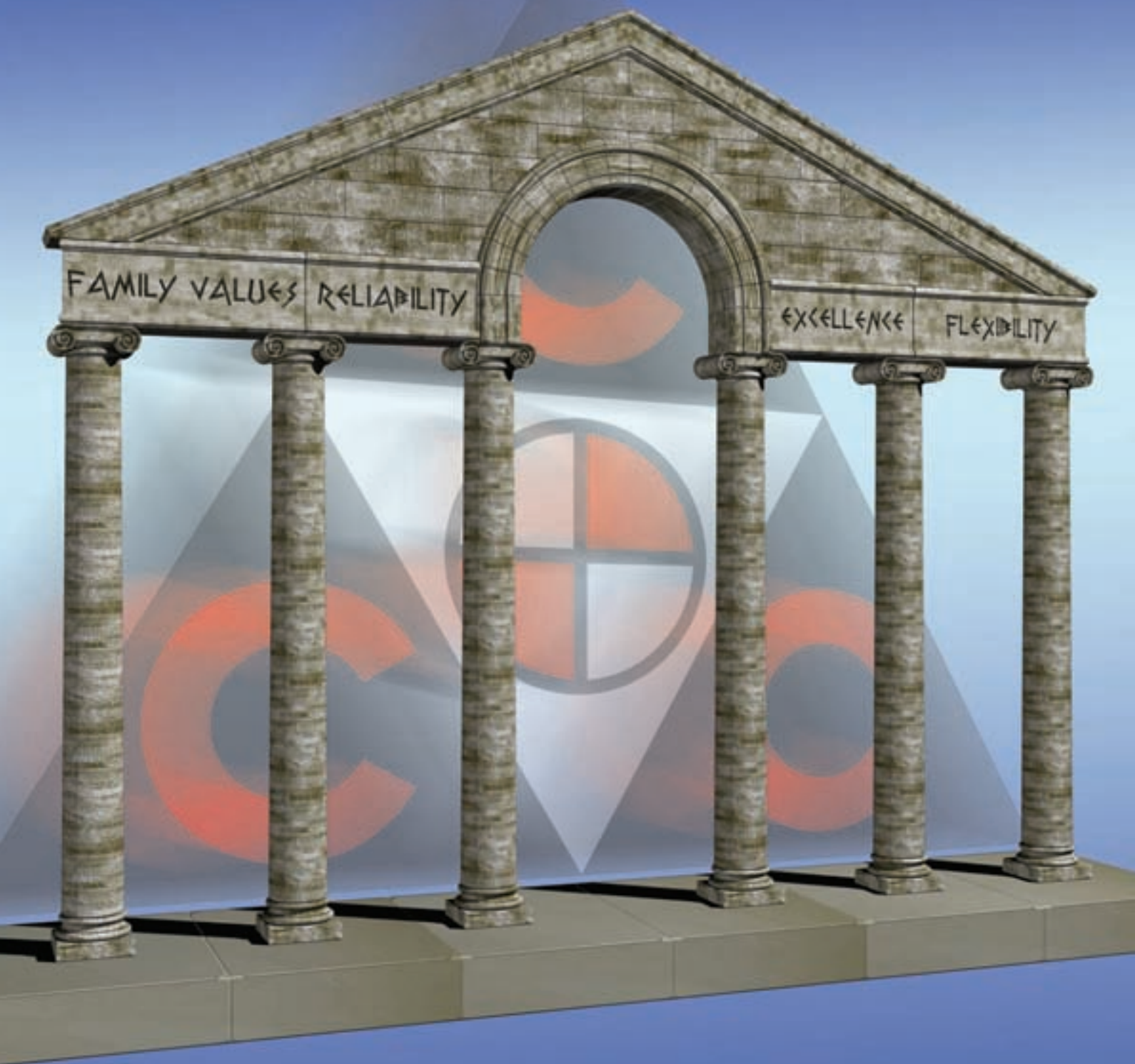
We encourage you to retain your company's investment by proactively capturing that knowledge and imparting that wisdom to the incoming generation of operators. Work with an instructional design leader in the industry who provides the knowledge engineering and differential learning tools to cost-effectively capture, retain, access and transfer the process-, job-, event- and unit-specific knowledge needed to improve ongoing operating margins.

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Improving VGO hydrotreater operation

A practical, industrial data-derived tool can give refiners confidence in simulating the actual benefits of additional hydrogen for improved VGO hydrotreater performance.

A lumped parameter dynamic simulation modelling approach is employed

Darius Remesat
Koch-Glitsch Canada

A lumped parameter dynamic model, using both Microsoft Excel and AspenTech HYSYS software, for industrial refinery/upgrader vacuum gas oil (VGO) hydrotreaters has been developed from proprietary and public steady-state hydrotreater models. The model is based on industrial plant data and tracks changes in intrinsic reaction rates based on catalyst deactivation, wetting efficiency, feed properties and operating conditions to provide useful information, such as required operating temperature, outlet sulphur composition and chemical hydrogen consumed.

The model credibly simulates local disturbances and represents the three distinct operating zones during the hydrotreater run length: start-of-run (SOR), middle-of-run (MOR) and end-of-run (EOR). This correlative, partially predictive model can be applied to demonstrate the tangible economic benefits of increasing hydrogen use to improve the operation of a hydrotreater by increasing run length and/or improving crude processing.

Hydrotreating developments

Hydroprocessing has become a key refiner/upgrader operation due to two key developments. First, transportation regulations for refined products have evolved to significantly reduce the maximum amount of sulphur allowed (eg, <30 ppm gasoline in North America and <10 ppm diesel in Europe). Second, it is becoming necessary for refiners to process heavier, more sour crudes due to reduced availability of sweeter (low sulphur) crudes. As a consequence, there is a need to remove more sulphur than previously required.

Unfortunately, refiners/upgraders rarely achieve their run lengths and crude throughput objectives for VGO hydrotreaters.¹ The performance shortfall is mostly due to disturbances (crude flow, feed compositional, sulphur, metals, and/or hydrogen partial pressure changes) that reduce the effectiveness of the catalysts. Most

public domain dynamic hydrotreater research is based on pilot plant data that do not translate well to industrial applications. A key element of this tool's development entailed gathering a substantial amount of relevant industrial data (14 operating industrial VGO units, with permission to publish data from six operators) specific to VGO hydrotreaters.

Methods and materials

The VGO hydrotreater model developed:

- Uses lumped parameters that match data available from industrial operations
- Uses a mix of industrial correlations, kinetic theory and academic research findings
- Factors in changes in operating conditions in response to disturbances in operation
- Incorporates changing reaction rate, wetting efficiency, catalyst deactivation in the three zones of the hydrotreater run life (ie, SOR, MOR and EOR)
- Uses parameters for all key process variables (sulphur, hydrogen partial

pressure, temperature, hydrogen-to-oil ratio)

- Is run in dynamic mode to track the key variable product sulphur and the representative value of performance weighted average bed temperature (WABT)

- Incorporates familiar software (Excel and HYSYS) for easy translation into existing operations and acceptance by users

- Is correlation based, demonstrating semi-predictive tendencies

- Is used to represent a trickle fixed-bed reactor in operation.

Data gathered

Detailed industrial VGO hydrotreater data, under confidentiality agreement, were obtained and used from six operators. In addition, data from eight other plants was used in testing the developed model. Catalyst, process and laboratory data, plus equipment information were among the needed and gathered data. Table 1 provides a sample of the information gathered from the industrial operating units.

Catalyst/reactor information gathered from six industrial plants

Unit	Plant A	Plant B	Plant C	Plant D	Plant E	Plant F
Reactor diameter, ft	13	12	12.5	12	11	14
Catalyst type	NiMo on Al	NiMo on Al	CoMo on Al	NiMo on Al	NiMo on Al	CoMo on Al
Catalyst volume, ft ³	4424	2865	5926	6523	2415	4189
Catalyst weight, lb	207 928	110 016	266 650	316 650	128 478	163 371
Catalyst density, lb/ft ³	47.00	38.40	45.00	48.54	53.20	39.00
Cycle length, years	2.60	2.00	1.80	1.08	3.00	2.28
Reaction type	HDS	HDS	HDS	HDS	HDS	HDS
Desired product S, wt%	0.04	0.05	0.03	0.03	0.04	0.04
Typical feed S, wt%	1.70	0.80	1.50	2.20	1.40	0.90
SOR average temp, °F	605	590	660	580	631	610
Typical LHSV, Hr ⁻¹	0.76	1.23	0.54	0.41	0.88	1.63
Feed type	LGO	LGO	LGO	LGO	LGO	LGO
Suggested reaction order	1.65	1.50	1.60	1.70	1.55	1.40
Activation energy, cal/mole	27 000	29 000	32 000	24 500	26 500	27 500

Table 1

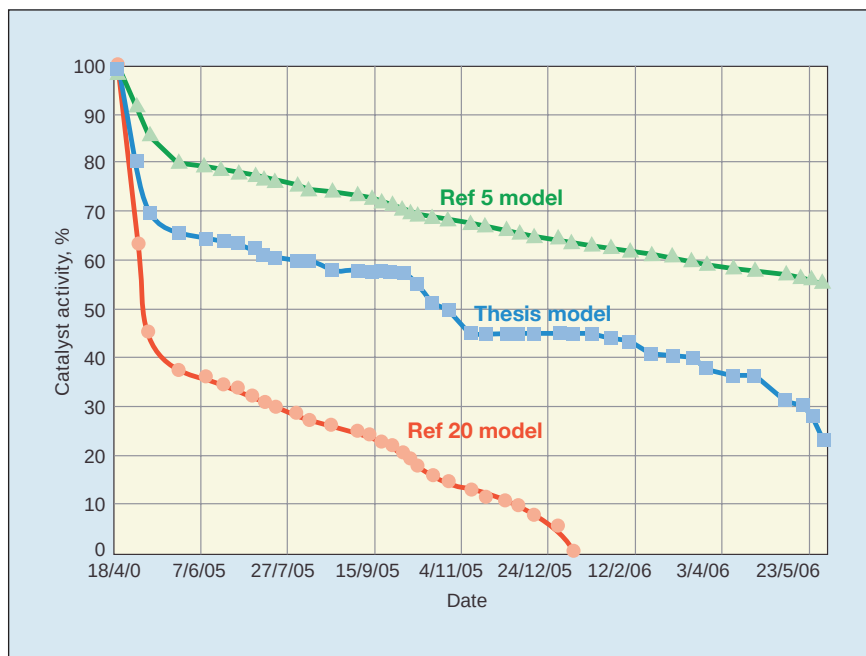


Figure 1 Catalyst activity profiles generated from various models evaluated incorporating catalyst deactivation using Plant D data

Dynamic approach to industrial hydrotreater kinetics

To dynamically track catalyst behaviour by calculating outlet sulphur composition from known or observed results of an industrial hydrotreater, the key product variable (S_p) was created in the form of Equation 1. The model involving Equation 1 takes into account process data, including temperature (T) and liquid hourly space velocity (LHSV) available from the plant data-gathering system; determines the impact of internal and external mass transfer resistance in a lumped parameter evaluation (η_e); and provides a relationship for catalyst deactivation embedded in the reaction rate expression k_{hds} :

$$S_{pi} = *k_{hds(i-1)} \frac{1}{LHSV_i} e^{\frac{b}{T_{i-1}} - \frac{b}{T_i}} f_i^p \frac{P_{i-1}}{P_i} f_i^g \frac{G_{i-1}}{G_i} + \frac{1}{S_{pi}^{2\eta_{ei}-1}} 4 \quad (1)$$

In reviewing plant performance, pressure (P) and gas-to-oil ratio (G) were included in Equation 1, along with their respective exponential factors (p and g) to better model the operation. Note that the variables P and G are key contributors to hydrogen effectiveness in the hydrotreating reaction.

To address the lumped sulphur composition provided from the industrial units, dibenzothiophene (DBT) was chosen as the sulphur component on which to base the overall sulphur reaction kinetics. It is hypothesised that by using the slower

DBT hydrogenation route to represent the overall sulphur conversion, treating all the sulphur as DBT should provide a representative conversion of all the sulphur. All the sulphur species that are easier to convert than DBT will be considered totally converted and lumped into the amount of DBT converted. The reversible dehydrogenation portion of this reaction provides a realistic representation of the reduced driving force of hydrodesulphurisation at higher temperatures.²

Catalyst deactivation

A crucial step in developing an accurate hydrotreater model is developing a realistic representation of catalyst deactivation and including it in the reaction rate expression (k), illustrated in Equation 1. Overall, 30 correlations³ were modified or developed to provide the k_{hds} in Equation 1.

Instead of using classical representations (eg, Thiele modulus) for the S-shaped catalyst deactivation curve, operator steady-state correlations were used as a starting point, since they provided a match to the type of data available from the operating units. Figure 1 illustrates various representative catalyst activity models, using Plant D data, considered for use in this research. The Reference 20 line based on publicly available literature has a very steep SOR and exhibits a classical S-shaped curve for catalyst deactivation, predicting EOR prematurely.⁴ The Reference 5 line is from an industrially focused consultant.¹ There appears to be a factor for SOR deactivation, but the remainder of the curve is essentially a negatively sloped straight line.

It was apparent that no previously developed publicly available or steady-state catalyst activity correlation would match the industrial data gathered and thus meet the objective of this research.

Enhancements to the base MOR correlations were made to better represent SOR and EOR catalyst deactivation in a VGO hydrotreater. Variables (eg, metals, olefinic content, aromatic content, temperature, hydrogen partial pressure, hydrogen-to-oil ratio, LHSV, sulphur content, nitrogen content, H_2S formation, aromatic saturation and API) that should be impacting catalyst deactivation in the SOR and EOR regions were evaluated and input into a dynamic-based format that resembled catalyst vendor steady-state correlation formats.

The catalyst activity profile from this tool is included in Figure 1 for comparison purposes. This model appears to capture and represent disturbances in the reactor more accurately than any other models evaluated.

Model particulars

For the outlet sulphur composition from

Average calculated parameters for sulphur product composition

Plant	Average p	Average g	Average b , °F	API SOR	Viscosity, SSU @ 100°F
A	0.46	0.50	21 500	30.1	58
B	0.63	0.54	23 700	27.3	478
C	0.51	0.64	23 350	19.5	453
D	0.89	0.53	23 100	27	243
E	0.38	0.47	21 700	30.8	46
F	0.39	0.55	24 700	25.8	1525
R	0.41	0.51	24 400	29.2	1310
S	0.59	0.63	23 270	20	430
T	0.36	0.53	23 000	26.7	300
U	0.53	0.59	24 000	23	1000
W	0.44	0.56	24 000	25	900
X	0.38	0.60	24 600	22.3	1650
Y	0.37	0.52	23 400	28	500
Z	0.78	0.63	24 600	21	1568

Plants A-F, full data sets published; plants R-Z, data in this table is permitted to be published.

Table 2

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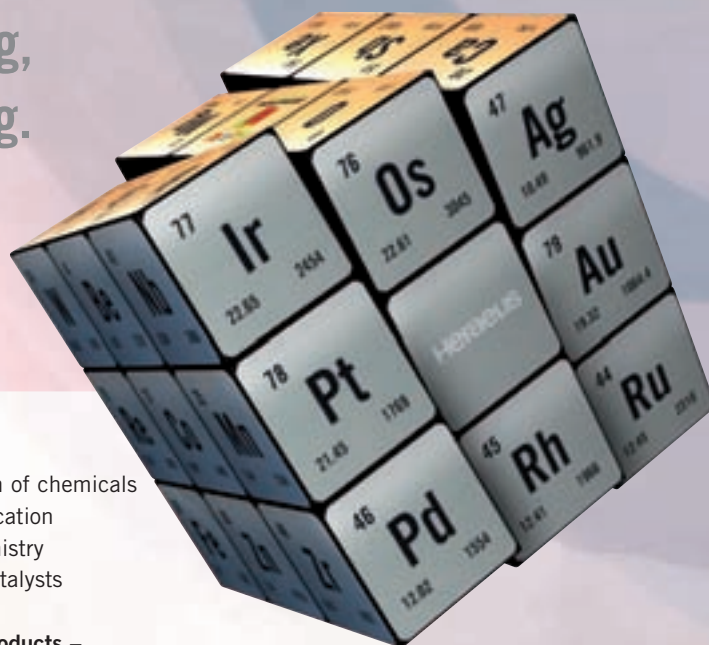
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the VGO trickle bed hydrotreater, represented as Equation 1, the parameters b (temperature), p and g were tested with the operating data from all 14 plants to determine a feasible way to represent these parameters for each VGO hydrotreater. Table 2 shows the final parameter values used for the 14 plants from which significant data were obtained (six plants allowed detailed publishing of the results). The parameters were evaluated separately with the data sets and then together to check for cross-correlation between the parameters. The parameters were adjusted during the simulation run for each plant.

Equation 2 provides a calculation to determine parameter p , based on hydrogen partial pressure (P_{H_2} , psig) and lumped mass transfer variable (η_e). Both of these variables are crucial in converting sulphur in the hydrotreater, and thus are incorporated in the calculation for parameter p :

$$p = -\frac{P_{H_2} - i e^{\eta_e}}{4500} \quad (2)$$

Equation 2 was based on a steady-state catalyst vendor correlation for this parameter in VGO hydrotreater service. The wetting efficiency factor was included (η_e), since the overall reaction relies on reactants contacting the catalyst for the reaction to proceed. A reduction in contact will reduce the impact of any hydrogen partial pressure benefits.

For the temperature factor b , there appears to be a relationship to the crude's viscosity (μ). The viscosity at SOR for each crude is included in Table 2. A logarithmic relationship, with an R^2 of 0.978 for the 14 plant data set (R^2 of 0.980 for the six plants published in this study), has been fit, resulting in Equation 3:

$$b = 866.24 \ln(\mu) + 18162 \quad (3)$$

Equation 4, for parameter g , hydrogen-to-oil ratio, appears to be linearly related to the API of the crude (ie, the more dense the crude, the larger the required hydrogen-to-oil ratio). Typically, more hydrogen is needed for hydrotreating heavier crude, since these types of sulphur molecules are embedded in the heavier crude molecules and more hydrogen is required.^{4,5} As a result, the relationship between hydrogen-to-oil ratio and API (crude specific gravity) is appropriate. The linear relationship between parameter g and the API gravity of the crude feed can be described by Equation 4 (R^2 of 0.9854 from 14 plants):

$$g = -0.0141 \text{API} + 0.9146 \quad (4)$$

This linear relation (Equation 4) does not apply to ultra-low sulphur (ULS)

Statistical results for sulphur and WABT from each plant studied, model vs plant

	Plant A	Plant B	Plant C	Plant D	Plant E	Plant F
Sulphur R^2	0.86	0.92	0.90	0.93	0.95	0.88
WABT R^2	0.91	0.925	0.925	0.927	0.935	0.916

Table 3

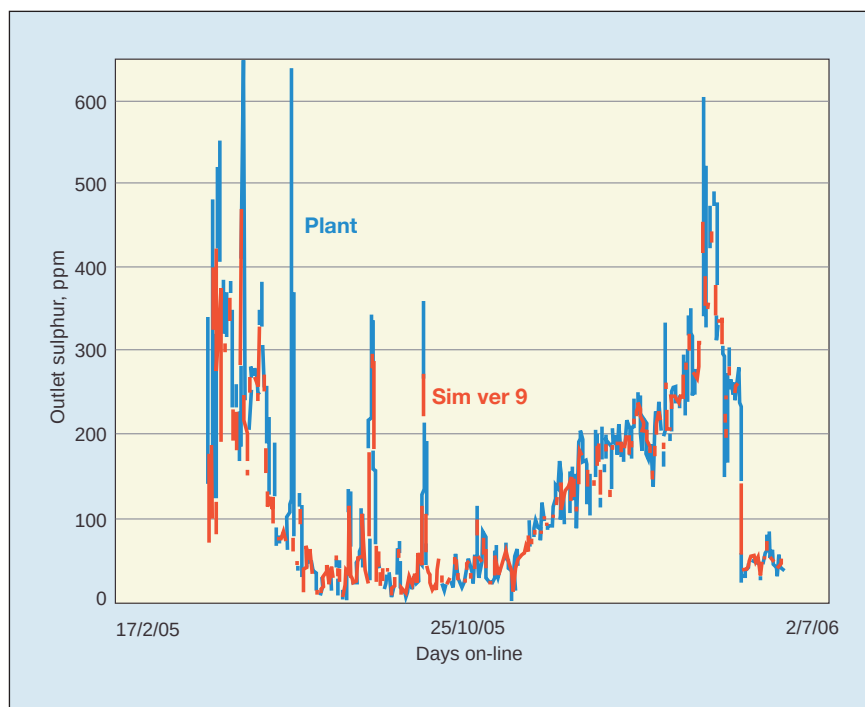


Figure 2 Plant D: product sulphur composition, model vs plant data

applications. The sulphur product specification for the VGO hydrotreaters studied was in the range of 300–500 wppm, well above the ULS specifications of less than 10 wppm.

Plant results — entire run length

The model output provides the WABT and sulphur outlet product, both variables that are constantly measured at industrial operations. The sulphur in the product is the primary specification for the VGO hydrotreater, while the reactor temperature is directly related to the catalyst activity (as catalyst activity goes down, reactor temperature goes up). The WABT of the reactor is plotted over time, which is a key variable the operators use to control product sulphur. This temperature is an indirect indicator of catalyst deactivation. As catalyst activity decreases (from coking, fouling or plugging), the reactor temperature is typically raised to try to increase the activity of the remaining active catalyst (prior to the need to reduce crude flow to the reactor).

Data for six plants were compared to model predictions for the plant WABT and product sulphur composition. Table 3 provides a summary of the statistical analysis used to compare the model

predictions to the plant data.

For the product sulphur, the model showed a R^2 of approximately 0.86–0.88 for two plants (A and F) and over 0.90 for the other four plants. For the WABT, the model had an R^2 in the range of 0.91–0.935. Overall, the model provides a credible match of the overall plant operation, especially considering that the model uses a lumped parameter approach and there are inaccuracies in the measurements and operator choices (on temperature), which as shown are not always the best method of mitigating a disturbance.

Plant D sulphur and WABT results

Plant D operated its VGO hydrotreater for one year and four and a half months, well below the desired run length of four years. The results of the model predictions, shown in Figure 2, for the product sulphur concentration were an R^2 of 0.93 for the product sulphur. Between 20–130 ppm, the model better matched the data with an R^2 of 0.957. For less than 20 ppm, the R^2 was 0.85, while above 130 ppm the R^2 was 0.895. The model was not as effective in capturing the spikes above 130 and below 20 ppm. The lumped approach in the model and the inaccuracy in the lab

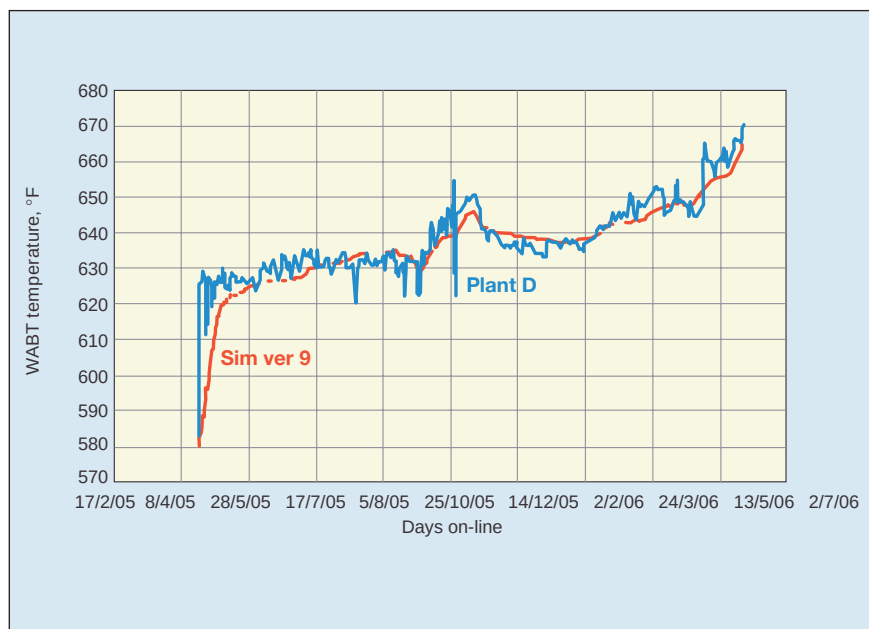


Figure 3 Plant D: WABT, model vs plant data

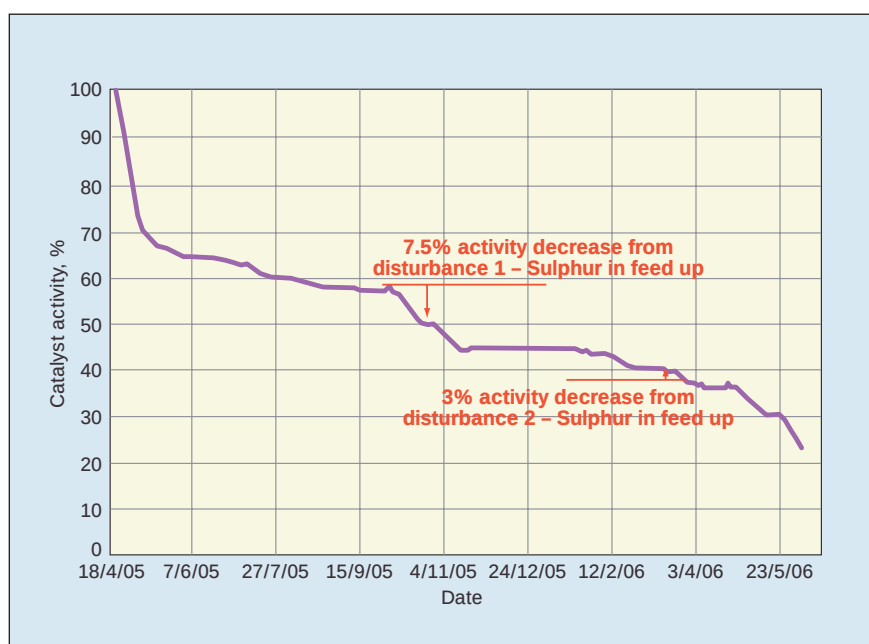


Figure 4 Plant D: catalyst deactivation from model

Performance comparison between the two data sets for Plant D

	Plant D: base	Plant D: new run
Time started	Apr 05	Nov 06
Time ended	Jul 06	?
T start, °F	580	602
T end, °F	670	?
R ² sulphur	0.917	0.927
R ² temperature	0.916	0.934
SOR range, °F	580–630	602–655
SOR T delta, °F	50	53
Catalyst type	Version 7	Version 8b
Viscosity, SSU-100°F	243	243
API SOR	27	27.1
Parameter <i>b</i> , average	23 000	23 000
Parameter <i>p</i> , average	0.9	0.92
Parameter <i>g</i> , average	0.54	0.54

Table 4

samples at the extreme points are likely contributors to the increased deviation by the model outside the 20–130 ppm range.

Figure 3 shows how the model WABT predictions compared to the Plant D data. The R² of 0.927 indicates a very good model prediction given the lumped approach, quality of industrial-scale plant data and operator error contributing to the inaccuracies in the model. The model captures the operating trends (changes in crude flow and contaminants in feed) and thus provides an insight into catalyst deactivation during the entire run length. This newly available information can be used to determine ways to mitigate the impact of catalyst deactivation.

Catalyst activity

Catalyst activity is directly related to the WABT, so WABT is a primary, easily attainable, yet indirect variable for operations to control catalyst activity or the rate of deactivation. Analysis of the catalyst activity profile is helpful in deciding when to schedule a unit shutdown and how to mitigate further deactivation. Figure 4 shows the catalyst activity/deactivation profile for Plant D from the model. This figure shows clearly the impact of the disturbances during the life of the catalyst. At disturbance 1, a rapid increase in sulphur causes a 7.5% reduction in catalyst life. If this impact can be mitigated during the disturbance, catalyst life can be extended. The two disturbances noted in Figure 4 reduce catalyst life by 10.5%, or four months. This information can be critical in deciding what steps operations can take to improve the performance or prepare for a shutdown.

Predictability of developed correlative model

The developed model in this research is correlative. An exercise was performed to determine if the model could also be considered partially predictive. A new data set was obtained from Plant D, which had a different catalyst (updated version of existing catalyst) and a different starting temperature. The parameter correlations developed from the entire sets of plant data obtained were used. The model was able to deal with a different catalyst and starting temperature while using the same model parameters from a different data set to obtain a representative and semi-predictive evaluation of the operation. The key point of this evaluation is that the model calculations do not rely on any correlative analysis with this data set. Table 4 compares the performance of the model with the base Plant D data and the new plant data.

Based on the catalyst activity profile to date, the model predicts a run length

of 2.4 years, just short of the three-year design rate, but more than double the previous data set of 1.08 years.

Application of the model

The developed model provides a valuable software tool that can be used by operators to understand the impact of changing a key process variable on the overall economics of the VGO hydrotreater operation. Operators can feel more comfortable justifying a process change to improve VGO hydrotreater performance (eg, throughput), since the model is based on industrial data and can track disturbances and the overall performance of the reactor. Table 5 shows a summary of the economic benefits that can occur by using increased hydrogen purity at the same hydrogen flow rate (and thus higher hydrogen partial pressure) for all six plants.

For the value calculation in Table 5, an average price of \$8.84/kscf for 99% hydrogen and a \$25/bbl crude upgrade value was used. The additional crude that could be processed ranged from an average of 1.5–3.6 kbpd, with the value (revenue from added crude production — cost of 99% pure hydrogen from a third party) for each plant ranging from \$13.5–45.3MM CAD over the run length for each plant (or \$6.7–22.6MM per year).

Refiners/upgraders can also increase recycle pressure and thus reactor pressure to boost hydrogen partial pressure and improve catalyst performance. A booster compressor is typically added to the recycle circuit. The model can be used to make a comparison between raising hydrogen partial pressure via increased reactor pressure and raising hydrogen partial pressure via increased hydrogen purity. This is an important analysis in determining which route, if any, to take to improve VGO hydrotreater performance. Table 6 shows the results of increasing hydrogen purity (from Table 5) to 99% if the recycle pressure is increased by 15%. The increased recycle pressure creates an increase in catalyst activity, resulting in an average rise of crude flow of 0.7–1.7 kbpd.

The rise in crude flow from increased recycle pressure is 43–54% of the rise in crude flow from increased hydrogen purity. The impact of increased hydrogen purity in the developed model translates into a more effective way of mitigating catalyst deactivation versus simply raising the reactor pressure.⁶

Conclusions

By using industrial data for validation purposes, and creating a model that responds to various disturbances during the entire hydrotreater operation, refiners/upgraders will now have the necessary software tool to justify the

Value of increasing H₂ purity via increased crude throughput

Plant	Avg % H ₂	H ₂ flow, mmscfd	Avg crude, kbpd	Avg crude increase, kbpd	\$MM for entire run length	\$MM/yr over run length
A	83	33	15.8	2.5	33.7	13.0
B	77	21	13.5	3.2	45.3	22.6
C	76	28	14.4	2.2	20.3	11.3
D	88	35	13.1	2.5	13.5	12.5
E	86	23	11.3	1.5	20.0	6.7
F	91	48.6	26.5	3.6	39.9	17.5

Table 5

Comparing increasing recycle pressure vs increasing H₂ purity

Plant	Existing reactor		Model - 99% H ₂		Model - P up 15%	
	Pressure, psig	P _{H₂} , psig	P _{H₂} , psig	Avg crude increase, kbpd	P _{H₂} , psig	Avg crude increase, kbpd
A	675	560.3	668.3	2.5	644.3	1.2
B	1065	820.1	1054.4	3.2	943.1	1.7
C	970	737.2	960.3	2.2	847.8	1.2
D	1550	1364.0	1534.5	2.5	1568.6	1.1
E	460	395.6	455.4	1.5	454.9	0.7
F	475	432.3	470.3	3.6	497.1	1.6

Table 6

use and have confidence to introduce the concept of increased hydrogen (purity and thus partial pressure) to improve hydrotreater operation. A representative dynamic model for industrial refinery/upgrader hydrotreaters has been developed based on 14 actual operating hydrotreaters (six of which can be published). The model accurately simulates local disturbances and performs well over the entire run length of the hydrotreater by competently representing the actual catalyst deactivation and incorporating a wetting efficiency factor to handle mass transfer resistances. This robust model can be applied to demonstrate the tangible economic benefit of increasing hydrogen (purity and flow) use to improve the operation of a hydrotreater by increasing run length and/or improving crude processing. The model can also be used:

- As a decision-making tool based on process variable changes
- As a training and learning tool to gain operating experience
- As a troubleshooting tool to identify faulty measurements, thus aiding operators in operating the hydrotreater more effectively.

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“The developed model provides a valuable software tool that can be used by operators to understand the impact of changing a key process variable on the overall economics of the VGO hydrotreater operation”

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Clean diesel hydrotreating

Design considerations for clean diesel hydrotreating. Critical issues are discussed when designing a hydrotreating facility to produce diesel fuel with very low levels of total sulphur

Ed Palmer, Stan Polcar and Anne Wong
Mustang Engineering

For over three decades, refiners worldwide have been implementing various projects in their facilities to accommodate a variety of regulations to improve the quality of transportation fuels in order to reduce vehicle emissions. One of the key areas of interest has been the reduction of sulphur in diesel fuel to very low levels. For example, since mid-2006, the maximum sulphur content of on-road diesel fuel in the US has been limited to 15 wppm. Similar regulations are in place or are in various phases of implementation in many countries.

Design considerations

Middle distillates contain various types of sulphur species, including mercaptans, sulphides, thiophenes and aromatic

sulphur compounds. Sterically hindered dibenzothiophenes are a group of aromatic sulphur compounds that are among the most difficult to remove when hydrotreating to very low sulphur levels. This is particularly true for diesel fuels that contain significant quantities of cracked stocks, such as FCC light cycle oil (LCO), which contains a large concentration of aromatic sulphur compounds. The effective removal of these species requires tailored catalysts and process conditions, as well as consideration of other factors such as feed nitrogen content and aromatics equilibrium.

There are numerous issues to be addressed in the design of a hydrotreater, including:

- Feed characteristics and variability
- Other product quality requirements, especially cetane index
- Catalysts selection
- Optimisation of reactor process variables
- Equipment design requirements
- Reliability
- Minimising product contamination
- Handling of off-spec diesel product.

All of these factors should be carefully considered during the front-end process design.

Process flow

Figure 1 shows a simplified process flow diagram for a diesel hydrotreater. Fresh feed from the surge drum is heated with stripper bottoms, then mixed with

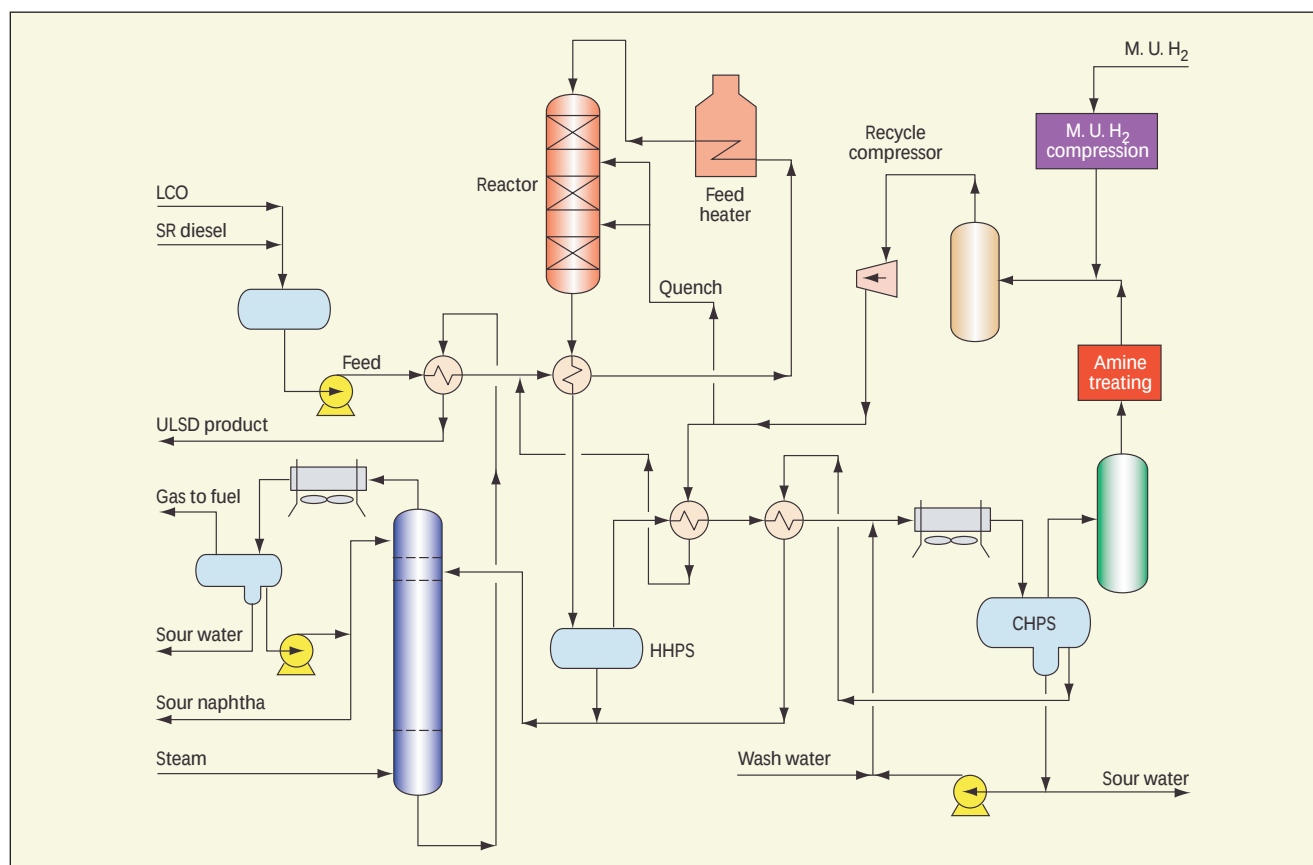


Figure 1 ULSD hydrotreater HHPS/CHPS

Maximum operating pressures for 321 SS and 347 SS stainless steel

	600lb flanges		900lb flanges		1500lb flanges	
	321 SS	347 SS	321 SS	347 SS	321 SS	347 SS
600°F	975	1030	1460	1550	2435	2580
650°F	950	1015	1425	1520	2375	2530
700°F	930	995	1395	1490	2330	2485
750°F	915	985	1375	1475	2290	2460
800°F	900	975	1355	1460	2255	2435
850°F	895	970	1340	1455	2230	2425

Table 1

recycle hydrogen. The combined feed is further heated by reactor effluent, then brought to reactor inlet temperature in the charge heater. Reactor inter bed quench may be required in one or more locations, depending on the volume of cracked stocks (FCC LCO, light coker gas oil) in the feed. This flow diagram shows recycle gas being used as quench. Reactor effluent exchanges heat with the combined feed and flows to the hot, high-pressure separator (HHPS). Vapours from the HHPS are used to heat recycle gas and stripper charge before being cooled in the reactor effluent air cooler (REAC) and entering the cold, high-pressure separator (CHPS). Wash water is injected upstream of the REAC to remove ammonium bisulphide. HHPS liquid is combined with heated CHPS liquid and flow to the product stripper.

Vapours from the CHPS are contacted with amine in a scrubber for hydrogen sulphide removal and flow to the recycle compressor suction drum. Make-up hydrogen is compressed and combines with the recycle gas in the suction drum. Some of the recycle gas may be purged from the compressor suction drum to improve the purity of the recycle gas hydrogen. If needed, the quantity will depend on the reactor hydrogen partial pressure requirements and the purity of the make-up hydrogen.

In the product stripper, superheated steam is introduced into the bottom of the tower to effect the removal of hydrogen sulphide. Stripper overhead vapours are condensed and flow to the stripper accumulator. Accumulator vapour and liquid (wild naphtha) are processed in other off-site facilities. The stripped diesel product is used to heat the feed, it is cooled, then it flows to drying facilities (not shown). This could be a coalescer/salt dryer or a vacuum drying system.

Feed and product characteristics

Sulphur, nitrogen and aromatics content are the most important feed characteristics that impact the process design for diesel hydrotreating facilities. The nitrogen content of the feed has a significant impact on the required operating pressure for a new design.

Nitrogen has to be removed to essentially the same level as sulphur to reach the ultra-low target. This means the catalyst employed and the hydrogen partial pressure selected must be consistent with a high nitrogen removal operation. Normally, the bulk of the feed nitrogen is contained in light coker gas oil and FCC LCO. The aromatics content of the feed will govern the chemical hydrogen consumption at the low space velocities and high hydrogen partial pressures required for very low sulphur diesel production.

Generally, cracked stocks can be included in the feed up to the level limited by the product cetane index or gravity without having a significant impact on hydrotreater design. There is a small increase in the gravity and cetane index during the hydrotreating reaction. If a significant improvement in cetane (say, three to five units or more) or gravity is required, a multi-stage design using aromatics saturation catalysts in the second stage may be the more economical option. The final choice will be driven by the magnitude of the improvement in gravity and cetane required.

Obviously, the design product sulphur target is a key issue, not only from a process design standpoint, but also for off-site storage and transfer. For the ultra-low sulphur diesel (ULSD) programme in the US, most new and revamp facilities have been designed for a product sulphur content of 8–10 wppm to ensure a final product sulphur content of 15 wppm at the point of sale.

Pilot testing of the feed is practically mandatory to confirm reaction process conditions. Testing for variations in feed characteristics, especially FCC LCO and coker light gas oil back-end distillation, should also be considered, because the separation achieved in the products fractionators from these facilities is notoriously poor. This can result in a temporary spike in the content of the most difficult-to-treat sulphur compounds in the hydrotreater feed and requires an increase in reactor temperature. This will increase the catalyst deactivation rate and, hence, directionally reduce the cycle length.

Reaction process variables

The key reaction process variables are:

- Space velocity
- Hydrogen partial pressure
- Make-up hydrogen purity
- Ratio of total hydrogen to reactor/chemical hydrogen consumption
- Cycle length
- Reactor temperature.

For feeds that have a significant aromatics and/or nitrogen content, a nickel-moly (Ni/Mo) or nickel promoted cobalt-moly (Co/Mo) catalyst will be used, along with an appropriate selection of graded catalysts in the top of the bed to mitigate reactor pressure build-up.

For a given cycle length and treating severity reactor space velocity, hydrogen treat gas quantity and hydrogen partial pressure are the variables that are optimised during the process design along with reactor temperature. As the hydrogen partial pressure is increased, the catalyst deactivation rate is reduced. Thus, the space velocity can be increased accordingly for a constant cycle length. However, this is at the expense of higher hydrogen consumption. Another important variable is the ratio of total hydrogen supplied to the reactor bed to the chemical hydrogen consumption for that bed. This value should be between five and six for feeds with significant quantities of cracked stocks. This ratio is normally a “fall-out” number during the process design, but there are instances where it can control the design hydrogen circulation rate, particularly for cases where high purity make-up hydrogen is used exclusively.

From a practical viewpoint, one should be aware of the limiting pressure of the alloy piping flanges in the reactor section when setting the hydrogen partial pressure and total operating pressure. This includes piping from the combined feed exchangers to the feed heater, from the heater to the reactor, and from the reactor to the combined feed exchangers (especially when the feed contains significant quantities of cracked stocks). This piping will be a 300 series stainless steel, and for 600 psi ANSI flanges this corresponds to a maximum operating pressure of around 800 psig at the reactor inlet when using 321 SS (Table 1) and 880 psig when using 347 SS. For 900 psig flanges, the reactor operating pressure can be increased to about 1200 psig when using 321 SS and 1300 psig when using 347 SS. This takes into consideration pressures during relieving conditions. These criteria should not necessarily govern the selection of the operation pressure. However, just barely exceeding these limits and requiring the next higher rated ANSI flange class in the reactor loop will be very costly. Actual pipe wall thickness is calculated for the design conditions and the limiting value used for the piping specification in the reactor

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loop alloy sections. The piping material selection between 321 and 347 stainless steel can be optimised, based on design and operating temperature. Type 347 has a higher allowable stress value, as shown in Table 1.

For revamp designs, the hydrogen partial pressure achievable is restricted by the existing equipment and piping mechanical design and hydraulics in the reactor loop. A higher treat gas rate can be used to increase the hydrogen partial pressure, but this is usually limited because of the associated increase in the reactor loop pressure drop and the corresponding maximum operating pressure of the various system components.

Make-up hydrogen purity impacts the hydrogen partial pressure for a fixed reactor operating pressure. Lower purity make-up hydrogen requires higher hydrogen circulation rates to maintain the target hydrogen partial pressure and may even require a purge stream from the cold separator. If the make-up hydrogen purity is too low, there is no combination of recycle rate and purge that can be used to achieve the target reactor outlet partial pressure. For a revamp design, increased make-up hydrogen purity is the most effective means of increasing the hydrogen partial pressure.

For new designs, the cycle lengths have typically been set at 24–36 months. This has been based on the logic that, at some point, the cycle will be limited by factors other than catalyst activity: namely, reactor pressure drop. Hydrogen partial pressure has a major impact on cycle length from a catalyst activity standpoint. For a fixed space velocity, the cycle length increases with hydrogen partial pressure.

Maximum reactor outlet temperature at end-of-cycle catalyst conditions is generally set at 725–750°F to avoid aromatics saturation equilibrium constraints. This is also influenced by the quantity of cracked stocks in the feed and the crude source. Hydrotreating catalyst performance correlations for reactor temperature are usually based on the weighted average bed temperature (WABT). WABT is calculated as the reactor inlet temperature plus two-thirds of the reactor temperature rise. The temperature rise is usually limited to 40–50°F per bed by quenching. Thus, for a 50°F temperature rise and a 725°F maximum reactor outlet temperature, the end-of-run WABT would be:

$$\text{WABT} = (725 - 50) + 2/3(50) = 708^\circ\text{F}$$

The start-of-run WABT has to be sufficient to obtain the required removal of sulphur and nitrogen. Cycle length is determined by the catalyst deactivation rate at the design space velocity and

hydrogen partial pressure. During the cycle, the increase in WABT will be 30–50°F, with lower deactivation rates occurring at higher hydrogen partial pressures.

Reactor design

Initially, the reactor diameter is set to obtain a superficial mass velocity (mass flux) in the range of 2000–5000 lb/hr/ft². A value of 3500 lb/hr/ft² allows for a reasonable turn-down rate and some up side allowance. The mass flow includes all hydrocarbon and hydrogen at the reactor inlet. If the required diameter is larger than the limit for which the reactor can be shop fabricated and shipped to the plant site (12–14ft for over-land shipment), a two-train design may be considered. For diesel hydrotreaters, this is normally in the range of 30 000–40 000 bpsd per reactor train. For plants that have adequate water access and dock facilities, larger reactors and thus larger single-train capacities can be considered.

For diesel hydrotreating, the flow through the reactor is two phase, so an appropriate correlation, such as that by Larkins,⁴ is used for estimating the pressure drop. Inter-bed quench should also be considered for the pressure drop calculation. The catalyst physical properties have a significant impact on the reactor pressure drop. This includes void fraction and equivalent particle diameter. In order to ensure good distribution, most ULSD catalyst beds are dense loaded instead of sock loaded. The calculated clean pressure drop should be in the range of 0.5–1.0 psi per foot of catalyst bed (clean).

According to the required catalyst volume, the bed heights are established based on either the heat of reaction/maximum temperature rise or a bed height of 30–40ft. The clean pressure drop is then estimated for each bed. The maximum overall pressure drop is determined for the design of the bed support and to compare with the crush strength of the catalyst. This value is the sum of the following:

- Fouled bed pressure drop at 175% of calculated clean drop
- Dead weight of catalyst and support material
- Coke deposits at 30% of catalyst dead weight
- Liquid hold-up
- 15 psi allowance for depressurisation.

The pressure drop for the feed distributor/redistributors, quench internals and collector are added to the bed values to arrive at the overall fouled reactor pressure drop. The design of the feed distributor and redistributors is crucial for obtaining the target product sulphur level. The distributors and quench internals are usually catalyst vendors' proprietary designs.

There are several ways to provide internal quench to the reactor to limit the temperature rise. The common method is to utilise hydrogen-rich recycle gas/make-up hydrogen. The quench gas also causes additional vapourisation of some liquid in the reactor, which provides an extra heat sink for reaction heat removal. Another less common approach is to recycle CHPS liquid to the reactor. As noted previously, quench is added to limit the reactor bed temperature rise to 40–50°F.

The reactor metallurgy is typically 11/4 Chrome-1/2 Moly with 1/8in 347 stainless overlay or cladding. The choice often depends on the thickness of the vessel, which will affect the cost. Cladding is usually more economical for vessels with wall thickness up to around 4.0in. For greater thickness, overlay is normally used. For thick-wall reactors with a minimum design metal temperature of less than 0°F, 2 Chrome-1 Moly metallurgy may be the better choice.

Feed exchangers

The feed exchangers are generally specified to optimise heat economy. However, enough duty should be allowed for the charge heater to have a reasonable amount of turndown and overall heat balance control. The feed exchange should not be more than about 80–85% of the total duty needed to heat the feed to reactor temperature at end-of-cycle conditions.

For very low sulphur diesel product, the reactor feed/effluent exchangers' mechanical design requires special attention to minimise leaks. Many refiners prefer a pull-through tube bundle with a floating head because this design is easier to clean and handle. However, the floating head cover is a potential source for leaks. A U-tube bundle avoids this potential problem and is less expensive. Also, tubes should be seal welded to the tube sheet to prevent leaks from the rolled tube joints.

Materials selection for the feed/effluent exchangers is based on predicted corrosion rates for the service conditions. The feed/effluent exchangers have several shells in each train in series with varying metallurgy. The cold shells are all carbon steel. The intermediate temperature units normally have 11/4 chrome shells and 400 series tubes. The hot shells are 11/4 chrome with 300 series stainless cladding and 300 series stainless tubes.

Charge heater

As previously noted, the feed heater design duty should not be any less than approximately 20% of the combined feed duty to the reactor inlet temperature at end-of-cycle conditions to allow for

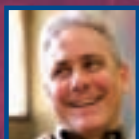


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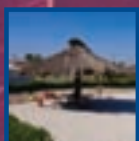


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turndown and heat balance control. A design margin of 10% of the combined feed exchanger duty should be added to accommodate accelerated exchanger fouling and loss of reactor heat of reaction caused by removing highly reactive feeds such as FCC LCO and coker light gas oil. The design duty of the charge heater should be checked to ensure it is sufficient to bring the unit up to operating temperatures from a cold start in a reasonable length of time.

Typically, the number of heater passes matches the number of parallel feed/effluent exchanger trains. The feed and recycle hydrogen can be flow controlled for each train ahead of the exchangers, which will prevent any maldistribution of the two-phase stream entering the heater passes. When there are more heater passes than feed effluent exchanger trains, particular care must be made to ensure equal distribution of vapour and liquid to each heater pass. The limit for one heater pass is in the range of 15 000–18 000 bpsd of fresh feed at typical diesel hydrotreater conditions. This limit is based on 8in diameter maximum heater tubes and an overall pressure drop of 40–50 psi. Heater tube metallurgy is typically 347 stainless steel.

Environmental issues such as NO_x and CO emissions are also a concern in the charge heater design. NO_x emissions limitations are usually addressed by installing low NO_x or ultra-low NO_x burners. CO emissions can be a concern

with heaters with a required turndown to less than 50% of design. This can be the case with a charge heater with a low SOR duty and a high design duty. In this case, the turndown can be 10–20% of design. Maximising energy efficiency can lead to low SOR duty. High design duties are a result of off-design cases such as loss of reactive feed or cold start-up.

Reactor products separation

There are several alternative arrangements for handling the reactor effluent after the combined feed exchangers. In general, the decision is whether or not to use an HHPS in addition to a CHPS, or a CHPS only. The HHPS is usually operated around 500–550°F and, thus, the vapours can be used to heat recycle gas and cold separator liquid. The HHPS improves the overall heat economy and results in a somewhat smaller product stripper and auxiliary equipment. This arrangement will also directionally improve the oil-water separation in the CHPS. For heavy gas oil hydrotreating, a hot separator is practically mandatory to have adequate oil/water separation. This is less of a concern for diesel hydrotreating, unless there are significant quantities of cracked material, which decrease API gravity. Disadvantages of this design are a 5–10% lower recycle gas purity, which requires higher recycle hydrogen compressor horsepower. The addition of a HHPS can be a viable option for debottlenecking an existing hydrotreater that is

hydraulically limited in the reactor loop. This revamp would require, however, a modest increase in inlet flow and power for the recycle compressor.

Other options include the addition of hot and cold low-pressure separators. These designs marginally unload the upper part of the stripper and result in improved LPG recovery. Figure 1 illustrates an ULSD hydrotreater with HHPS/CHPS, Figure 2 an ULSD hydrotreater with CHPS only and Figure 3 a hydrotreater with HHPS/CHPS/CLPS.

The HHPS base material is 11/4 Cr-1/2 Moly normally with clad or overlay. The lining is 300 or 400 series stainless, depending on the actual predicted corrosion rate. For equipment in wet sour service, hydrogen induced cracking (HIC) resistant carbon steel material should be specified. This requirement applies to the CHPS. A 300 series stainless steel mesh pad is installed in the CHPS to assist in coalescing the wash water. The boot of the CHPS should have 1/4in corrosion allowance.

Reactor effluent air cooler

Regardless of the reactor products separators configuration, a final cooling step is eventually used prior to separating liquid and vapour. An air cooler is typically used, sometimes supplemented with a water trim cooler. Metallurgy selection of the piping and equipment in this area requires special attention because of the presence of ammonia and hydrogen sulphide in the reactor

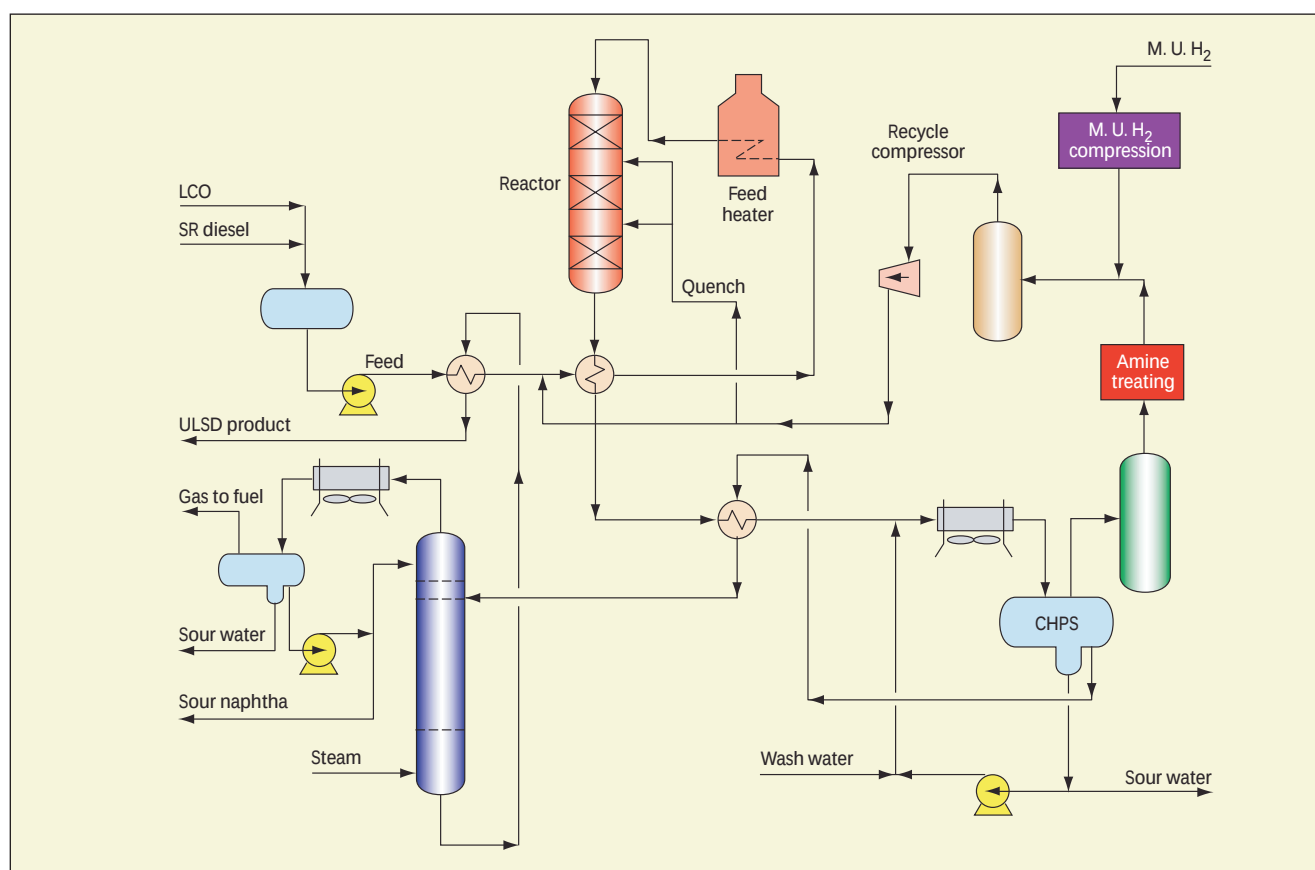


Figure 2 ULSD hydrotreater with CHPS only

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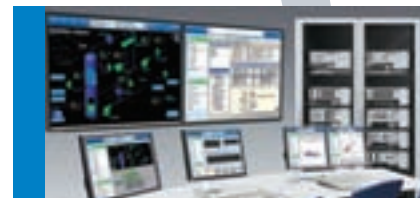
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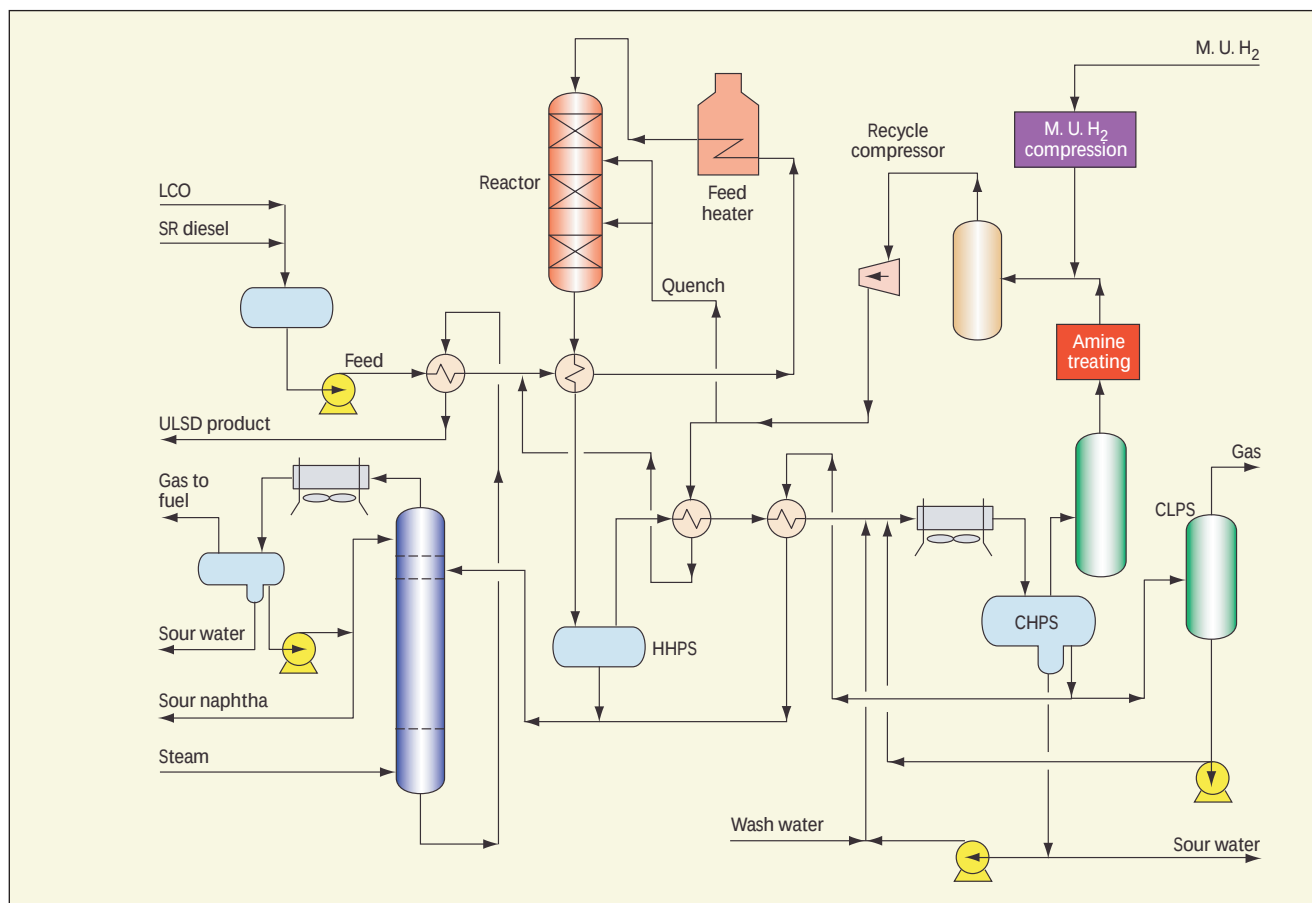


Figure 3 ULSD hydrotreater with HPPS/CHPS/CLPS

effluent. As this stream is cooled, these two compounds combine to form ammonium bisulphide (NH_4HS), which condenses as a solid on the inlet piping and in the cooler tubes. To prevent plugging and under-deposit corrosion, recirculating wash water is injected ahead of the cooler, which introduces a corrosive aqueous solution in the stream.

Tube metallurgy selection is based on the product of the mole percentage of ammonia and hydrogen sulphide in the total stream before water injection. The target maximum value for this product, also known as K_p , is 0.15 (5) before alloy metallurgy is considered:

$$K_p = \text{Mol \% H}_2\text{S} \times \text{Mol \% NH}_3 < 0.15$$

Other criteria include:

- Determine make-up water quantity to limit NH_4HS concentration in the condensed water phase to 4 wt%. Assume equal molar amounts of ammonia and hydrogen sulphide in the CHPS water and that essentially all of the ammonia is dissolved in the water
- Determine circulating water quantity as that needed to maintain a minimum of 20–25% of the total water injected in the liquid phase ahead of the condenser
- Mixed-phase velocities in the piping and tubes should be limited to 20 ft/sec for carbon steel and 30 ft/sec for alloy.

Minimum velocity should be 10 ft/sec

— Symmetrical piping in and out of the condenser

— Wash water source can be stripped sour water, but should be from a stripper dedicated to hydrotreating spent wash water service

— Wash water can be injected into the main effluent line upstream of the air cooler or independently into each air cooler nozzle through a distribution device such as a spray nozzle or restriction orifice. Injecting in the piping gives more time for mixing and vapourising the water and is less expensive. Injection into individual air condenser nozzles ensures good distribution in each of the air cooler bays.

If alloy construction is required, typical alloys used are Incoloy 800 or 825 and duplex stainless steel 2205.

High-pressure separator liquid level control valve sizing

In the high-pressure separator, the operating pressure is greater than the critical pressure of the liquid. The high-pressure separator liquid level control valve is in flashing liquid service. Typically, both the vapour pressure and critical pressure are required to determine the effective pressure differential in the sizing of any control valve in flashing liquid service. In this case, the ratio of vapour pressure vs critical pressure is greater than one. This unusual situation

is not acceptable in most control valve sizing programmes. To bypass this problem, one of these two pressure values will need to be artificially manipulated. If the vapour pressure is artificially reduced to below the critical pressure, the effective pressure differential may be over-estimated and the control valve may be undersized. Based on actual experience, the control valve vendors recommend that the critical pressure is raised to equal to the vapour pressure when specifying instrument process data.

Compression

The choice of recycle compressor design is based on inlet flow and head requirements. To use a centrifugal compressor, adequate suction flow is required, but the head should be low enough to limit the number of stages, such that a single body machine can be used (usually maximum of ten stages). In the past, most diesel hydrotreaters did not have an adequate volume of recycle gas for a centrifugal compressor. New, larger ULSD hydrotreaters circulating 3000–5000 SCF of gas per barrel of feed will be candidates for a centrifugal compressor. If a reciprocating compressor is used for recycle, it will normally be combined with the make-up service in a multiple-throw machine. For reciprocating compressors over about 500 HP, two 60% capacity machines are

Typical pressure drop allowance for reactor loop equipment and piping in a hydrotreater with reactor inlet pressure of 1100 psig

Equipment item	Pressure drop, psi
Combined feed exchangers (both sides)	40
Feed heater	50
Reactor (fouled)	75
HHPS vapour/recycle hydrogen (both sides)	20
HHPS vapour/CHPS liquid	10
Reactor effluent air cooler	10
Amine/knock-out drums	5
Piping	23
Total reactor loop pressure drop	233

Table 2

Maximum pressure and typical design temperature for critical piping services in the reactor section

Pipe section	Design pressure, psi	Design T, °F	Max allowable, psi
Exchange to heater	1252	700	1260
Heater to reactor	1200	775	1242
Reactor to exchange	1123	825	1233

Table 3

typically provided. For smaller compressors, two 100% units are used.

The make-up compressor discharge may be routed to either the recycle compressor suction or discharge. Make-up gas flowing to the suction will increase the purity and volume of the recycle gas and decrease the molecular weight. Potentially, this could be a problem for a centrifugal recycle compressor, since the

lower molecular weight directionally requires more head and potentially more stages. This is not as serious an issue with a reciprocating machine. However, higher hydrogen purity will increase the discharge temperature, which is limited per API-618 to 275°F.

Normally, the make-up would be routed to the recycle compressor discharge unless this causes an additional stage of

make-up compression. This approach has the advantage of maintaining some hydrogen flow capability through the reactor loop following a recycle compressor emergency outage.

Reactor loop hydraulics

A hydraulic profile is established for the reactor loop in order to set the recycle compressor head requirements and to establish the design pressure of the piping and equipment.

The reactor inlet pressure is set based on conditions established by the catalyst supplier and, as noted previously, considering the pressure limits of standard piping flanges. Table 2 shows the typical pressure drop allowance for the reactor loop equipment and piping in a hydrotreater with a reactor inlet pressure of 1100 psig.

A point-to-point pressure profile is shown in Figure 4. Data shown are for the normal case (EOR) and for the relieving case when the CHPS is at 10% above operating pressure. Table 3 is a tabulation of the maximum pressure (at relieving conditions) and typical design temperature for critical piping services in the reactor section. This is compared to the maximum allowable pressure for 900 psi, type 321 stainless flanges.

This analysis shows that the assumed pressure profile is consistent with the use of 900 psi flanges in the reactor loop alloy piping. The relieving pressure

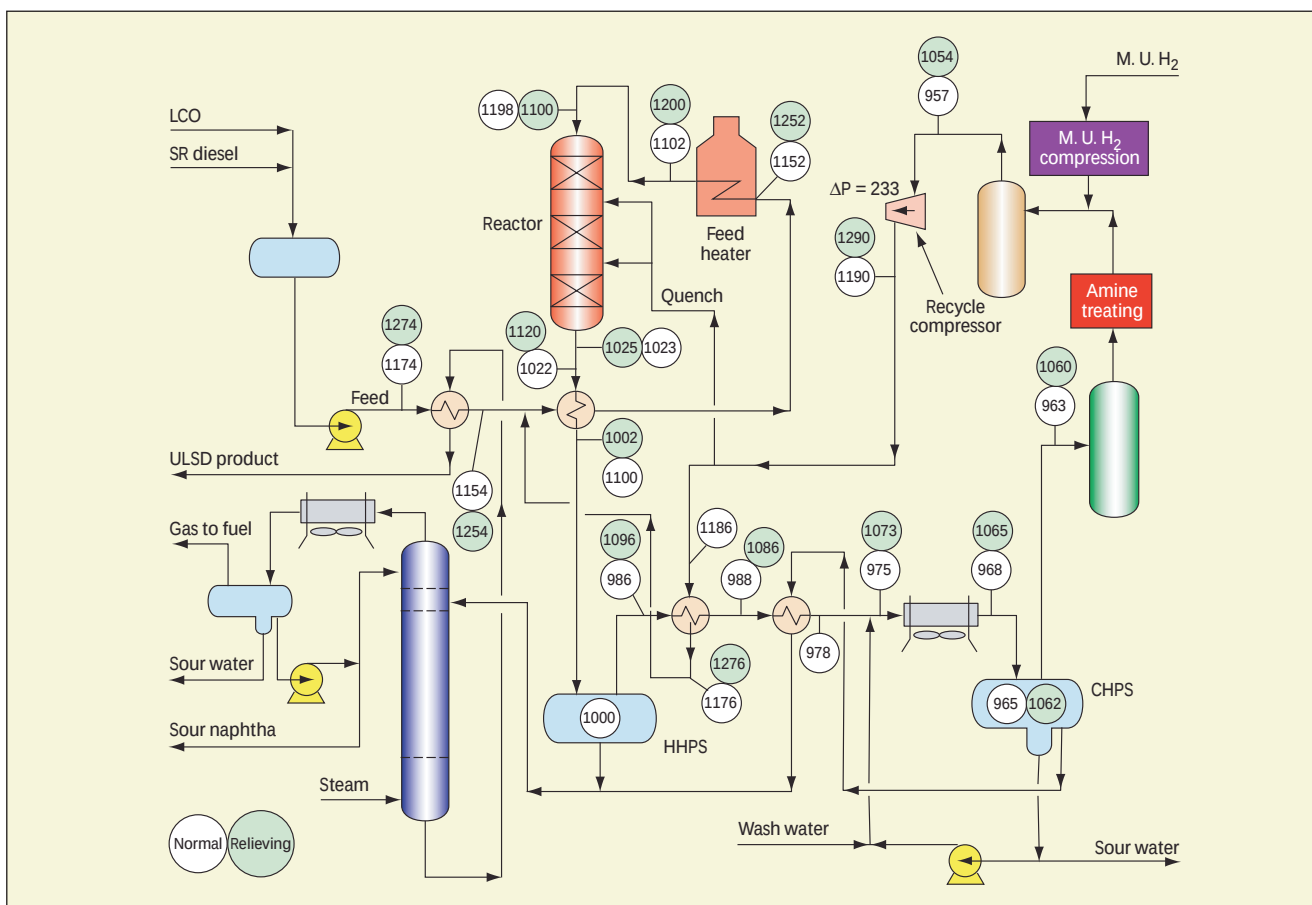


Figure 4 Normal/relieving pressure profile

Estimated equipment/materials delivery matrix

Equipment materials	Current quoted deliveries	Vendor data submittal (current durations)
Compressors (reciprocating)	70–92 weeks ARO	20 plus weeks ARO
(centrifugal)	70–84 weeks ARO	20 plus weeks ARO
Compressors (air)	52–64 weeks ARO	12–16 weeks ARO
Centrifugal pumps (API)	36–52 weeks ARO	16 plus weeks ARO
ANSI pumps	22–30 weeks ARO	10–12 weeks ARO
Agitators/mixers	26–28 weeks ARO	6–8 weeks ARO
Reactors (ULSD/alloy)	18–24 months ARO	6–8 weeks ARO (outline)
Reactors (2 1/4 Cr. - vanadium enhanced)	24–36 months ARO	6–8 weeks ARO (outline)
Large towers (all metallurgies)	54–68 weeks ARO	6–8 weeks ARO (outline)
Pressure vessels (carbon steel)	26–36 weeks ARO	4–6 weeks ARO (outline)
Pressure vessels (alloys)	48–56 weeks ARO	4–6 weeks ARO (outline)
Fired heaters	52–60 weeks ARO	12–14 weeks ARO
(heater tubes - high alloy)	36–48 weeks ARO	(mill delivery)
Shell & tube heat exchangers (carbon steel)	40–52 weeks ARO	6–8 weeks ARO
Shell & tube heat exchangers (alloys)	52–80 weeks ARO	6–8 weeks ARO

(ARO: After receipt of order)

Table 4

profile will be used to set the design pressure of the equipment in the reactor loop. Also, early in the process design, following completion of the heat and weight balance and a preliminary process flow diagram (PFD), a sized equipment list will be developed, which will allow plot plan studies to be completed. Preliminary piping sketches of the reactor loop will be developed and the allowance for piping pressure drop rechecked prior to purchase of the recycle compressor. The reactor loop hydraulics will be checked a final time following receipt of equipment vendor information and completion of piping isometrics for the reactor loop.

Note that the design pressures in the reactor loop were established by assuming the CHPS relief valve set pressure is 10% above normal operating pressure. In fact, this margin can be 5% by using a pilot-operated relief valve, which will lower the design pressure of the reactor loop equipment. Designing for a 10% margin for a grass-roots facility allows room for future capacity increases while staying within equipment design pressure limits. API recommended practice RP 521 appendix G recommends the design pressure to be 105% of the settling-out pressure, which would make the design pressure about 115% of the normal operating pressure. In the beginning of the process design stage when equipment design conditions are being established, there is not sufficient information available to accurately calculate the settling-out pressure. However, when the heat and material balance and PFD are completed, preliminary equipment sizing information and assumptions about pipe quantities along with the reactor loop pressure profile can be used to estimate the settling-out pressure. When actual

equipment and piping design information is available, the settling-out pressure is re-estimated to determine what margin is available compared to the CHPS relief valve set point. If the settling-out pressure exceeds the set pressure, a step-wise calculation or dynamic simulation can be used to estimate the relief rate.

Product stripper

In the product stripper, hydrogen sulphide formed in the reactor is removed from the diesel product along with light hydrocarbons. The removal of light material has to be sufficient to meet a flash point specification of 130°F. This also ensures removal of essentially all of the H₂S. Approximately 30 trays are required in the column. Overhead products include a sour gas, unstabilised naphtha and sour water. Equipment is included to provide intermittent water wash of the condenser.

Steam or vapours from a fired reboiler are used as the stripping medium. Due to temperature constraints (about 700°F maximum), the operating pressure of a reboiled stripper is limited to around 40–50 psig. Unless the refinery has a low-pressure gas recovery system, a small compressor and spare will be required to handle the off-gas. A steam stripper can be operated at over 100 psig, which allows routing into an existing refinery sour fuel gas system.

Diesel product from a steam stripper has to be further treated for water removal. This can be vacuum drying or coalescing, followed by salt drying. If this system is already in place, the steam stripping option would definitely have a lower capital cost compared to a fired reboiler. A steam stripped tower will also be a little smaller than a reboiled tower. If the product drying system is not in

place, the fired reboiler option should be considered. This will also create less sour water to process.

The product stripper material of construction is killed carbon steel with 410 SS trays and caps. Some part of the stripper column may need to be lined if the H₂S concentration is high. The overhead condenser and receiver are in wet sour service and HIC-resistant steel is required. The overhead receiver boot has a 1/4in corrosion allowance. R/F >0.10 is typical for both steam stripper and reboiled stripper.

Feed filtration

Even though distillate stocks are relatively clean, feed filtration is important to reduce exchanger/reactor plugging. A cartridge filter with 25 micron retention is typical for this application. Cracked feeds, if routed directly from the upstream facilities, should not be cooled.

Equipment delivery

Due to high worldwide demand, getting the necessary equipment delivered to the site could be a major challenge for any project. Construction and installation schedules are often governed by the delivery of long-lead items. Table 4 gives an estimate of current equipment and materials delivery.

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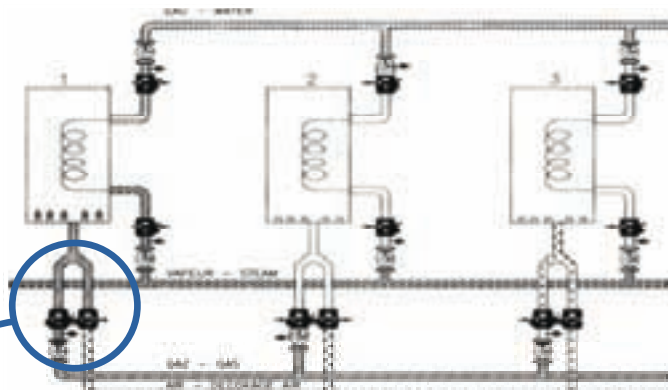


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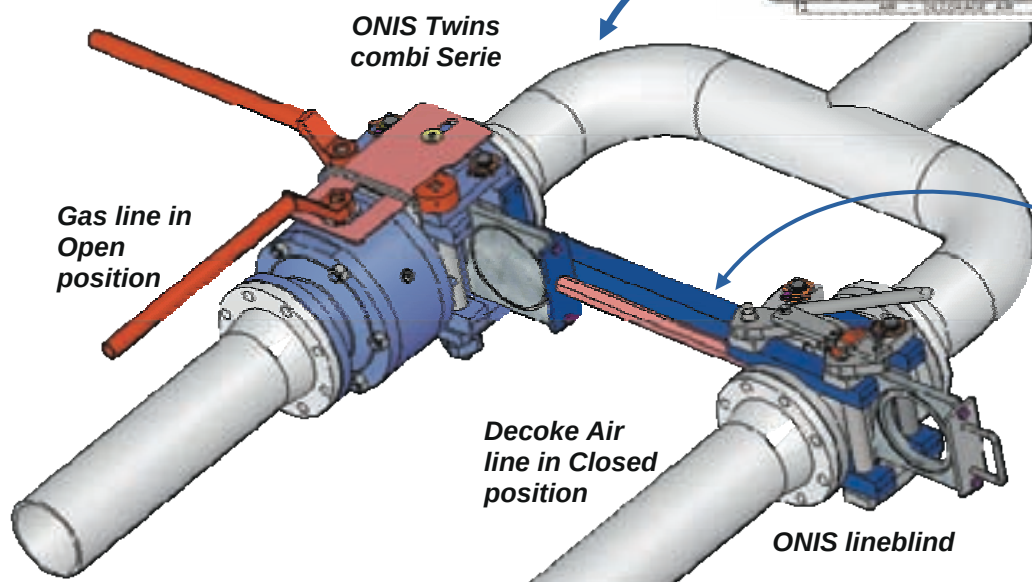
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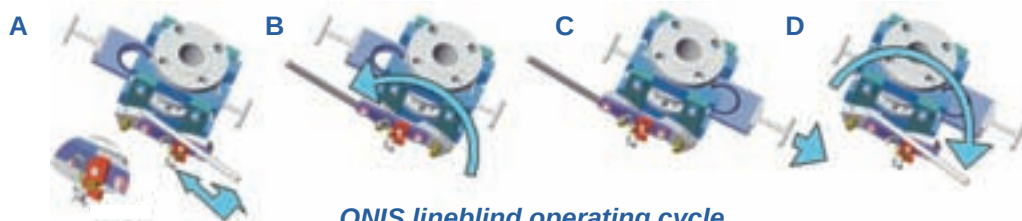


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Pygas upgrading for European steam crackers

Upgrading secondary by-products from naphtha-based steam crackers is imperative to remain profitable in a competitive petrochemical field. This article presents available technology options for BTX recovery, styrene extraction, C_5 olefin upgrading and more

Joseph C Gentryn and Meijuan Zeng
GTC Technology

In order to maintain competitiveness in the ethylene business for European steam crackers, more emphasis must be placed on upgrading all of the by-products that are generated by liquid crackers. Producers who do not upgrade these by-products will face increasing pressure on plant margins due to competition from the low-cost regions of the world.

Ethylene is one of the world's most important chemical feedstocks. Together with propylene, it accounts for 50–60% of all organic petrochemical production. Most ethylene is produced via the steam cracking of hydrocarbon feedstocks such as ethane, propane, butane, naphtha or gas oil. Steam cracking of saturated hydrocarbons has been the dominant technology for several decades. It involves thermal pyrolysis in the presence of steam to dehydrogenate the saturated hydrocarbon. Ethane crackers primarily produce ethylene and only small amounts of co-products, whereas liquid crackers produce a range of olefins and aromatics, including butadiene, propylene and benzene.

West European ethylene production is approximately 24 MM tpa, which represents a 21% market share of worldwide production. Naphtha and condensates together provide 74% of the feed to the European crackers; 13% of the feedstock is from NGL (ethane, propane and butane), with the balance being gas oil. On average, from 2008–2011, ethylene capacity is expected to increase by 3%.

In a relative sense, European steam crackers use more liquids in the feed slate (eg, naphtha or gas oil) than Middle Eastern producers, which use cost-advantaged NGLs. NGL-fed plants or gas crackers are less complicated because they require only a water quench system and fewer process units for the by-products. The main attraction for gas crackers is the lower feedstock cost, which is often subsidised by national governments and is lowest in the Middle East.

Downstream processing of cracked hydrocarbons from liquid feedstocks (naphtha and gas oil) is somewhat more complex than the processing of gaseous feedstocks because heavier components are present. In this case, a primary fractionator is installed upstream of the compressor to remove fuel oil, which is produced in considerable amounts when cracking naphtha or gas oil. This fuel is partly used in the direct quench operation, while the remainder may be sold or used as fuel for steam generation. The primary fractionator also produces a gasoline stream, called pyrolysis gasoline or pygas, which is rich in aromatics (benzene, toluene and C_8 aromatics). This pygas portion of the cracker products contains a host of valuable petrochemicals that can be recovered if they are available in sufficient quantity and a suitable recovery method is chosen.

Figure 1 provides a guideline of which products may be economically recovered as a function of ethylene rate. With today's typical increased cracker size, many of these products are economical to produce. When the ethylene rate

exceeds 400 KTA, butadiene, benzene and toluene production become economically feasible. At 600 KTA and above, styrene extraction, production of C_9 resins, xylenes, benzene derivatives and C_4 derivatives become economic. Isoprene, dicyclopentadiene (DCPD) and piperylene recovery will be economical at 800 KTA ethylene feed. The steam cracker C_5 s have a variety of end uses. These are often overlooked or considered as orphan streams due to a lack of knowledge about end markets and processing methods.

Polyisoprene is a substitute for natural rubber, which is being constrained by land use in Southeast Asia that has been set aside for palm oil plantations. The supply/demand balance for isoprene has tightened in recent years, sometimes resulting in sharp upward shifts in pricing. Piperylenes (cis and trans 1,3 pentadiene) are used as a reactive monomer in the manufacture of plastics, adhesives and resins. DCPD is used for printing inks and as a precursor to unsaturated polyester resins.

After ethylene and propylene, benzene is the next most widely produced steam

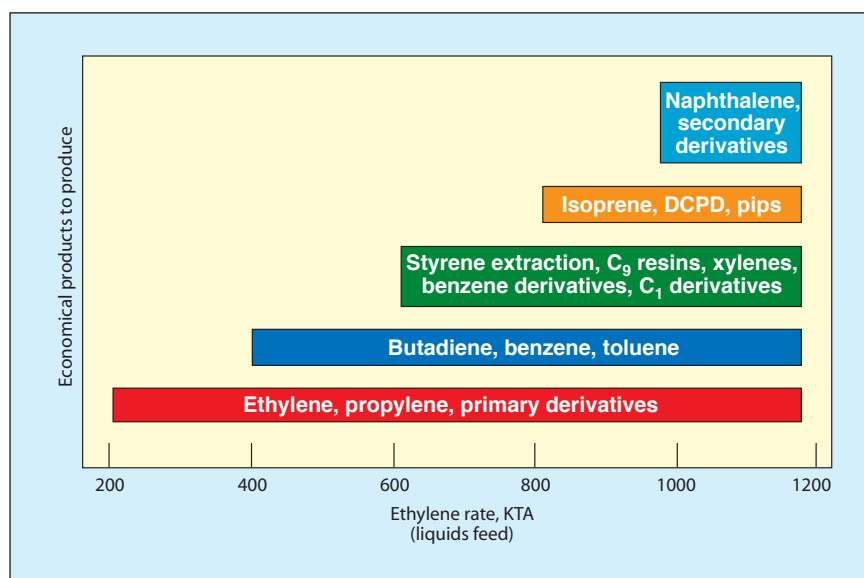


Figure 1 Economical products as a function of ethylene rate (liquids feed)

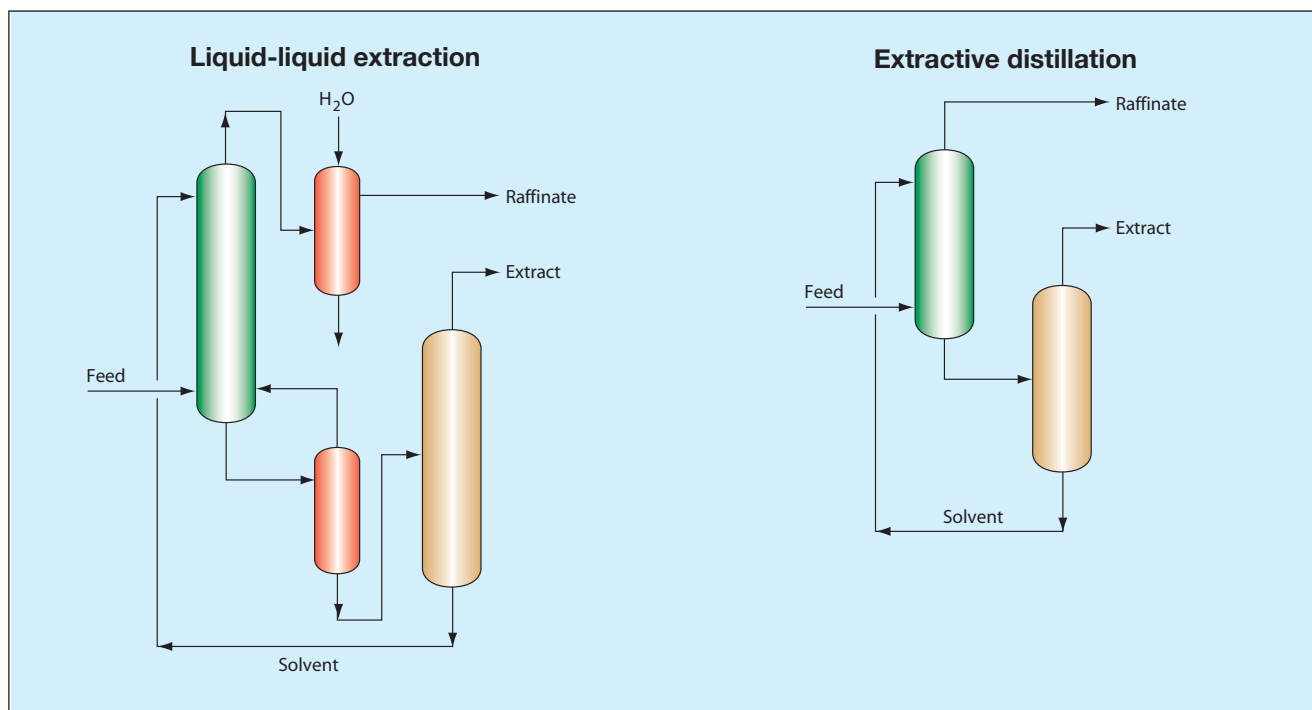


Figure 2 Liquid-liquid extraction and extractive distillation

Properties of Tectiv-100 extractive distillation solvent

Physical properties	High-boiling; polar; non-nitrogen-containing components
Toxicity	Low
Corrosivity	Mild against carbon steel
Stability	Thermally stable at design/operating conditions
Reactivity	Non-reactive to feed components
Effective range	15% to >99% aromatics in the feed

Table 1

cracker petrochemical. Benzene has been denigrated as a cancer-causing dangerous product. Government legislators have deemed that the benzene content in motor gasoline should generally be lower than 1 wt% worldwide and 0.62% in the US to protect the citizens in these areas. While this has dampened the spirit for aromatics recovery, benzene, toluene and xylene (BTX) production is very much alive and needed, and somewhat encouraged by the need to remove the components from gasoline. In order to maintain competitiveness in the ethylene business, more emphasis must be placed on upgrading all of the by-products that are available in the value chain of liquid crackers.

BTX recovery

Figure 1 is not exact for every producer, but is a useful guideline to highlight what typical commodity products could be recovered. Individual plant sites will have different economies based on local supply/demand, logistics of product movements and construction costs. The first priority for component recovery from the pygas is BTX. Most plants already have aromatics extraction units

or sell the BTX cut to other units that recover the aromatics. Two technologies are used for BTX recovery:

- Liquid-liquid extraction (LLE)
- Extractive distillation (ED).

The schematics of these two processes are shown in Figure 2. In the last few years, nearly all new units have been designed using ED technology, which offers a simpler design and better process performance.

GTC offers the proprietary GT-BTX process for aromatic recovery by ED. The working principle of ED is the alteration of the relative volatility of components in the presence of a highly selective solvent. In a mixture containing aromatics and non-aromatics, the relative volatility of the non-aromatic components is enhanced over that of the aromatic components in the presence of a solvent. This enhancement allows the non-aromatics to be distilled overhead in a conventional distillation column, while the aromatics are recovered in the column bottoms. The solvent used in the GT-BTX process is the proprietary blend, Tectiv-100, which makes it possible to achieve the process performance with BT- or BTX-containing feedstocks. Tectiv-100 can

process wide-cut feeds instead of benzene-only in the ED configuration. Previous generations of solvents could be used only with fractionated narrow-cut feeds or with very high aromatic content to avoid the situation of three-phase distillation. The primary properties of the solvent Tectiv-100 blend are shown in Table 1.

The flow scheme of the GT-BTX process is quite simple (Figure 3). It consists of two towers: an extractive distillation column (EDC) and a solvent recovery column (SRC). The EDC cleanly separates the aromatics and solvent into the bottoms from the solvent-free non-aromatics in the overhead. The second column strips the aromatics from the solvent, which is recycled back to the first column.

Since the proprietary GT-BTX system requires only two major unit operations, it is easier to design and operate than the LLE processes. In LLE systems, the solvent makes an incomplete separation of the components at both ends of the extraction column, thus requiring the additional steps of extractive stripping and water washing of the raffinate. In GTC's ED system, the ED column cleanly removes the non-aromatics from the aromatics, and the aromatics and solvent from the raffinate, in a single operation. Therefore, ED designs require fewer pieces of equipment and a much lower capital cost than a LLE system or other ED systems that require washing of products or reprocessing of the raffinate.

Several variants of this technology can be used to revamp older LLE units based on sulpholane, NMP, NFM or glycol solvent systems. GT-BTX Plus technology is used to separate aromatics



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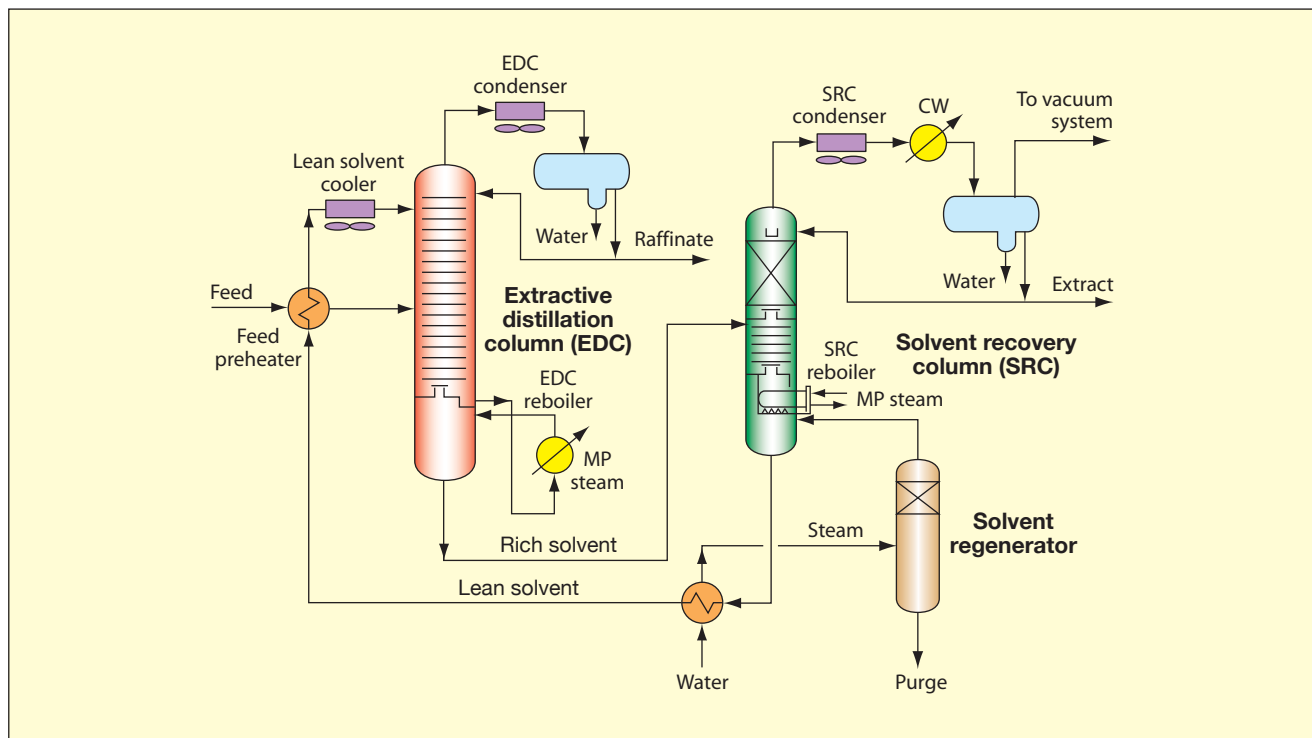


Figure 3 Process flow scheme for GT-BTX process

plus sulphur from feedstocks that contain olefins.

Styrene recovery

The next profitable component to recover is styrene, extracted from the C_8 fraction of raw pygas. In a typical pygas operation, the styrene is hydrogenated to ethylbenzene (EB) in the pygas hydrotreater units to reduce the gum-forming potential of the gasoline. Unfortunately, this downgrades the component value, consumes valuable hydrogen, uses capacity in the pygas hydrotreating unit and decreases the potential value of the remaining xylenes. Styrene cannot be purified by conventional distillation because of the presence of many other components with close boiling points.

New technology that recovers the styrene from pygas via the ED method is now being commercialised. The proprietary GT-Styrene technology is the most cost-effective process for recovering styrene from untreated pygas. The economics are good for reasonable-sized crackers using liquid feedstock.

The styrene extraction technology is applied to upgrade the styrene to petrochemical value and to improve the quality of the mixed xylenes. Figure 4 shows the conceptual arrangement, while Table 2 gives prospective economics at recent pricing. A proprietary solvent system, Techtiv-200, is used to change the relative volatility of the pygas components and allow the styrene to be selectively extracted. The cash cost economics are favoured over conventional styrene production from benzene plus ethylene in all pricing

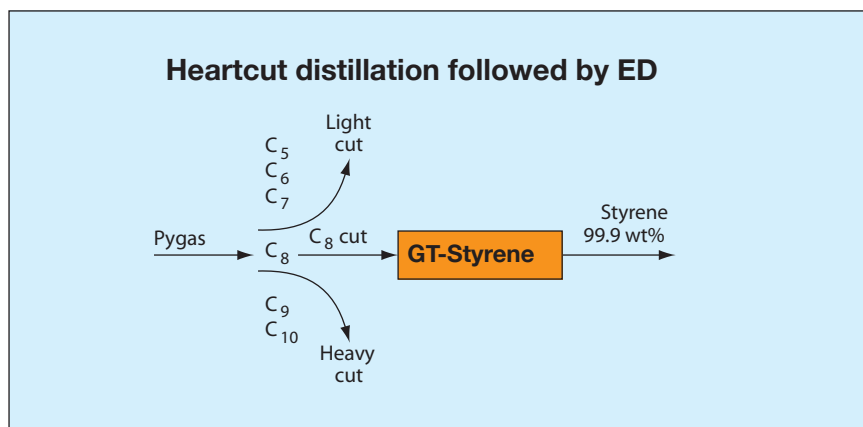


Figure 4 Conceptual arrangement for proprietary GT-Styrene process

scenarios.

The process also provides other advantages by upgrading the xylenes (with lower EB content), reducing hydrotreater operating costs and hydrogen consumption, and increasing hydrotreating capacity. Styrene is produced at high purity, suitable for

polymerisation, at a significant upgrade over its alternate value as a gasoline-blending component.

The analysis indicates that the extraction technology provides profitable production of styrene at relatively small capacities. Prime candidates for the technology are ethylene producers that can generate sufficient pygas feedstock to produce at least 20 000 t/yr of styrene. This would include major naphtha-based steam crackers in Europe, Asia and the Americas. The required capacity for GT-Styrene is at least 15 000 t/yr contained styrene in pygas.

Olefin conversion to aromatics

Other low-value steam cracker products can be converted to additional BTX components with a novel aromatisation technology. This process converts olefins in the C_4 - C_8 range into a mixture of C_6 - C_9 aromatics. Typical feedstocks are the

Prospective economics at current pricing

Parameters	GT-Styrene
Capital cost, \$	30 MM
Feedstock cost, \$/tonne	850
Processing cost, \$/tonne	250
Total production cost, \$/tonne	1100
Sales price, \$/tonne	1600
Net margin	12.5 MM
Pre-tax ROI, %	42

Basis: 250 000 MT/yr styrene

Table 2

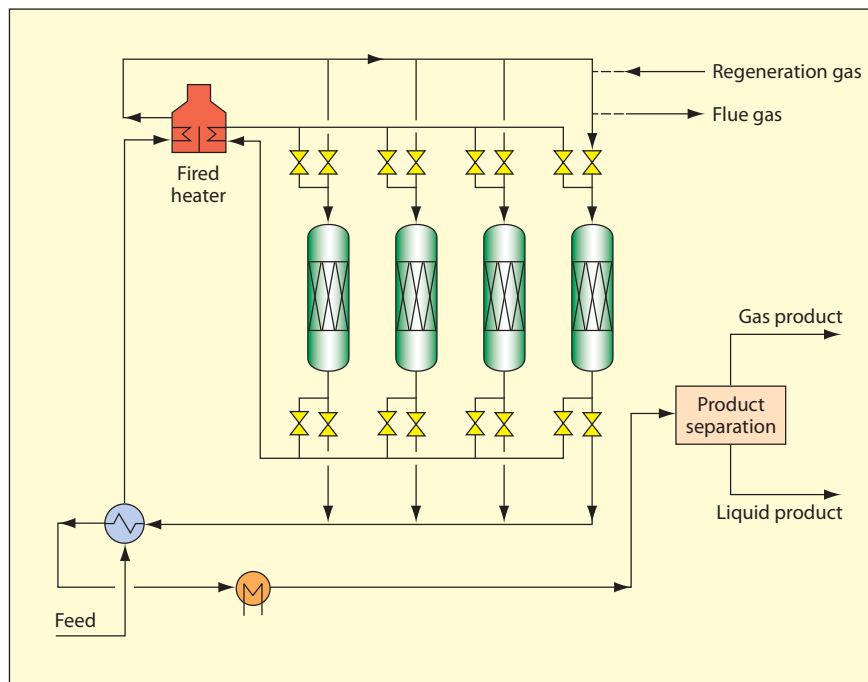


Figure 5 Scheme for the aromatisation process

mono-olefin C_4 or C_5 fractions, or the olefinic C_6 - C_8 fractions from partially hydrotreated pygas. C_4 s usually come from the raffinate after BD extraction, the raffinate after i-butene extraction for MTBE, or a mixture of the above. C_5 s include raffinate after isoprene and CPD extraction, partially hydrotreated C_5 s, or a mixture of these. C_6 - C_8 s are the olefins from partially hydrotreated pygas. Another feed source is from refinery FCC gasoline after removal of the aromatics. In the aromatisation process, olefins and naphthenes convert at approximately a 1:1 ratio into aromatics. The products are rich in xylenes and xylene precursors, and therefore useful

for feeding into a paraxylene complex. Figure 5 highlights the aromatisation process.

The aromatisation takes place in a single-stage adiabatic fixed-bed reactor, which operates in a cyclic mode of regeneration. The operation is very simple, with no hydrogen required. The reactor is operated at 460–540°C and the pressure is 1–4 bar. Catalyst lifetime is greater than two years. The liquid yield of aromatics is approximately 47–55%, depending on feedstocks. By-products are dry gas and LPG, with yields of 15–20% and 30–35% respectively. Separation of liquid aromatics products may be accomplished by simple fractionation.

EB Dealkylation

Further down the C_8 chain, pygas xylenes can be selectively dealkylated to produce isomer-quality material. Typically, pygas C_8 streams have high EB content and are not desirable for use as paraxylene plant feed. The proprietary EB Dealkylation process was developed for increasing PX production capacity by converting EB into benzene plus ethane. Benzene product is high purity (99.8 wt%) without extraction. The ethane can be combined with cracker feed to produce additional ethylene. The technology features a proprietary catalyst with high activity, low ring loss and superior long cycle length.

Figure 6 shows a typical configuration of EB Dealkylation with the GT-BTX and GT-Styrene technology. The feedstock is pygas C_8 . In the hydrogen environment, EB is dealkylated to benzene with per pass conversion up to 100%, which results in very low EB content in the mixed xylene product. The xylene loss and ring loss are very low even at high EB conversion. The low EB xylene product can be either sold on the market at a premium price or used in a paraxylene recovery plant to debottleneck production. Benzene and the small amount of toluene generated can be sent to the fractionation section to produce on-spec products. Highlights of the EB Dealkylation process are:

- Simple, low-cost fixed-bed reactor design
- Flexible feedstocks and operation
- Stable catalyst with long operating life
- Low hydrogen consumption
- Moderate operating parameters.

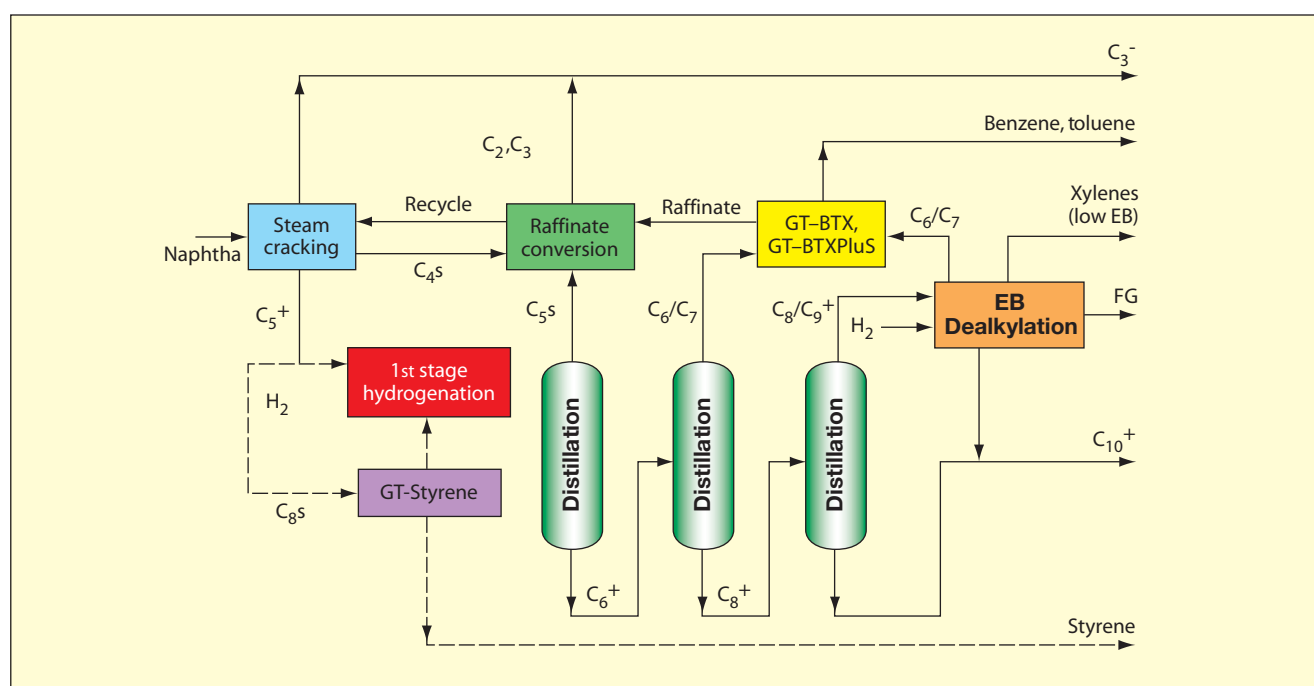


Figure 6 Combinations of GT-BTX, GT-Styrene and EB Dealkylation

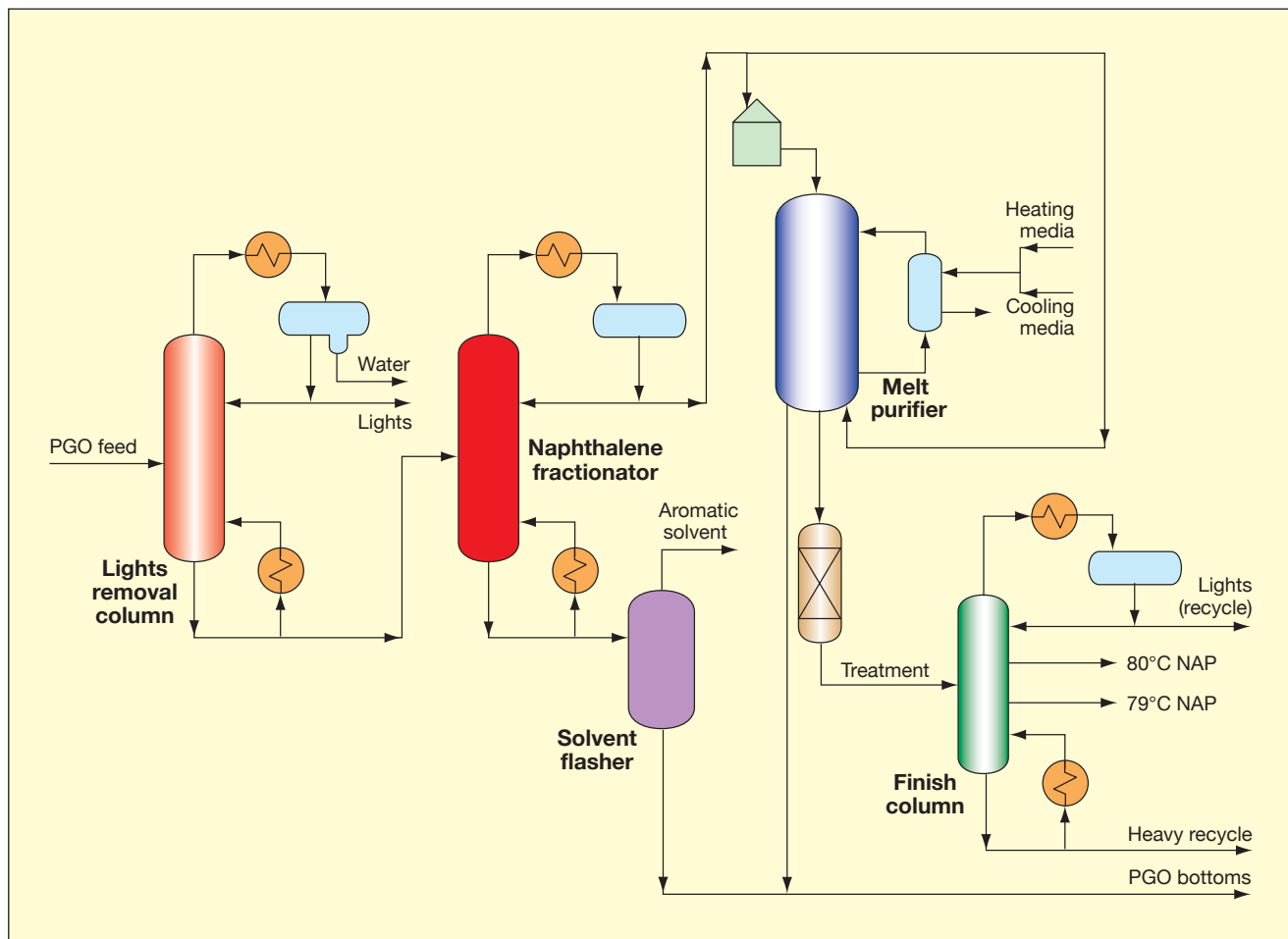


Figure 7 Naphthalene separation process

Naphthalene

In the heavier cut of pyrolysis gas oil (PGO), naphthalene can be recovered. When a cracker size crosses the 1000 KTA mark, naphthalene recovery is economically feasible. The method of choice is a static-melt crystallisation process, such as that used at the largest North American producer's site. This operation produces refined naphthalene with a MP of 80°C, along with aromatic solvents and speciality fuel products. Various product derivatives can further increase the profitability of naphthalene recovery. The generic flow scheme of heartcut fractionation followed by crystallisation is shown in Figure 7.

Naphthalene is available in three grades (MP based): 78°C, 79°C and 80°C. Refined naphthalene from PGO feedstock is clear, with low levels of sulphur. Major sections of the process involve prefractionation and crystallisation operations. Prefractionation uses distillation to produce a concentrate of naphthalene. The melt purifier employs progressive freezing in a static device with no moving parts and low equipment cost. Optional operations are used to produce 79°C and 80°C naphthalene from 78°C naphthalene.

The process design using static melt purification is the cheapest way to produce high purity naphthalene. With

the static freezing technique, slurry handling is avoided, which simplifies the operation. The system is also reliable. No moving devices such as filters or centrifuges required, so the investment and operating costs are reduced.

Conclusions

Although European crackers may be disadvantaged on the basis of pure ethylene production, these units can maintain a viable and profitable operation if the by-products are strategically upgraded. Many of the secondary products are economical to produce at ethylene rates as low as 600 KTA. The key to realising this value is an understanding of the range of products that are possible to produce and utilising the latest process technology for the petrochemical upgrades.

BTX recovery is basic for all crackers, and it is economical at a cracker capacity as low as 400 KTA. ED technology has replaced LLE due to its simplicity and increased performance in separating close boiling components. ED technology also makes styrene recovery from pygas viable for reasonable-sized crackers using liquid feedstock. Advanced aromatisation technology transforms low-value steam cracker C_4 - C_8 products to higher-value BTX components. EB Dealkylation is useful to produce high-quality xylenes

with benzene by-product. Naphthalene recovery from PGO is profitable when the cracker size crosses the 1000 KTA mark. Otherwise, PGO is traditionally consumed as fuel for boilers or sold at heating value.

In summary, there are a number of new processes that are applicable to the C_5+ spectrum of by-products from naphtha-based steam crackers. In order to maintain a competitive position, a cracker operator needs to consider taking advantage of all the possible upgrade opportunities presented.

This article is based on a presentation at the recent ERTC Petrochemical Conference in Cannes, October 2008. GT-BTX, Techtiv-100, Techtiv-200, GT-BTX Plus, GT-Styrene and EB Dealkylation are marks of GTC Technology.

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Control of primary fractionator fouling

Optimal operation and chemical treatment of primary fractionators requires an in-depth knowledge of many parameters. A combination of analytical tools and benchmarking information can help predict fouling severity

Bob Presenti, Dan Frye and Sandra Linares-Samaniego
Nalco Company

The ethylene industry remains extremely competitive. Fouling in primary fractionators costs ethylene producers millions of dollars annually in lost production, product downgrades, reduced energy efficiency and unplanned shutdowns. The primary fractionator in a liquid cracker represents one of the largest potential material and energy cost debits if fouling is not controlled. While the fouling mechanisms in primary fractionators have been studied extensively over the past few decades, they are by no means fully understood.

The overlying problem for most ethylene producers is the ability to effectively monitor the impact of fouling on primary fractionator performance. Often, proper instrumentation is either unreliable or non-existent and plant operators are challenged to answer the questions “Is my tower fouling?” and, if so, “What do I do to stop it?”. As part of Nalco’s Best Practices primary fractionator treatment programme (PrimAct), benchmarking, analytical and monitoring tools have been developed to give ethylene producers an improved tool to evaluate fouling tendencies. This in turn helps us understand and optimise the economic impact of fouling and operational optimisations.

Fouling in a primary fractionator

Primary fractionator fouling can be broken down into two distinct problem areas: top section fouling and bottom section fouling. The fouling mechanisms in the top and bottom sections of a primary fractionator are quite different. Analyses of top sections of fractionators across the industry indicate that the predominant fouling mechanism is the deposition of cross-linked polystyrene-type polymers formed through free radical polymerisation, whereas fouling in the bottom section of the primary fractionator is caused by the

agglomeration and deposition of polynuclear aromatic hydrocarbons (PNAs).

Top section fouling is usually identified by increased differential pressure (DP) and increased overhead endpoint. While increased DP can limit the throughput and decrease the unit run length, an elevated pygas endpoint can lead to emulsions in the quench water loop and product downgrades downstream.

Fouling in the bottoms section of a primary fractionator will cause changes in the viscosity control of the circulating quench oil, loss of heat recovery, a decrease in dilution steam production, an increase in pump energy usage and poor filter operation, as well as many other issues.

Stream characterisation and benchmarking

The primary fractionator is usually the first tower after the transfer line exchanger (TLE) or furnace. The primary functions of this unit are heat recovery and crude fractionation of the furnace effluent. Basic plant configurations vary widely from plant to plant, but most fractionators have a top stream, bottom stream and a light fuel oil stream. Due to the variability in design and operating conditions, a comprehensive approach to primary fractionator treatment and monitoring that includes the characterisation and benchmarking of the process streams was undertaken. Figure 1 shows the sampling points and summarises some of the tests undertaken on each of these streams.

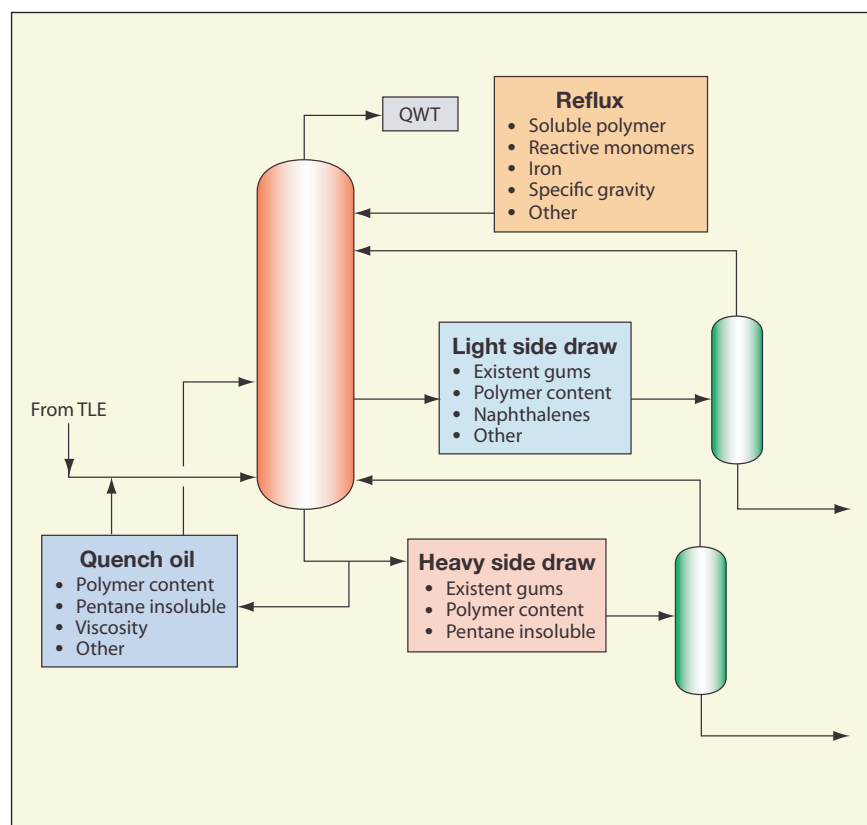


Figure 1 PF survey sampling points and testing

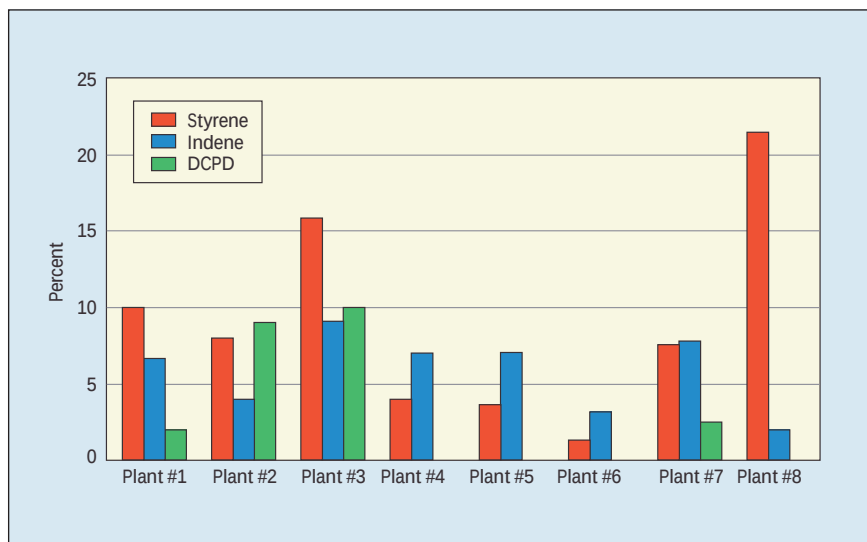


Figure 2 Average reactive monomer in reflux

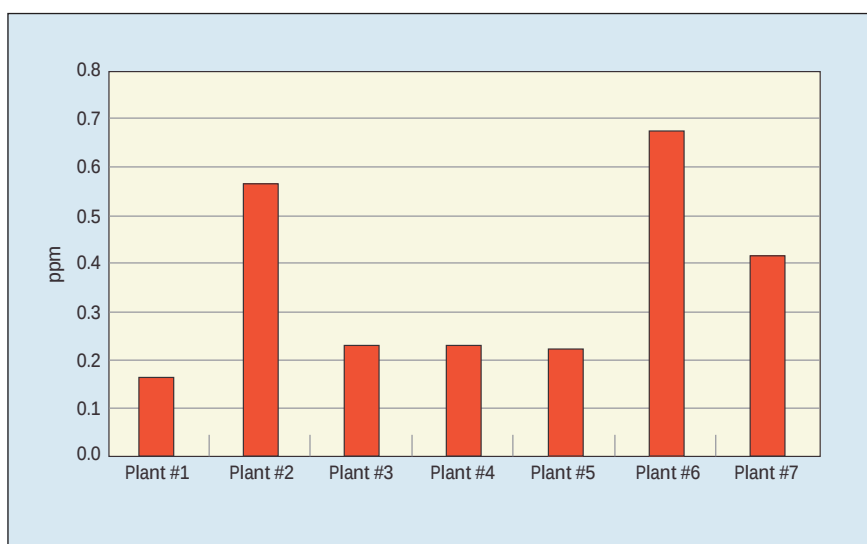


Figure 3 Average iron levels in reflux

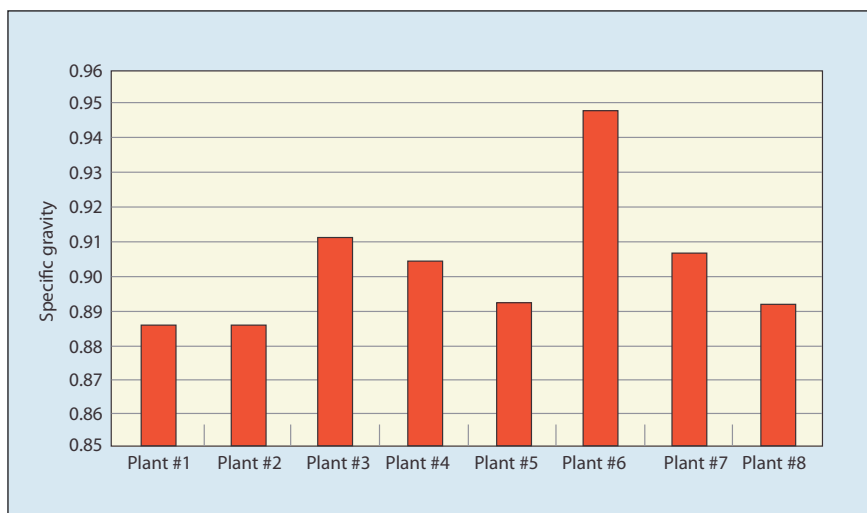


Figure 4 Average specific gravity of reflux

A database of analytical results from ethylene plants throughout the world is being compiled and continues to grow, as over 400 samples have been analysed to date. This database allows for continuous expansion of knowledge

and serves as a benchmarking tool for other units. Currently, the database is comprised of towers that have experienced fouling problems as we work with each ethylene producer to improve reliability. A portion of the

benchmarking data for reflux streams is included on the following pages in Figures 2 to 5.

Reviewing the benchmarking data in Figures 2 to 5 reveals that stream characterisation is plant specific and that further investigation is required before the fouling severity in a tower can be predicted based on analytical data. Still, several observations exist based on Nalco's initial survey of reflux streams:

- Styrene content alone does not predict fouling severity, as polystyrene is very soluble in styrene

- Styrene and indene levels are independent of each other (Figure 2). Indene will cross-link with polystyrene to form a polymer that is less soluble in the liquid stream

- DCPD is present when the reflux contains recycle streams (Plants 1, 2, 3 and 7 in Figure 2). DCPD reacts via a Diels-Alder mechanism to both form polymer and cross-link with other oligomers and polymers like polystyrene

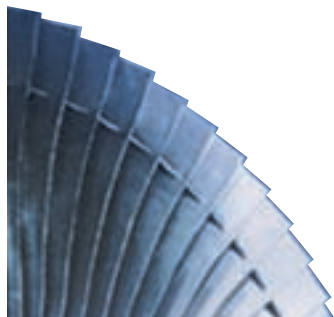
- Iron does not appear to exist in significant quantities (Figure 3).

Specific gravity of the reflux stream (Figure 4) is indirectly controlled as each ethylene operator attempts to maximise pygas flow while maintaining stream endpoint within a targeted range. As specific gravity approaches 1.0, the potential for emulsion and separation problems in the quench tower and downstream equipment increases.

Figure 5 summarises the soluble polymer levels in the reflux using a Nalco proprietary lab method. This data is interesting not only because it demonstrates significant variation in soluble polymer from plant-to-plant, but also because the levels in some of the reflux streams are much higher than previously anticipated. This suggests that in addition to the polymerisation occurring inside the tower, polymer is being formed at varying levels outside of the primary fractionator and transported back to the tower via recycle streams or the quench tower gasoline reflux.

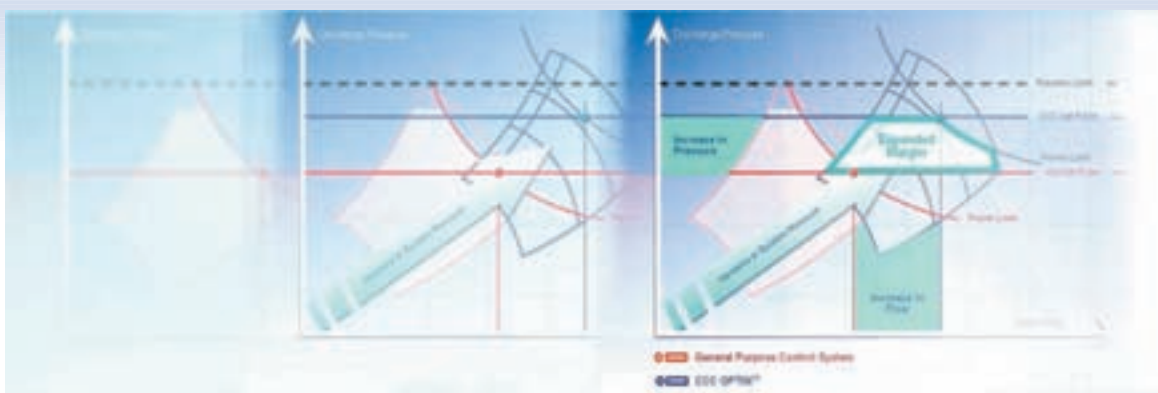
Field monitoring techniques development

Many ethylene producers have become frustrated with conventional monitoring techniques like delta pressure (DP) as a measure of fouling in the upper section of a primary fractionator. Two goals to address this problem have been identified. The first involves the application of statistical modelling to improve the ability to detect fouling in DP trends. The second is to develop other monitoring techniques to support the DP analysis. Figure 6 outlines Nalco's initial statistical modelling of



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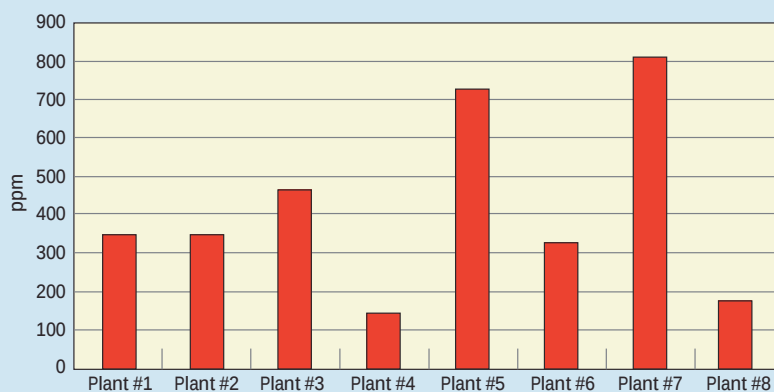


Figure 5 Average soluble polymer in reflux

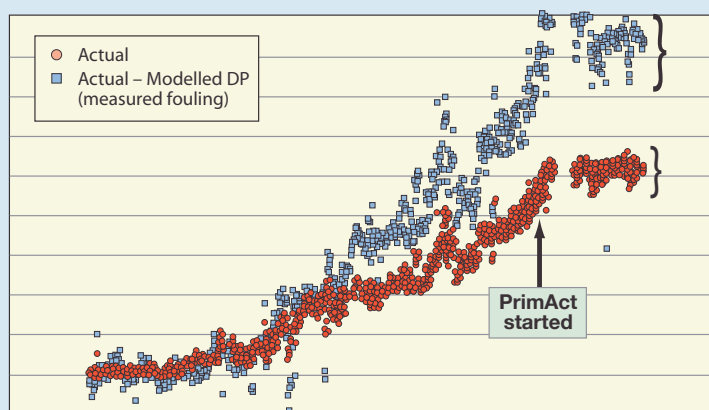


Figure 6 Actual modelled DP using statistical modelling

one plant's primary fractionator tower DP.

Using statistical modelling software, three separate models were created and compared. The models helped smooth the DP trend and remove hydraulic impacts. This analysis offers an improvement over traditional flow-corrected multivariate regressions of tower pressure drop by addressing limitations due to non-linearity and autocorrelation of "independent" variables typical of actual plant operations.

In addition to focusing on statistical modelling, two proprietary field analytical methods were developed to measure the polymer content in the reflux and the light side stream. The results from the new field methods have correlated strongly with other proven soluble polymer methods, such as that outlined in Figure 5, but the advantage to the field methods is that results can be obtained within minutes on-site. These methods allow for robust comparison of relative polymer content

with respect to a baseline, thus providing a tool for monitoring operational or chemical treatment changes in the unit, as can be observed from Figures 7 and 8.

Primary fractionator monitoring

Figures 7 and 8 illustrate that the field methods were useful tools to evaluate operational modifications, as well as changes in chemical treatment. In the previous example, the data was used to

"The optimal operation and chemical treatment of primary fractionators is a very complex issue that requires an in-depth knowledge of many parameters"

understand questionable tower DP data, a problem that haunts many ethylene producers. By trending the ratio of the amount of polymer exiting the upper section in the light fuel oil to the amount of polymer entering the tower in the reflux (fouling ratio), we were able to measure analytically the impact of chemistry and operational changes. A higher fouling ratio translates to more polymer being produced in the upper section of the tower. In the end, the reduction in fouling ratio supported the statistical modelling trends, showing that PrimAct had reduced fouling and flattened a previously upward DP trend. The field methods were also used to test the efficacy of the inhibitor used in the PrimAct program. Figure 8 outlines the results of a plant test, where samples were taken before and after increasing the inhibitor dosage. In this fouled tower, the plant theorised that polymer was entraining overhead. This theory was substantiated, as both the reflux and light fuel oil levels decreased when the inhibitor dosage increased.

Current landscape

Currently, Nalco's industry database includes 15–20 primary fractionators as of the end of 2008 and is expected to continue expanding. The knowledge gained thus far has allowed for the development of the previously discussed monitoring tools and their implementation at four plants, yielding a better understanding of fouling and its impact on plant total cost of operation (TCO). At one plant where fouling was an issue and potentially threatened ethylene production targets, the combination of the field polymer method, economic tools and the chemical treatment programme allowed the plant to survive until the scheduled turnaround. At other plants, anywhere from \$3–10 MM of annual TCO savings have been identified to justify chemical treatment, so that operational optimisations can proceed. Examples of TCO items include the following:

- Reduction of polymer formation in the top section to allow more pygas production
- Controlling the bottom temperature at a higher level without fouling or loss of viscosity control.

As the industry database expands, it will provide an enhanced capability to help ethylene producers compete in the highly competitive ethylene market.

Conclusion

The optimal operation and chemical treatment of primary fractionators is a very complex issue that requires an in-depth knowledge of many parameters, as well as a deep understanding of parameter interplay. For this reason, a comprehensive Best Practices primary

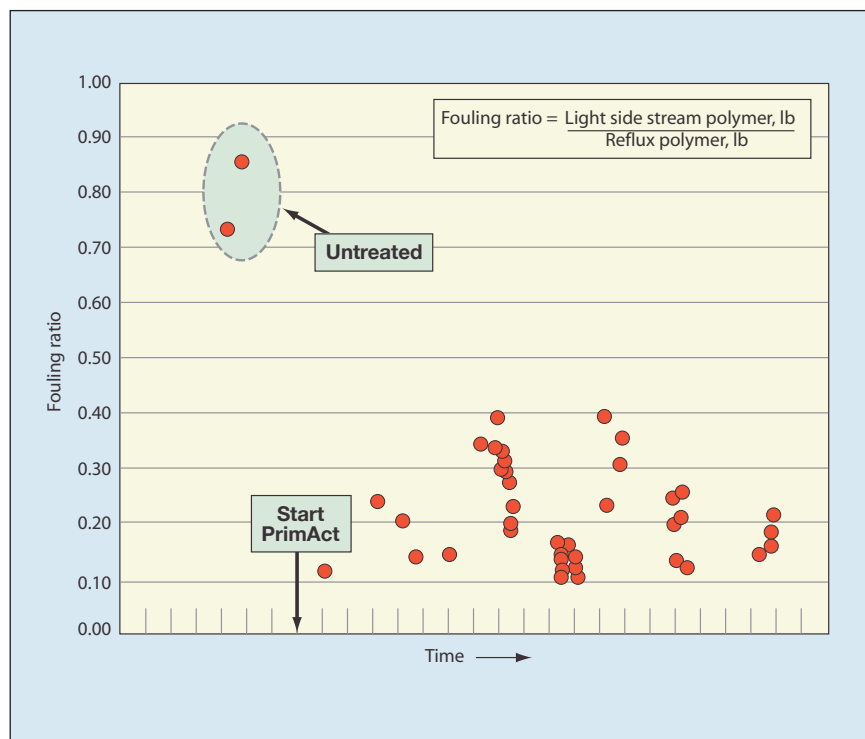


Figure 7 Fouling ratio improves with Nalco PrimAct

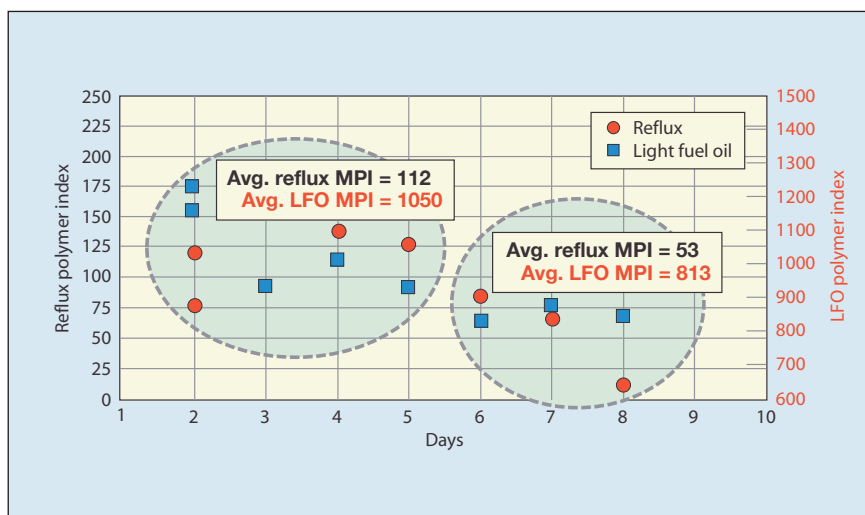


Figure 8 Polymer levels decreased when Nalco PrimAct inhibitor was increased on the fifth day

fractionator treatment programme requires a flexible and wide-ranging approach that includes the development of analytical and monitoring tools, benchmarking data and modelling tools. While only a small portion of the current work has been described and discussed, it nonetheless reveals an example of the challenging nature of the problems faced, as well as the possibilities that further understanding of the system can afford. The first goal has been to innovate with new monitoring techniques that translate to economic optimisations. Looking forward, Nalco believes the combination of these analytical tools with benchmarking information will help towards predicting fouling severity.

This article is based on a presentation from the October 2008 ERTC Petrochemical Conference in Cannes, France. PrimAct is a registered trademark of Nalco.

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Reducing FCC regenerator emissions

There are several ways of meeting emission limits, but SO_x and NO_x reduction additives are very attractive as they require little or no capital investment and have reasonable operating costs, resulting in an overall lower cost than a WGS or SCR

Chris Kuehler, Pieter van de Gender and Subramani Ramachandran
Albemarle Corporation

Increasingly severe regulation of sulphur oxide (SO_x) and nitrogen oxide (NO_x) emissions from FCCUs is being implemented around the world. Although there are a variety of approaches for meeting emission limits, the use of SO_x and NO_x reduction additives appears to be very attractive technically and economically.

SO_x and NO_x emissions from many industrial sources have long been regulated worldwide. In the US, in addition to possible state and local regulations, SO_x and NO_x emissions from FCCUs have been most recently impacted by an Environmental Protection Agency (EPA) programme of civil enforcement of the Clean Air Act (CAA). Citing alleged violations of the CAA, the EPA has entered into settlements (consent decrees), which provide for both possible fines and mandatory implementation of pollution control technology.

Since March 2000, the EPA's national Petroleum Refining Priority Program has resulted in 21 settlements with US refiners, accounting for approximately 86% of the nation's refining capacity.¹ These settlements, covering 95 refineries, will result in an estimated \$5 billion investment in control technology with an annual reduction in SO_x emissions of 245 000 tonnes. The consent decrees cover a variety of emission sources, but there is a heavy focus on the FCCU.

The consent decrees generally prescribe the implementation of emission reduction technology, but in some cases refiners accept hard limits for the FCCU flue gas, which they meet by methods of their choice. The ultimate SO_x emission target for all refiners is 25 ppmv. The corresponding target for NO_x emissions is 20 ppmv.

In the 27 countries of the European Community, the emissions situation is addressed by the Integrated Pollution Prevention and Control (IPPC) Directive adopted in 1996 by the EU and subsequently transposed into the national legislation of EU Member

States.² Integrated pollution prevention and control is based on a permit system for installations. The Directive does not set standards or thresholds for the prevention and control of emissions, or for other environmental aspects, but leaves this responsibility to the Member States. The IPPC Directive applies to both new and existing installations (ie, those built before 2000), where the operators intend to carry out changes that may have significant negative effects on human health and the environment. Member States were given a transitional period until October 2007 to ensure all other existing installations fully comply with the Directive.

In contrast to the US, where the consent decrees set limits on individual FCCUs, most countries in Europe look at emissions from a "bubble" point-of-view. Local authorities issue permits based on Best Available Technique (BAT). BATs, documented in Best Available Technology Reference documents (BREFs), have been developed for individual industrial processes by the exchange of information among experts from industry, Member State authorities, research institutes and non-governmental organisations (NGOs). The original BREFs are currently being updated.

In the rest of the world, a variety of local, regional and national systems regulate gaseous emissions from FCCUs. In South America, each country has different regulations. For example, in Brazil, SO_x from the FCCU is limited to 1200 mg/Nm³, while in the industrial regions near Buenos Aires, Argentina, there is a 500 mg/Nm³ regulation.

SO_x emissions

SO_x emissions from industrial sources have been a problem since the Industrial Revolution, with the most visible manifestation being acid rain caused from burning coal. In recent years, more focus has been put on other industrial sources such as petroleum refineries, where a major source of SO_x is typically the FCCU.³

Coke formed in the FCCU cracking process is subsequently burned to both regenerate the catalyst and supply the heat required for vapourisation and cracking. Depending on the character of the feed, 5–10% of the feed sulphur reports to the coke and is quantitatively oxidised to SO₂ and SO₃ (SO_x). Left uncontrolled, SO_x concentrations in the regenerator flue gas can reach into the thousands of ppm, depending on feed quality.

FCCU SO_x reduction technology

The means for reducing SO_x emissions from the FCCU regenerator fall into three categories:

- Lowering the sulphur in the feed
- Treating the flue gas downstream from the FCCU
- Use of a SO_x reduction additive within the FCCU.

Lowering the feed sulphur can be achieved through the purchase of lower sulphur feeds and by hydrotreating. Both of these approaches can be expensive, although they bring other benefits, such as improved yield structure and lower sulphur levels in liquid products, and they must be judged on the overall economics. If the refiner is faced with a low SO_x emission limit, it may also be difficult to meet with these approaches alone.

There have been a variety of processes developed for the removal of SO_x from flue gas, but the dominant technology has been the wet gas scrubber (WGS) using caustic as a reagent to regenerate the scrubbing liquid. This technology has been commonly mandated under the consent decrees and is included under BATs in the EU. In a later portion of this article, the economics of this technology relative to SO_x reduction additives are discussed.

Background to SO_x reduction additives

An SO_x reduction additive (or SO_x transfer additive) is designed to pick up

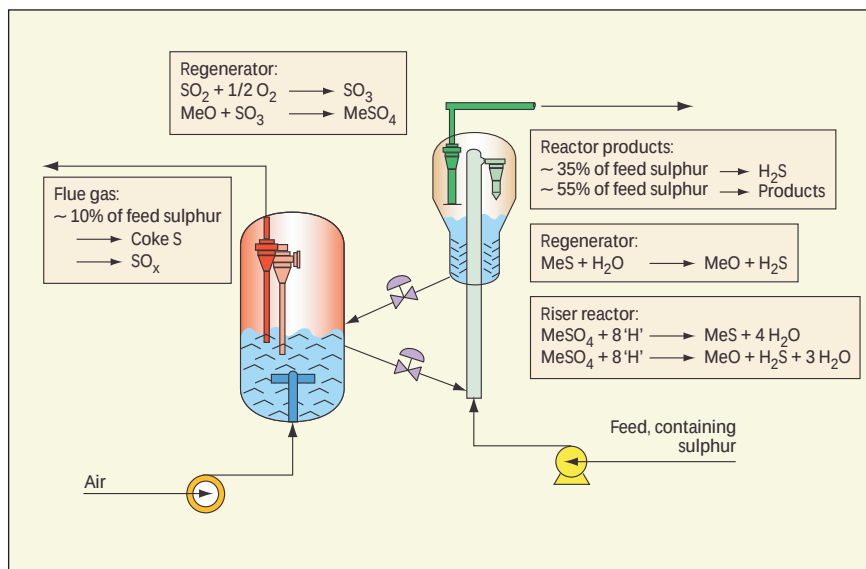


Figure 1 Sulphur in fluid catalytic cracking

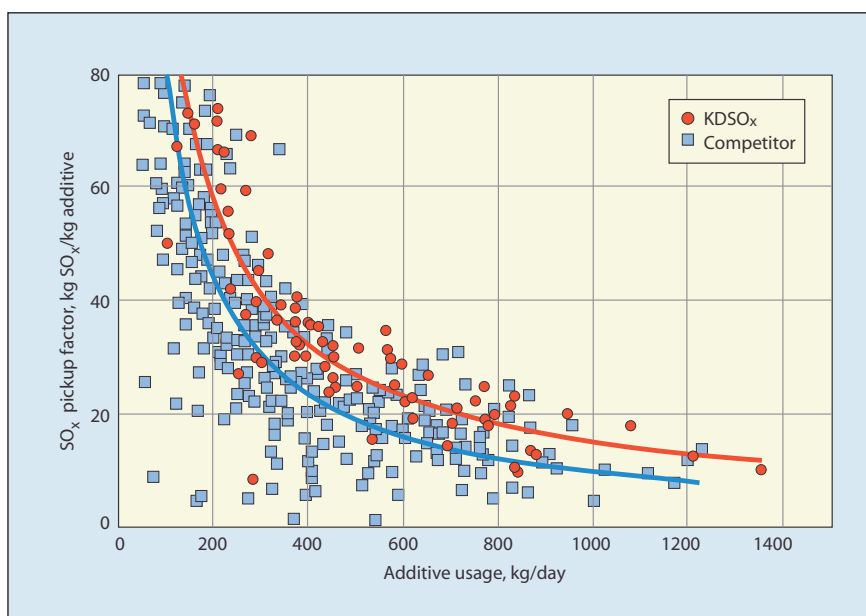


Figure 2 Comparison of KDSO_x to competitive additive

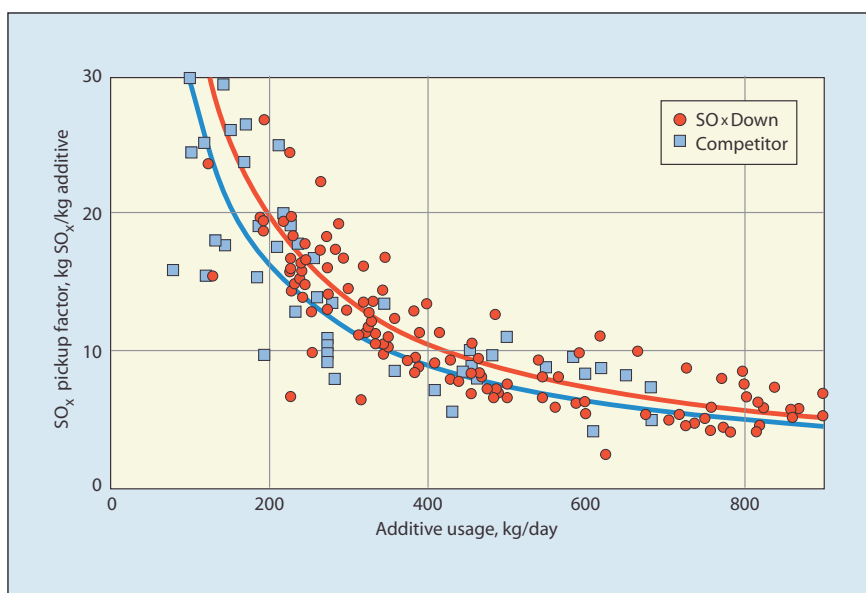


Figure 3 Comparison of SO_xDown to competitive additive

SO_x in the FCCU regenerator and release it as H_2S in the reactor. This is illustrated schematically in Figure 1. In the late 1970s, Akzo Nobel Catalysts (now Albemarle) developed and patented the use of hydrotalcite (HTC) as a SO_x reduction additive⁴ and has continued to develop this technology.⁵ This is a layered magnesia-alumina system with the advantage of being rich in magnesium, which results in improved SO_x pickup compared to competitive technology.

Since this development, Akzo Nobel licensed the HTC technology to the industry. In 2002, the company began marketing its own additives (KDSO_x/SO_xDown) with improvements in SO_x pickup efficiency and physical properties that ensured retention of the additive in the unit. In subsequent years, HTC technology has accounted for approximately 70% of the SO_x reduction technology used in the refining industry. SO_xDown is a subsequent improvement of the KDSO_x additive.

A common measure used to gauge the effectiveness of a SO_x reduction additive is the pickup factor (PUF). This is defined as the weight of SO_x removed per weight of additive used. The weight of SO_x removed is calculated by estimating the mass rate of SO_x that would have been emitted using correlations for uncontrolled SO_x and then subtracting the mass rate of SO_x leaving the regenerator while using the additive. The PUF can vary with operating conditions, in particular additive loading.

Case study 1 VGO operation with a high sulphur feed

Data comparing KDSO_x and a competitive additive are shown in Figure 2 for a 50 000 bpd UOP high efficiency configuration operating in full combustion. Feed sulphur is fairly high at 2.0 wt%. The PUF for KDSO_x is approximately 40% higher than of the competitive product.

Case study 2 Resid operation

The next example comes from a modified Kellogg Model III unit feeding some resid. Regenerator temperature is typically higher than 732°C. A high regenerator temperature can significantly reduce the effectiveness of a SO_x reduction additive. In addition to increasing the hydrothermal deactivation rate, the equilibrium of SO_3 to SO_2 is less favourable. Figure 3 illustrates that at severe regenerator conditions, SO_xDown shows a 20% advantage over a competitive product. Even so, an ongoing R&D programme has been devoted to new products aimed at improving SO_x reduction in situations where SO_x additives have been previously challenged.



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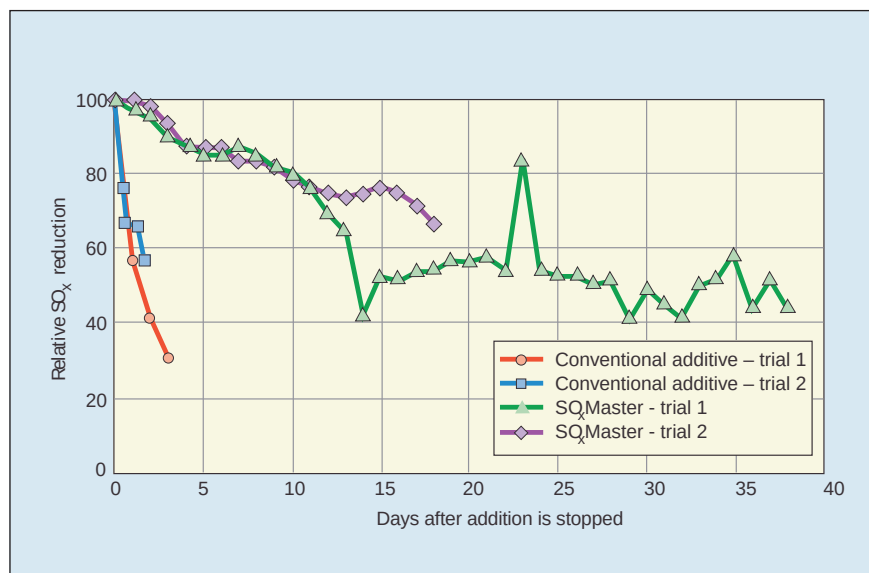


Figure 4 Commercial examples of SO_xMaster performance

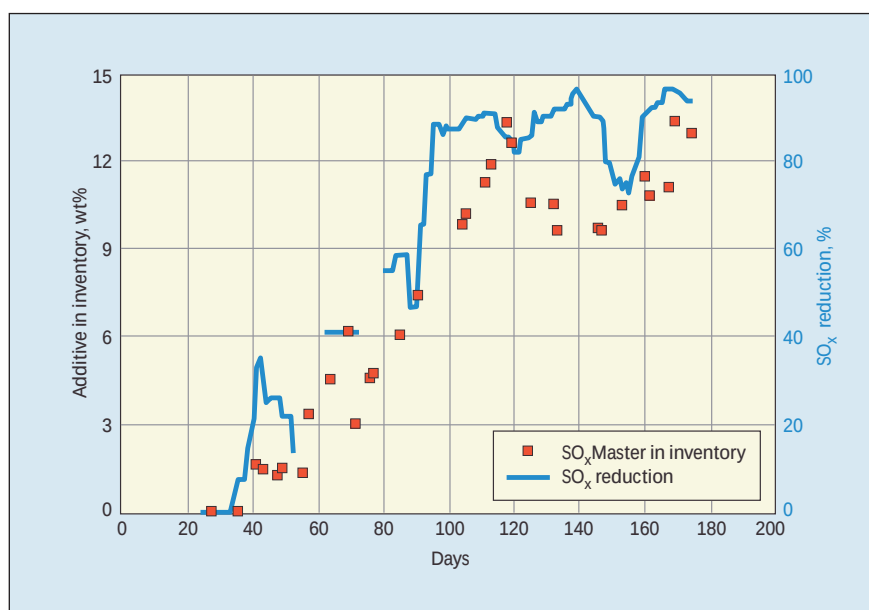


Figure 5 Commercial examples of SO_x reduction using SO_xMaster

Enhanced SO_x reduction

The intrinsic activity of SO_x reduction additives has improved considerably over the past few decades. Many refiners have no doubt benefited from these conventional SO_x additives. In parallel to these additive developments, there is an awareness that many FCCUs are failing to meet SO_x reduction targets, such as when:

- Operating in deep partial-burn mode
- Operating at high regenerator temperatures
- Operating with low daily replacement rates
- The refinery/FCCU is subject to very low SO_x emissions.

For these more difficult applications, additional capabilities that are not available from conventional SO_x additives are required, which is why Albemarle developed the SO_xMaster additive. It includes features that are not available from conventional additives, including:

- Superior stability under commercial FCC conditions
- Improved regenerability
- A lower sensitivity to the availability of O_2 in the regenerator (better performance in partial-burn units).

SO_xMaster is suited for R2R FCC applications, which run with partial burn in R1 (first regenerator) and high temperatures in R2 (second regenerator). Additional benefits with this more sophisticated formulation, compared to conventional additives, are its contribution to E-cat activity and unit conversion. Hence, FCC catalyst consumption can be reduced. It also has a lower CO promotion activity.

The use of conventional additives in deep partial-burn regenerators can upset the CO_2/CO balance, leading to higher CRC and regenerator temperatures. The use of SO_xMaster will have a much smaller effect on regenerator operation in deep partial burn. Figure 4 shows the

deactivation of SO_xMaster and conventional additives in commercial units. Data from four commercial trials are shown: two trials with conventional additives and two with SO_xMaster . These commercial data demonstrate the superior stability of SO_xMaster . Conventional additives lose half of their initial activity within days. With SO_xMaster , lower SO_x emissions continue for several weeks or months after additive addition is stopped.

Case study 3

FCCU in deep partial burn

In case 3, an FCCU processes heavy VGO with an average sulphur content of 1.8 wt%. The regenerator runs in deep partial-burn mode; the average CO content of the flue gas during the trial was 7.3 mol%. Average riser and regenerator temperatures were 527°C and 691°C respectively. The inventory refreshment rate in this unit is high: daily additions are about 4% of the unit inventory.

Figure 5 illustrates the SO_x reduction that was achieved. This refinery managed an impressive 90% reduction in SO_x emissions compared to the typically maximum achievable of 40%. This example clearly demonstrates that SO_x reduction improves as the level of SO_xMaster in the unit inventory is building up. With conventional additives, SO_x emissions are strongly dependent on daily additive dosage. With SO_xMaster , due to the longer half life, additive built up in the inventory also contributes to the overall SO_x reduction achieved.

Case study 4

FCCU in full burn with very low daily replacement

In case 4, an FCCU changes frequently between high sulphur (HS) and low sulphur (LS) VGO. The regenerator is operated in full combustion. Several SO_x additives from different suppliers have been tried in this FCCU without success due to the low inventory replacement rate. Daily additions are only about 0.5 wt% of the unit inventory. SO_xMaster was recommended to achieve the target 50% SO_x reduction with HS feeds.

During the trial, the average sulphur content was 1.6 wt% for HS and 0.5 wt% for LS feeds. Average riser and regenerator temperatures were 508°C and 673°C respectively.

Figure 6 shows the results of the SO_xMaster trial. As predicted, SO_x emissions during HS campaigns could be halved with 10–12 wt% additive. Of course, SO_x reductions are even better with LS feeds, thanks to lower uncontrolled SO_x emissions. On average, the SO_x reduction during LS campaigns was 80%.

This commercial trial again shows that the percentage SO_x removal is not determined by daily additive additions, but correlates with the amount of SO_xMaster in inventory.

Selection of the best SO_x additive

Until recently, all available SO_x additives had high initial intrinsic activity but limited stability under commercial FCC conditions. These types of additives are still the best choice for the easier applications, where relatively small quantities of additives are enough to achieve the target SO_x reduction. SO_xDown is recommended here, as it has the highest initial intrinsic activity. Situations that favour the use of high activity SO_x additives are:

- Regenerators that operate in full burn or at low CO levels
- Low to moderate regenerator temperatures
- Moderate to high daily replacement rates
- Moderate SO_x reduction targets.

There are also many cases where the high initial pickup of SO_x by fresh additives is not sufficient to meet SO_x reduction targets. Large amounts of fresh additive would be required in these cases, resulting in severe activity dilution of the FCC catalyst inventory. For these units, almost all the SO_xMaster additive that is present in the FCCU inventory contributes to SO_x reduction. In contrast to conventional additives, the SO_x removal is not determined by fresh additive additions, but by the total amount of additive in inventory. Situations that favour the use of SO_xMaster are:

- Regenerators that operate in deep partial burn
- High regenerator temperatures
- Low daily replacement rates
- Low SO_x emission targets.

Albemarle has developed a proprietary SO_x model that explains the commercial performance of additives in all FCCUs. This model accounts for the activity of fresh SO_x additives, the effect of operating conditions, and the deactivation and regeneration of these additives in commercial operations.

With this model, it can be determined if an FCCU requires a conventional SO_x additive, or if the high stability of SO_xMaster is the best choice.

SO_x reduction additives vs scrubbers

As discussed earlier, SO_x emissions are being increasingly regulated around the world. Fortunately, refiners have options to meet the mandates. Expanding on the list of options mentioned earlier, primary commercial options include, in descending order of capital investment (not necessarily in order of total costs vs benefits):

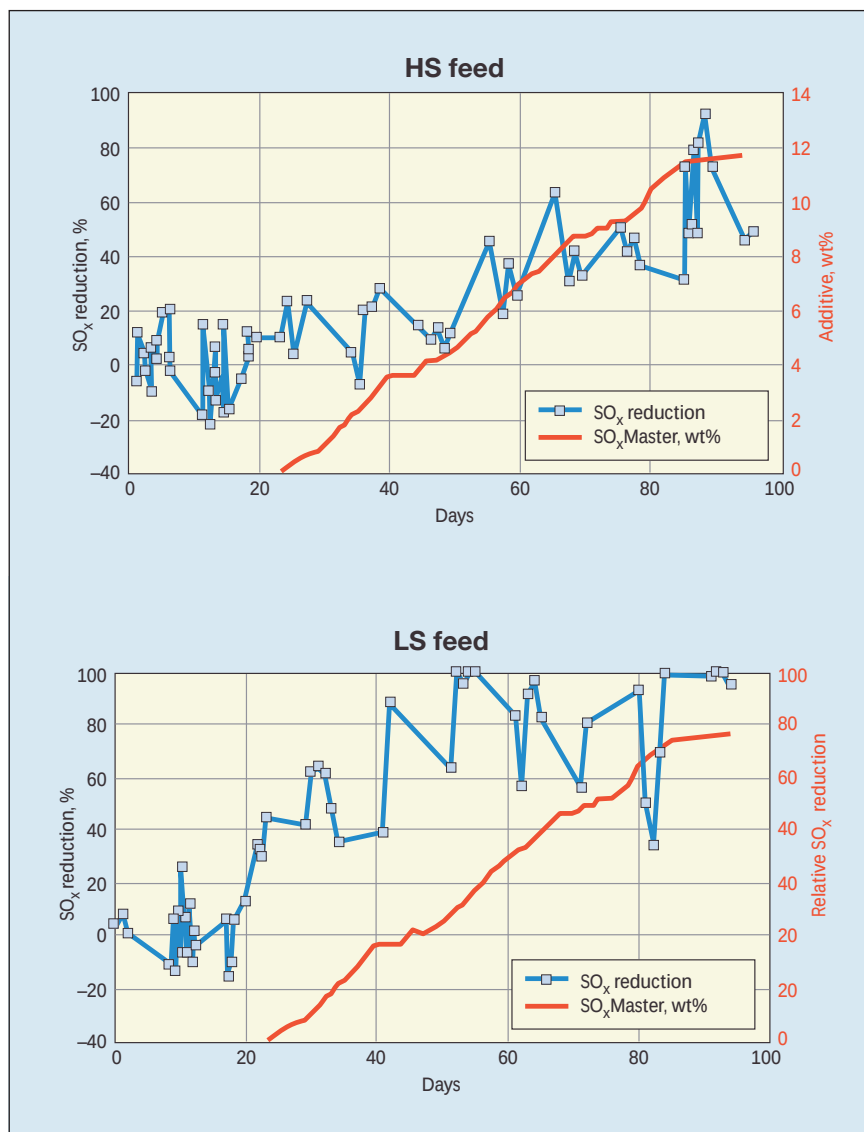


Figure 6 Results of SO_xMaster trial

- Hydrotreat FCC feed: big investment but normally high return value
- Flue gas scrubbing (WGS) with caustic: moderate investment, net costs
- FCC SO_x reduction additive: minimal/no investment, sulphur is recovered
- Low sulphur FCC feed selection: no investment, higher crude cost.

The first option often makes economic sense when adequate capital is available. The economics of the last option vary day-to-day with the spread between high and low sulphur crudes. The middle two options will be reviewed in this section, with a focus on the process and economic issues associated with their commercial applications.

In comparing the installation of a scrubber to using a SO_x reduction additive, a number of points need to be considered. Using additives to remove SO_x actually prevents pollution; scrubbers convert the air pollution to potential water pollution. A WGS consumes valuable resources such as energy and water, while additives do not. Additives require minimum

planning and are highly effective. They are in widespread usage under the consent decrees in the US and are included as a BAT in the EU.

The process aspects of a WGS also need to be considered. There can be pressure drop issues, especially if located downstream from a CO boiler. Use of caustic (NaOH) vs magnesium hydroxide (MgOH) is an economic vs operational issue. MgOH costs less but has poorer solubility, resulting in more erosion/fouling of pumps, control valves, exchangers and pipes. Sulphate deposition in the wash water piping system can lead to plugging of pipes and valves, and there is a need to avoid exceeding a certain level of concentration of solids (0.5 wt% is a typical maximum value). Even then, there are issues with the erosion of pump impellers in the circulation water pumps and the need for abrasion-resistant coatings. With everything in good order, there can still be problems with the formation of a visible plume from the WGS stack, with sulphites/sulphates deposition in the near vicinity.

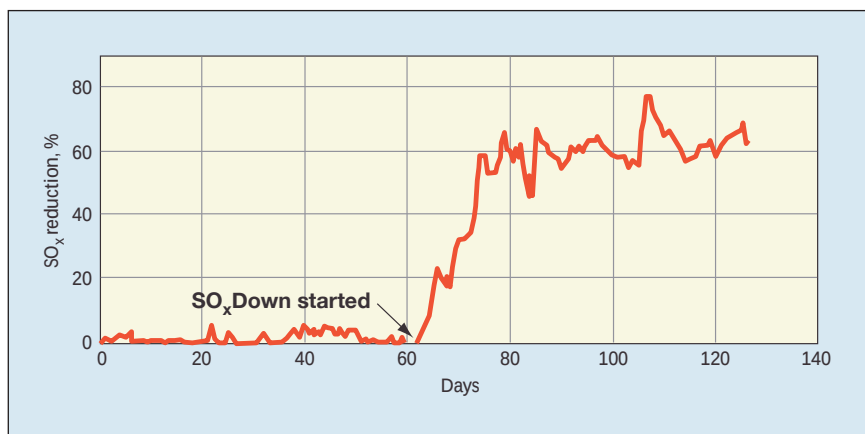


Figure 7 Effect of SO_xDown on SO_x levels

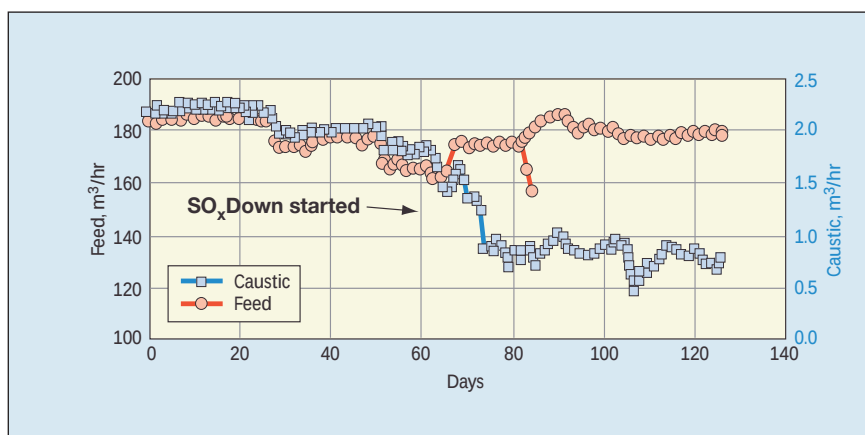


Figure 8 Effect of SO_xDown on caustic usage

Cost comparison of scrubber and SO _x Down				
% reduction		25%	50%	90%
\$ /kg SO ₂ removed (scrubber)	Total costs	3.7	2.2	1.6
	Operating costs	1.05	0.92	0.86
\$ /kg SO ₂ removed (additive)	Daily costs	0.40	0.46	0.70

Table 1

Other aspects to consider are:

- Operational flexibility during a shutdown, especially the need to have an emergency sump to store the water
- Sludge disposal costs
- Loss of the potentially valuable sulphur by-product.

SO_x additive usage with a commercial scrubber

It is clear that additive use could prevent (or at least postpone) the decision to install a scrubber. After the capital has been spent, however, it is still possible to compare additive use to scrubber operation, neglecting the sunk investment costs.

Typically, the major component of a scrubber's variable (operating) costs, caustic usage, is a direct function of the amount of feed sulphur reporting to flue gas. However, location specifics might influence the costs of power and

water, which can be substantial in some cases. Most of the remaining variable costs track caustic use (power, process water, water and solids disposal). The total variable costs are over 40% of the scrubber total cost (including amortised fixed investment) at design removal rate.

As an example, a recent application of SO_xDown in a Middle East refinery with an existing scrubber is reviewed. This FCCU processes 30 000 bpsd of 100% atmospheric resid, with a high sulphur content at 2.7 wt%, and 4 wt% Conradson carbon, operating in full burn. Severe corrosion was observed over a period of time, with sulphur deposits found in the regenerator. The refiner experienced frequent problems associated with corrosion, resulting in blocking of cyclone paths, catalyst losses and subsequent shutdowns. Detailed investigation had indicated that one

potential option for mitigating the regen side corrosion was to reduce SO_x in the regenerator itself through the use of a SO_x reduction additive. The refiner decided to use SO_xDown, while the effective SO_x reduction provided by the additive allowed the refiner to turn down caustic consumption.

Figures 7 and 8 illustrate the effect of the additive on SO_x levels and caustic usage. With a target removal rate of 50%, actual reductions averaging 67% were observed. At the same time, caustic usage was cut by more than 60%.

In the case of this refinery, using the additive permitted a 15% reduction in operating costs in the scrubber, with the sole yield shift a small increase in fuel gas H₂S, as expected. The additive use was more than paid for by the reduced scrubber costs. Lower SO_x also reduced the level of corrosion in the regenerator, an ongoing concern. Given these favourable results, the refiner continued to use SO_xDown even with a scrubber in place. This example clearly illustrates a case where refiner is finding it economically viable to use reduction additives even with an installed WGS.

Economic comparison of WGS and SO_x reduction additives

There are contrasting cost trends for WGS and SO_x reduction additive technologies. Additive costs increase more than linearly as the degree of removal increases. As you would expect, scrubber total costs decrease as the investment is amortised over larger amounts of removed sulphur, although the operating costs increase linearly. Additive use reduces these. More generally, you can estimate the economics for ranges of sulphur removal, comparing total scrubber costs to additive use. An added economic benefit that you need to consider is the value of product sulphur, which is generated from the extra H₂S in the sulphur recovery plant. This economic value also needs to be considered in the comparison, but is location specific. For example, China values this product, while some places (eg, Canadian oil sands plants) have little to no market for sulphur. Not considering the value for by-product sulphur, the economics have been compiled for several levels of removal efficiency: 25, 50 and 90%. Scrubber costs are taken from a Belco publication.⁶ Capital costs were escalated at a nominal 4%/y from 2000 to present, while operating costs were only adjusted for the increase in caustic, since this is the large part of such costs. Caustic price has increased in this period from approximately \$160/tonne to \$400/tonne.

Table 1 compares full costs of scrubber, operating costs only and the daily costs of SO_xDown. The overall conclusion is

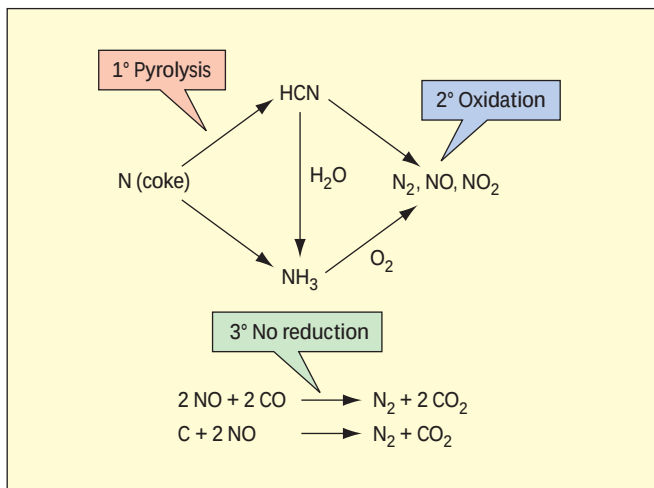


Figure 9 NO_x Formation in fluid catalytic cracking

that additives are very competitive to install in WGS systems, even at very high removal requirements. Even after a WGS has been installed, the specific costing situation can favour additive use through reduced scrubber operating costs. Scrubber costs are specific for each location (especially caustic and sulphur values), while additive costs are less variable.

NO_x formation in FCCU flue gas

Approximately half of the nitrogen in the feed to an FCCU reports to coke. When this coke is burned in the regenerator of a unit operating in complete combustion, about 10% of the coke nitrogen is released as NO_x (primarily NO). A simplified illustration of the chemistry is illustrated in Figure 9.

It is generally agreed that there is little, if no, contribution to NO_x from thermal oxidation of N_2 . NO_x is formed by oxidation of nitrogen compounds such as hydrogen cyanide (HCN) and NH_3 formed by pyrolysis reactions. It is consumed by reduction, primarily by CO. Thus, the concentrations of oxygen and CO in a regenerator are very important in determining the ultimate NO_x level in the flue gas. In addition, any catalysts present that will influence these reactions will affect NO_x .

In a regenerator operating in full combustion, the objective is to burn the coke as fully and effectively as possible to CO_2 to minimise CO emissions. The strategy for accomplishing this in a typical bubbling bed regenerator is to provide plenty of oxygen and catalyse the oxidation of CO using a Pt catalyst. In addition to being very active for CO oxidation, Pt is very effective for oxidising nitrogen-containing intermediates in this oxygen-rich environment. At the same time, CO concentration is very low and little reduction of NO_x occurs. This environment leads to high levels of NO_x .

If a regenerator is designed efficiently, it can operate with little or no CO combustion promoter. An example of this is the combustor design, which produces a relatively low level of NO_x . In any event, Pt promoter usage and excess oxygen should be minimised within constraints to reduce NO_x emissions.

A contrasting mode of regenerator operation is partial combustion. Insufficient oxygen is provided for complete combustion of the coke and the flue gas can contain up to 10 vol% CO. Typically, no Pt promoter is used. All of these conditions favour the minimisation of NO_x and, in fact, NO_x levels in the flue gas leaving the regenerator are typically very low. However, to meet CO emission limits and to recover the fuel value of the CO, the flue gas is usually incinerated in some sort of boiler. These typically operate at 900–1000°C and introduce the possibility for the generation of thermal NO_x . In addition, unoxidised nitrogen intermediates now have the opportunity to be converted to NO_x .

There are a number of regenerator configurations that operate with two stages, one in full combustion and one in partial, with various routings of the flue gas streams. The issues

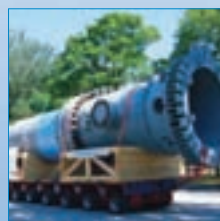
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with NO_x for these systems are covered by the individual arguments previously made.

Reduction in NO_x emissions

There are essentially four approaches to reducing NO_x in the FCCU regenerator flue gas:

- Optimisation of operating conditions
- Mechanical design changes
- Downstream flue gas treating
- Catalytic additives.

For a given regenerator configuration, minimising excess oxygen and Pt promoter usage are the simplest options for reducing NO_x emissions in full combustion. Of course, these must be done in the context of CO emission limits and afterburn constraints. In partial combustion, operations can be optimised in the CO boiler to minimise NO_x. Avoiding over-firing the boiler to raise additional steam is an example of this.

Mechanical design changes generally focus on spent catalyst distribution, combustion/lift air distribution and regenerator mixing intensity. All of these can be utilised in full burn to increase regenerator efficiency, allowing operation at the conditions that minimise NO_x previously described. A good example of achieving lower NO_x through improved combustion efficiency is the two-stage combustor design, which utilises a fast fluidised bed and catalyst recirculation. This regenerator can operate at low excess oxygen and generally without Pt promoter.

With proper distribution, the carbon on spent catalyst can also be utilised as a reductant via the second reaction in the figure above. A good example of this is the counter-current regenerator design in which the spent catalyst distributor is designed to distribute the carbon-rich catalyst evenly across the surface of the bed, reducing the NO_x in the flue gas leaving the bed. Baffles can be used in the bed to promote this counter-current operation.

In partial combustion, proper design of the CO boiler can minimise NO_x. Examples of good design practice include the use of low-NO_x burners for supplemental fuel gas and staged combustion, with optimised balance of the air to each stage.

Of course, taking advantage of mechanical improvements requires hardware modifications and capital expenditures. In many cases, a given regenerator configuration is simply not suitable for some of these design changes.

The third approach to NO_x reduction is treatment of the flue gas downstream of the regenerator and CO boiler. This generally requires capital investment and additional operating cost. The three processes developed to do this are:

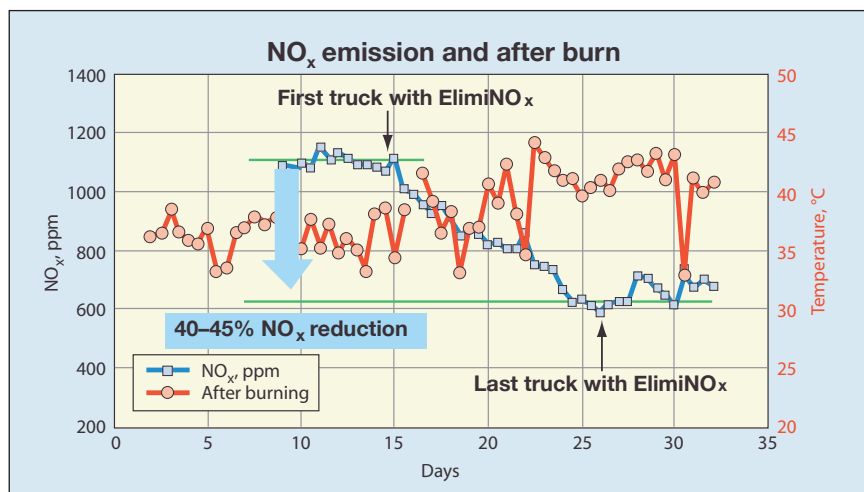


Figure 10 Effectiveness of ElimiNO_x in commercial application

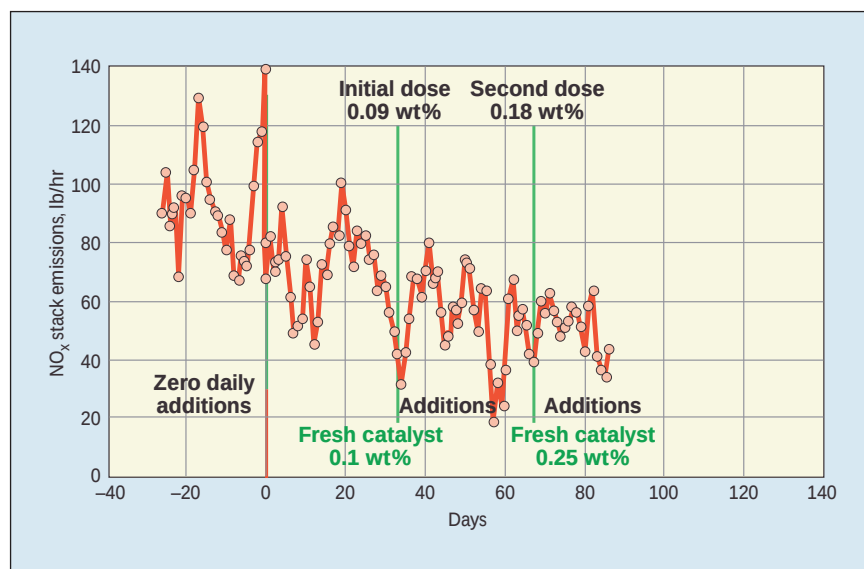


Figure 11 Effectiveness of KDNO_x in commercial application

Comparison of the various NO_x control approaches for a typical 28 000 bpd FCCU

Technology	Efficiency, %	Installation cost, \$ million	Operating cost, \$ million/yr	Specific removal cost, \$/tonne NO _x
SCR	85	2.1–6.3	0.21–0.84	3600
SNCR	60–80	0.6–2.6	0.09–0.70	3000
ElimiNO _x	40–70		0.32–1.76	1200–3600
KDNO _x	30–80		0.11–0.22	2400–3600

Table 2

- Selective catalytic reduction (SCR)
- Selective non-catalytic reduction (SNCR)
- LoTO_x (scrubber required).

In SCR, NO_x is reacted with ammonia and oxygen over a catalyst, most commonly vanadium pentoxide/titanium dioxide. Operating temperature is relatively low (350–375°C) for this catalyst system and efficiency can be quite high. Ammonia is added, but there is usually sufficient oxygen already in the flue gas. The net products are water and nitrogen; however, some ammonia remains in the flue gas. If there is SO₂ in

the flue gas, it can be converted to SO₃ by the SCR catalyst and this will react with the ammonia to form ammonium sulphate and bisulphate, which can cause plugging in downstream units and particulate emissions. Another drawback to SCR is the use of a structured catalyst support, which is sensitive to particulates in the flue gas.

In SNCR, NO_x is reacted with ammonia or urea at much higher temperatures than SCR (900–1000°C). A CO boiler with adequate residence time is required, so SNCR is generally only applicable in partial combustion. NO_x reductions are

lower than those achieved by SCR and the process suffers from the same ammonia slip problem.

LoTO_x involves reacting ozone with NO_x. A scrubber is required and operating costs can be high. This process has had limited application.

Catalytic additives for NO_x reduction

Albemarle offers two catalytic solutions for reducing NO_x in FCCU regenerator flue gas in full-burn operation: ElimINO_x and KDNO_x.

If an FCC is using a Pt-based CO combustion promoter, replacing it with ElimINO_x is the first step towards reducing NO_x emissions, effectively oxidising CO and controlling afterburn, but it is much less active for oxidising nitrogen compounds. Typically, NO_x levels while using ElimINO_x are 40–70% lower than those observed from a Pt-based promoter. Figure 10 illustrates the effectiveness of ElimINO_x.

ElimINO_x has been used successfully in more than 20 applications around the world and is approved for usage under EPA consent decree agreements. It has proven to be more active than competitive products, lowering required usage as much as 50%.

While ElimINO_x suppresses the formation of NO_x, KDNO_x reduces the level of NO_x by catalysing its reduction by CO. Figure 11 illustrates the effectiveness of KDNO_x in a commercial application.

In this case, NO_x was reduced by approximately 50% by using 0.25 wt% of KDNO_x on catalyst additions. The performance of a NO_x reduction additive is naturally sensitive to the concentration of CO, one of the reactants. Thus, conditions like low excess oxygen favour NO_x reduction, while poor air distribution renders the additive less effective. Performance is also influenced by regenerator design. Commercially, NO_x reductions as high as 80% have been observed, but there have been instances where reductions were quite low. Using ElimINO_x for combustion promotion favours the performance of KDNO_x. As with ElimINO_x, KDNO_x has been widely used and is approved by the EPA for consent decree applications.

Additives vs hardware

Additives like ElimINO_x and KDNO_x offer flexibility and the virtue of little or no capital expense. A loader may be required. However, as discussed earlier, they may not be effective in all applications and may not be able to reach very low NO_x limits.

SCR has the potential for consistently meeting low NO_x limits, but requires significant capital investment and maintenance. The units are sensitive to particulates and can produce particulates

themselves, as discussed earlier. SNCR requires a CO boiler. Both have an operating expense in the reactant.

Table 2 compares the economics of the various approaches for a typical 28 000 bpsd FCCU. The investment and operating costs for the hardware approaches come from the 2003 EU BREF escalated to 2008.⁷ The ranges represent potential variations in technology performance, degree of NO_x removal, and uncontrolled NO_x level. Operating cost for ElimINO_x is the incremental over using a Pt promoter.

The principle conclusion is that additive technology for NO_x reduction is economically competitive with hardware without the need for capital investment.

Conclusions

Increasingly severe regulation of SO_x and NO_x emissions from FCCUs is being implemented around the world. Although there are a variety of approaches for meeting emission limits, the use of SO_x and NO_x reduction additives appears to be very attractive. These options require little or no capital investment and have reasonable operating costs, resulting in an overall lower cost than a WGS or SCR. In contrast to hardware approaches, additives prevent pollution and do not transfer it to a potential liquid or solids disposal problem or increased particulate emissions. Energy and water resources

are not consumed by emission reduction additives. Even if a WGS exists, SO_x reduction additives can be cost effective through reduction in caustic costs.

SO_x Master (SO_x MASTER), SO_x Down (SO_x DOWN), ElimINO_x (ELIMINO_x), KDNO_x and KD₂SO₄ are marks of Albemarle Corporation.

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SO₂ scrubbing in refinery applications

Emissions control and by-product capture can add value from flue gas streams generated by FCCU, process heaters, sulphur plants and spent acid regeneration units. Process flow sheet information and utility consumption guidelines are presented for an SO₂ scrubbing system

Rick W Birnbaum
Cansolv Technologies

Tighter regulations, an increasing spread between sweet and sour crude prices, and attractive revenue opportunities for sulphur and its by-products have led refiners to increase their use of high sulphur fuels internally and install flue gas desulphurisation systems to capture SO₂.

The Cansolv SO₂ scrubbing system has been in use commercially since 2002 and a total of nine units are now operating worldwide. These units capture SO₂ from FCCU regenerator offgas, fluid coker CO boiler offgas, lead and copper smelter offgas, sulphur plant tail gas and sulphuric acid plant tail gas.

Higher API gravity and sulphur content

Environmental pressures and refining costs are two challenges that face refiners on a daily basis. The spread between sweet and sour crudes is increasing as supplies of sweet crudes become tighter. Environmental pressures continue to tighten, reducing the refiner's options to dispose of high sulphur products into the marketplace, into the air or into refinery wastewater streams.

Long-term trends for crude feed quality to refiners are clear. For example, the US EPA, through its Energy Information Administration (EIA), reports that the average diet of crudes fed to US refineries has become heavier and higher in sulphur content over the last 25 years. Figure 1 shows the overall trend. In 1984, the average refinery was fed 32.7 °API oil containing 0.9 wt% sulphur. In 2008, these numbers changed to 30.3 °API and 1.4 wt% sulphur. On a planning basis, it would not be inappropriate to anticipate that crude in 20 years' time might consist of 28.3 °API oil containing 1.8 wt% sulphur.

Oil price trends are also clear. The cost of crude is rising and the split between the cost of heavy and light crudes has grown to nearly \$10/Bbl. The incentive to configure the refinery to process these cheaper, opportunity crudes is significant. The cost base of a 250 000 bpd refinery,

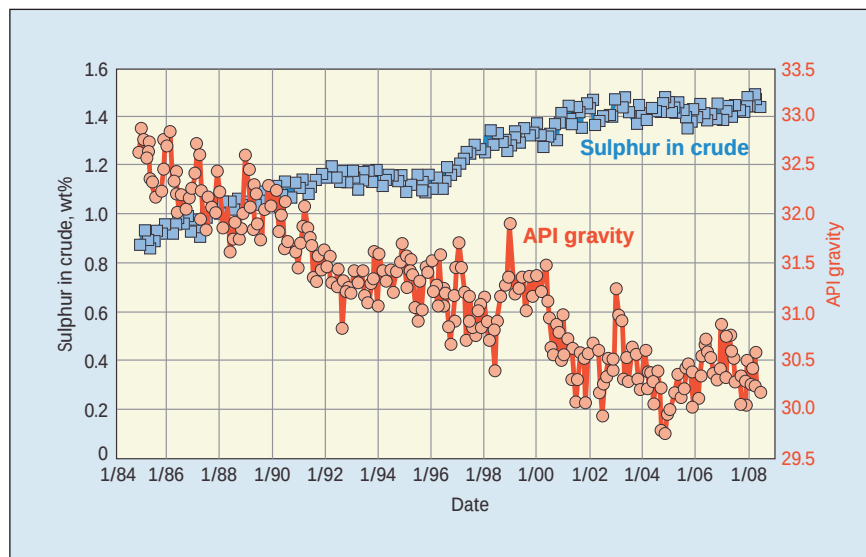


Figure 1 Trend of sulphur content and density of average US crude diet (Source: EIA)

for example, would drop by nearly \$900 MM annually if the refiner were able to take advantage of the full spread between light and heavy crudes.

However, various technical issues must be addressed in order to take advantage of the price gap between light and heavy crudes. By definition, heavy crudes produce a heavier slate of products containing greater amounts of sulphur. Major investments in bottoms processing capacity are required that would also need additional investments in hydrogen and hydroprocessing capacity for all products, and additional sulphur conversion capacity. Processing schemes must also be reviewed to ensure product quality does not suffer. Additional investment may be needed to preserve octane, cetane and vapour pressure requirements of distillate products or to remove benzene and other aromatics generated by new bottoms processing units. Changing markets for bottoms products, tighter environmental regulations and increasing costs for natural gas will require renewed examination of utility systems, such that:

— Shrinking markets for high sulphur residuum or coke will incentivise the

refiner to incorporate these materials into their refinery fuel balance. Cogeneration or heater refuelling projects can absorb part of an unmarketable bottoms stream, but additional SO_x, NO_x and particulate controls will be needed to accommodate the use of poorer quality fuels

— Increasing prices for natural gas or refinery gas will incentivise the refiner to conserve these commodities for use as hydrogen plant feed. Converting process heaters from gas to oil may be justifiable

— Demand for fertilisers by India, China and the worldwide biofuels markets is expected to continue to exert pressure on sulphur and its by-products for the foreseeable future. If by-product sulphur prices remain high, regenerable SO₂ capture projects will be better positioned to serve refinery-wide emission reduction campaigns

— Higher alkylate demand, higher sulphuric acid costs and tighter markets for acid may compel the refiner to install standalone spent sulphuric acid regeneration (SAR) systems. Excess acid capacity, beyond alkylation needs, would provide an additional outlet for

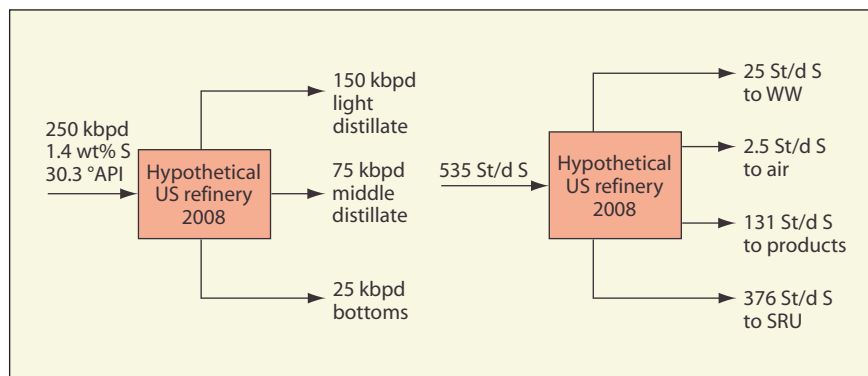


Figure 2 Crude and sulphur scenario for average US refinery in 2008

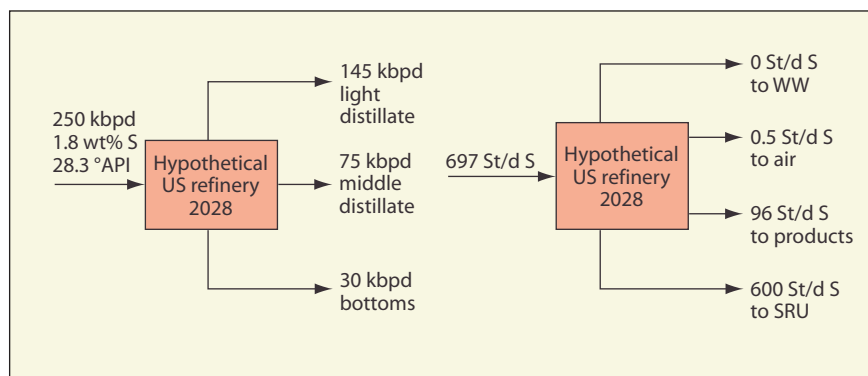


Figure 3 Crude and sulphur scenario for average US refinery in future

H₂S generated by the refinery, a partial backup to existing sulphur recovery units (SRUs) and a second revenue stream for sulphur.

Environmental pressures must also be addressed. Permits to expand or modify processing units will void “grand-fathered” emissions allowances and force the installation of additional end-of-pipe wastewater and flue gas treatment systems. Tighter environmental emission limits can be met by redirecting sulphur compounds that are now discharged into the wastewater and the air to other disposal points, such as the SRU.

Many of the strategic pressures facing the refiner will require additional attention to be paid to its overall sulphur balance. Non-regenerable SO₂ scrubbing systems will only increase costs as the cost for reagents such as sodium hydroxide, lime or limestone increase. Further, tighter environmental controls will likely limit the ability to dispose of gypsum to landfill or to dispose of sodium sulphate into refinery wastewater streams. Regenerable SO₂ scrubbing systems can help ease many of the environmental- and market-induced pressures that are associated with the use of greater quantities of opportunistic crudes. The Cansolv SO₂ scrubbing system has been able to satisfy all of these SO₂ capture needs previously described, including:

- FCCU and fluid coker CO boiler flue gas SO₂ scrubbing applications for two years
- Since 2002, for removal of SO₂

produced by a Claus SRU and a SAR unit

- An SO₂ scrubbing system will soon be operating in a coal-fired cogeneration facility in China. This unit captures SO₂ from a 240 MW power facility and directs the SO₂ by-product to a sulphuric acid unit. The by-product revenue from this project will pay for the capital costs within three years

- SO₂ scrubbing systems have also been licensed to refiners who will use it to capture SO₂ from flue gas generated by resid fired crude unit process heaters and utility boiler systems.

Refinery SO₂ scrubbing

Figure 2 shows the overall processing trend for a hypothetical 250 000 bpd refinery today. It assumes a 60%, 30%, 10% split between light distillate, heavy distillate and bottoms product distributions. For simplicity, volumetric shrinkages or gains between feed and product streams are not considered. Refinery gas production is ignored. A 250 000 bpd refinery is assumed to produce 250 000 bpd of products from the same volume of crude.

Figure 2 also shows the overall sulphur balance that might apply to such a refinery. A total of 535 short tonnes (St) of sulphur are contained in the crude feed. 5%, 25% and 70% of the sulphur entering the refinery with the crude is assumed to flow to air and wastewater streams, product streams and to the SRU respectively.

Figure 3 shows the overall processing

trend for the same refinery as it might appear in the future. The crude mix is heavier and contains more sulphur. The product volumetric split is now 58%, 25% and 17% between light, intermediate and bottoms products respectively.

Figure 3 also shows how the overall sulphur balance might look, assuming that sulphur emissions to air and water have been curtailed, FCCU SO₂ is captured in a regenerable scrubber and cogen facilities have been installed to burn up to 15 kbpd of residuum or its equivalent in coke. The total amount of sulphur fed to the refinery increases to 697 short tonnes per day (St/d). 1.0%, 14% and 85% of the sulphur entering with the crude leaves with waste streams, product streams or via the SRU respectively. Four significant changes to the refinery utility and sulphur systems are assumed to support the sulphur distribution scenario for the future refinery:

- Half of the 30 000 bpd bottoms stream is retained as fuel due to soft markets for high sulphur fuel oils. The balance is sold to remaining markets for high sulphur fuels. SO₂ is captured from the combusted resid flue gas stream in the SO₂ scrubbing system and directed to the SRU

- FCCU regen gas SO₂ is captured and directed to the SRU through the installation of a SO₂ scrubbing system

- A SAR has been installed to regenerate spent alkylation acid catalyst and to act as a contingency disposal point for acid gas in the refinery. SO₂ is directed to the acid plant from the SO₂ scrubbing system to secure a sulphur emission rate of less than 0.3lb of sulphur per tonne of acid made

- A SRU SO₂ tail gas unit is assumed to be required, which increases the refinery SRU conversion efficiency to over 99.9%. SO₂ is routed back to the SRU.

In each case, an SO₂ scrubbing system is required to manage the additional SO₂ that is emitted as a consequence of the changes. By directing resid to fuel systems, an additional 96 tonnes of sulphur must be captured as SO₂. Redirecting SO₂ from the FCCU scrubber away from the wastewater treatment systems increases the sulphur load on the SRU by 27 tonnes per day (tpd). The tail gas system adds an additional 12 tpd of SO₂ load on the SRU.

Four cases have been developed to illustrate how a regenerable SO₂ scrubbing system can be used for each case previously described. Inside battery limits (ISBL) costs have been estimated and operating costs have been derived to satisfy utility, operations and maintenance costs of the SO₂ system. Revenue from sulphur by-products is also estimated to illustrate how by-product revenues can impact project economics.

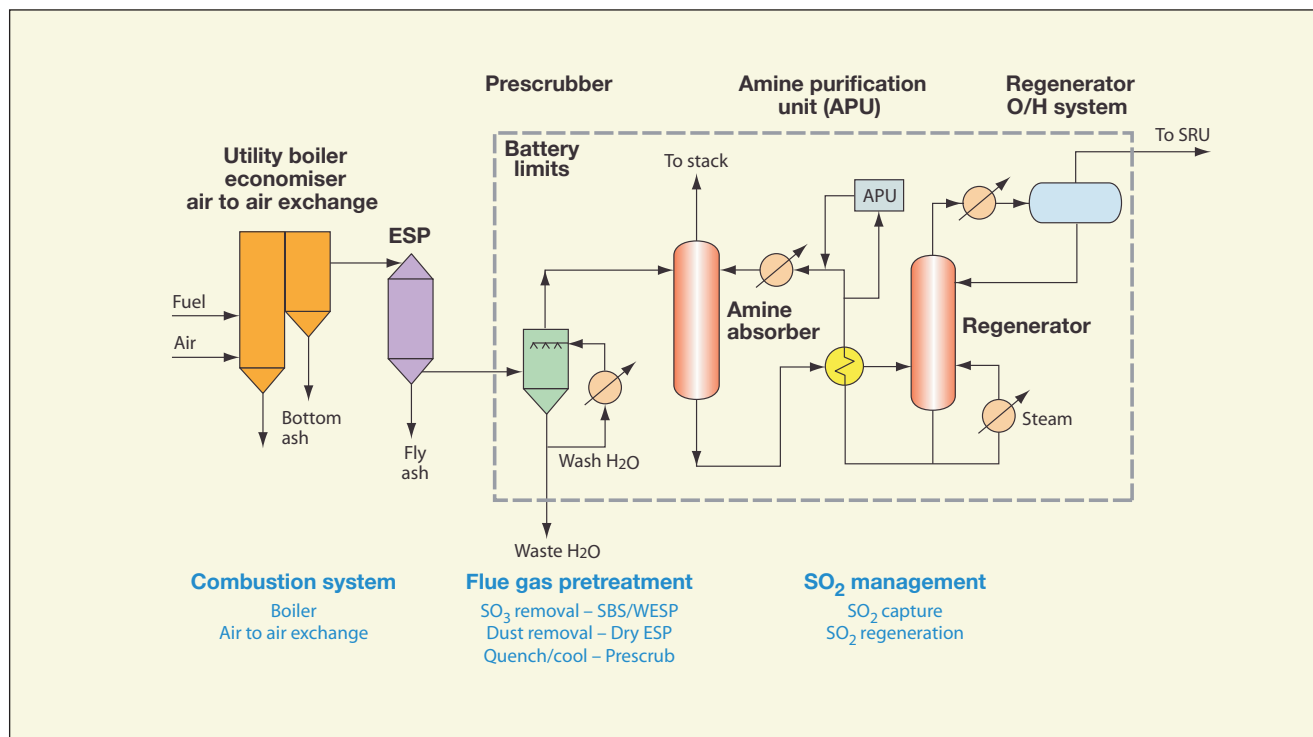


Figure 4 Cogen system flue gas treating flow diagram

By-product values

Changing crude prices have rippled through the economy and created similar, related waves in sulphur by-product pricing. In 2007, prices for sulphur were in the \$45/St (\$50/metric tonne) range. In late 2008, sulphur prices rose to as high as \$630/St (\$700/metric tonne). Sulphuric acid values have been similarly variable and have increased from \$90/St (\$100/metric tonne) to as high as \$329/St (\$360/metric tonne). It is widely expected that by-product values will fall, but specific values are more difficult to predict. For this discussion, it is assumed that sulphur prices will average \$250/St for the next 15 years.

Case study 1

SO₂ scrubbing in co-generation application

Cogen firing basis:

Resid feed rate: 15 kbpd
Sulphur in feed: 3.6 wt%
Heating value: 17 100 Btu/lb fuel
Total firing rate: 3402 MMBtu/hr — 350 MW equivalent at 9700 Btu/kW heat rate.

In this example, residuum is fired to a utility type boiler. Steam is raised to feed power turbines and to supply steam to the refinery. Flue gas is directed to an air-to-air preheater and then to an electrostatic precipitator, where solids are removed. The cool gas flows to the prescrubbing system and then to the SO₂ scrubbing system. The overall flue gas management systems are broken down into three discrete parts:

- The combustion system
- The flue gas pretreatment system
- The SO₂ management system.

Cost and utility data have been established for the flue gas prescrubber and the SO₂ absorption and regeneration system as identified as being contained in the battery limits in Figure 4.

The ISBL costs for the regenerable SO₂ scrubbing system amount to \$42.0 MM and the annual operating cost is \$14.6

SO₂ cost and utility consumption table: cogen case

Resid feed rate, kbpd	15.0
Firing rate, MMBTU/hr	3402
MW equivalent	350
SO ₂ captured, St/hr	7.9
Annual sulphur equivalent, St/yr	34 602
Flue gas flow rate, kscfm	884
Flue gas SO ₂ , vppm	1833
Capital cost, \$MM ¹	42.0
Annual op cost, \$MM ²	14.6
Annual by-product credit, \$MM	8.4
Net operating cost	6.2

Utility consumption	
Power, kW-hr/tonne SO ₂	970
Steam, '000 lb/tonne SO ₂	23.3
Cooling water, '000 gal/tonne SO ₂	234

1 Capital cost refers to inside battery limits (ISBL) total installed costs for a high labour efficiency, low material cost location. Owner's costs, incremental utility capital costs and overheads are not included. Costs are to be considered as ball park estimates only, for the four cases identified.

2 Operating costs are based on \$3.63/'000lb for steam, \$0.06/kWh for power and \$0.08/'000 gallons for cooling water. Operating and maintenance costs are not included, but are typical for low corrosion, petrochemical applications.

Table 1

MM for utilities, consumables, operation and maintenance. The revenue opportunity for sulphur generated from the capture of SO₂ amounts to \$8.4 MM annually. The project is a break-even proposition if sulphur revenue is more than \$520/St over the project life.

Case study 2

FCCU regen gas SO₂ scrubbing

FCCU SO₂ scrubbing basis:

Gas oil feed: 87 kbpd
Sulphur in feed: 2.4 wt%
Regen gas generated: 256 scfm
Flue gas SO₂ concentration: 2100 vppm
SO₂ content of regen gas: 2.6 St/hr

This scenario is based on the refinery generating up to 87 kbpd of catalytic feed from the crude charge of 250 000 bpd. If the sulphur content of the feed is 2.4 wt% and 10% of this is carried in the coke to the catalyst regenerator, a total of 2.6 St/hr of SO₂ must be removed from the regen gas.

Particulate management in the FCCU is critical because particulate emission concentrations can change quickly from low concentrations (0.04 gr/scf of gas, or 100 mg/Nm³) to several grains of particulate per standard cubic foot of gas as a result of regenerator cyclone failure or catalyst flow reversal. A venturi prescrubbing device in the flue gas conditioning system can accommodate these swings in particulate content of the flue gas.

Unlike the cogen case, additional flue gas cooling is required to ensure the gas enters the SO₂ scrubber at a low enough temperature for sufficient SO₂ removal.

The specific steam consumption for the cogen case is higher than for the



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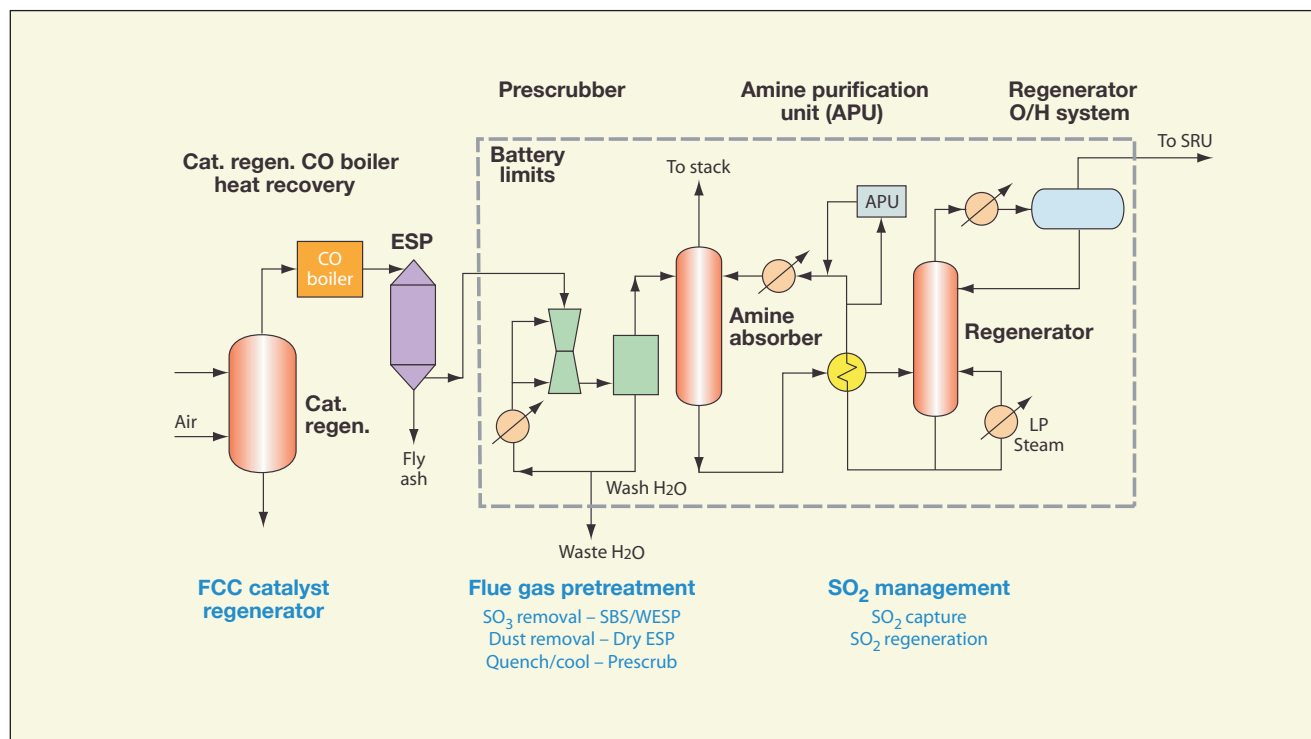


Figure 5 Process flow diagram: FCCU CO boiler flue gas DeSOx unit

FCCU case because the gas is not cooled, and higher amine circulation and steam flow rates are needed to be sure the gas is treated to specification levels of SO₂. The cooling water demand is greater for the FCCU case to reflect the additional cooling load in the prescrubber system.

Table 2 shows that the ISBL TIC capital cost of the regenerable SO₂ scrubbing system amounts to \$20 MM and that the annual operating cost is estimated to be \$5.7 MM. The price of sulphur must remain above \$590/St to break even for this case.

Case study 3

Spent acid regeneration

Spent acid feed basis:

Acid plant production rate: 400 St/d

Tail gas flow rate: 22 kscfm

Operating parameters for the FCCU CO boiler flue gas DeSOx unit

FCCU feed rate, kbpd	87.5
SO ₂ captured, St/hr	2.6
SO ₂ captured, St/day	62.4
Annual sulphur equivalent, St/yr	11 388
Flue gas flow rate, kscfm	256
Flue gas SO ₂ , vppm	2100
Capital cost, \$MM	20.0
Annual op cost, \$MM	5.7
By-product credit, \$/t S	250
Annual by-product credit, \$MM	2.9
Net operating cost, \$MM	2.8
Utility consumption	
Power, kW-hr/t SO ₂	1290
Steam, '000 lb/t SO ₂	17
Cooling water, '000 gal/t SO ₂	510

Table 2

Tail gas SO₂ concentration: 4500 vppm
Recovered SO₂: 12 St/day

Greater thermal processing and hydrotreating of cracked products reduce the octane content of light distillate streams. To maximise their return on octane, the refiner will need to consider upgrading their alkylation system, resulting in the consumption of greater amounts of fresh acid and the generation of increasing volumes of spent acid. Incorporating an acid plant into the refinery process scheme reduces the reliance on outside contractors to process spent acid and allows the refiner to direct some of their by-product H₂S or elemental sulphur to the acid plant and engage in what is now a lucrative market for sulphuric acid by-product. Alkylation units consume between 15lb and 20lb of acid per barrel. Hence, a 200 St/day spent acid regeneration unit would be required to satisfy the local requirements of the alkylation unit. For this discussion, it is assumed that an additional 200 St/day of acid can be sold to external customers to enhance the value proposition for the project.

Sulphuric acid plants are normally configured as single absorption and double absorption flow schemes. Single absorption plants are generally regarded as being able to achieve in excess of 99% conversion with fresh catalyst, and double absorption plants can achieve conversions in excess of 99.9%. Addition of an absorption step essentially is considered to be an equivalent process option to the use of a tail gas SO₂ capture and recycle flow scheme.

The regenerable SO₂ scrubbing system

allows conversions of greater than 99.9% of the feed to sulphuric acid and is capable of meeting a sulphur emission specification below 0.33lb sulphur per tonne of acid produced. Further, the integration of the system into the acid plant design disconnects emission values from catalyst performance and allows lean Cansolv solvent to be sourced from a common refinery SO₂ regeneration system. Figure 6 illustrates the flow scheme used for a spent acid regeneration unit and its SO₂ tail gas unit.

Table 3 shows some of the performance characteristics for SO₂ scrubbing in a hypothetical 400 St/day H₂SO₄ spent acid facility.

Specific consumption rates of steam and cooling water per tonne of SO₂ are very much advantaged in this system when compared to FCCU and cogen absorption because acid plant tail gas is concentrated in SO₂, contains no water,

Operating parameters for the SAR DeSOx unit

Acid plant production, St/day H ₂ SO ₄	400
SO ₂ captured, St/hr	0.5
SO ₂ captured, St/day	12
Annual sulphur equivalent, St/yr	2200
Flue gas flow rate, kscfm	22
Flue gas SO ₂ , vppm	4500
Capital cost, \$MM	4.7
Annual op cost, \$MM	0.4
Utility consumption	
Power, kW-hr/t SO ₂	114
Steam, '000 lb/t SO ₂	6.6
Cooling water, '000 gal/t SO ₂	59

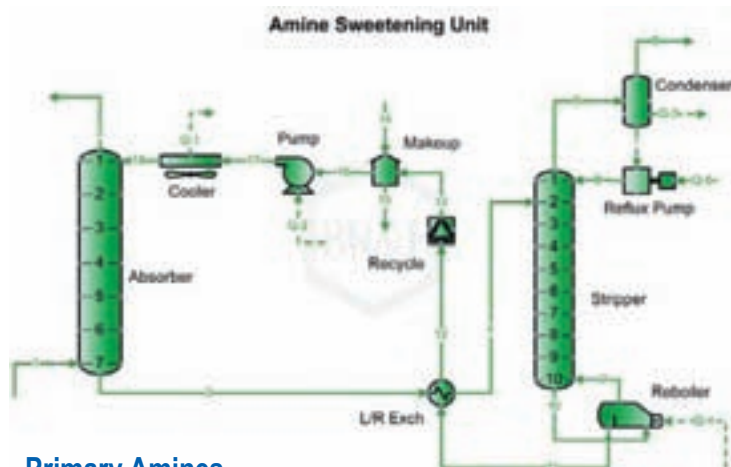
Table 3



PROCESS INSIGHT

Selecting the Best Solvent for Gas Treating

Selecting the best amine/solvent for gas treating is not a trivial task. There are a number of amines available to remove contaminants such as CO_2 , H_2S and organic sulfur compounds from sour gas streams. The most commonly used amines are methanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA). Other amines include diglycolamine® (DGA), diisopropanolamine (DIPA), and triethanolamine (TEA). Mixtures of amines can also be used to customize or optimize the acid gas recovery. Temperature, pressure, sour gas composition, and purity requirements for the treated gas must all be considered when choosing the most appropriate amine for a given application.



Primary Amines

The primary amine MEA removes both CO_2 and H_2S from sour gas and is effective at low pressure. Depending on the conditions, MEA can remove H_2S to less than 4 ppmv while removing CO_2 to less than 100 ppmv. MEA systems generally require a reclaimer to remove degraded products from circulation. Typical solution strength ranges from 10 to 20 weight % with a maximum rich loading of 0.35 mole acid gas/mole MEA. DGA® is another primary amine that removes CO_2 , H_2S , COS, and mercaptans. Typical solution strengths are 50-60 weight %, which result in lower circulation rates and less energy required for stripping as compared with MEA. DGA also requires reclaiming to remove the degradation products.

Secondary Amines

The secondary amine DEA removes both CO_2 and H_2S but generally requires higher pressure than MEA to meet overhead specifications. Because DEA is a weaker amine than MEA, it requires less energy for stripping. Typical solution strength ranges from 25 to 35 weight % with a maximum rich loading of 0.35 mole/mole. DIPA is a secondary amine that exhibits some selectivity for H_2S although it is not as pronounced as for tertiary amines. DIPA also removes COS. Solutions are low in corrosion and require relatively low energy for regeneration. The most common applications for DIPA are in the ADIP® and SULFINOL® processes.

Tertiary Amines

A tertiary amine such as MDEA is often used to selectively remove H_2S , especially for cases with a high CO_2 to H_2S ratio in the sour gas. One benefit of selective absorption of H_2S is a Claus feed rich in H_2S . MDEA can remove H_2S to 4 ppm while maintaining 2% or less CO_2 in the treated gas using relatively less energy for regeneration than that for DEA. Higher weight percent amine and less CO_2 absorbed results in lower circulation rates as well. Typical solution strengths are 40-50 weight % with a maximum rich loading of 0.55 mole/mole. Because MDEA is not prone to degradation, corrosion is low and a reclaimer is unnecessary. Operating pressure can range from atmospheric, typical of tail gas treating units, to over 1,000 psia.

Mixed Solvents

In certain situations, the solvent can be "customized" to optimize the sweetening process. For example, adding a primary or secondary amine to MDEA can increase the rate of CO_2 absorption without compromising the advantages of MDEA. Another less obvious application is adding MDEA to an existing DEA unit to increase the effective weight % amine to absorb more acid gas without increasing circulation rate or reboiler duty. Many plants utilize a mixture of amine with physical solvents. SULFINOL is a licensed product from Shell Oil Products that combines an amine with a physical solvent. Advantages of this solvent are increased mercaptan pickup, lower regeneration energy, and selectivity to H_2S .

Choosing the Best Alternative

Given the wide variety of gas treating options, a process simulator that can accurately predict sweetening results is a necessity when attempting to determine the best option. ProMax® has been proven to accurately predict results for numerous process schemes. Additionally, ProMax can utilize a scenario tool to perform feasibility studies. The scenario tool may be used to systematically vary selected parameters in an effort to determine the optimum operating conditions and the appropriate solvent. These studies can determine rich loading, reboiler duty, acid gas content of the sweet gas, amine losses, required circulation rate, type of amine or physical solvent, weight percent of amine, and other parameters. ProMax can model virtually any flow process or configuration including multiple columns, liquid hydrocarbon treating, and split flow processes. In addition, ProMax can accurately model caustic treating applications as well as physical solvent sweetening with solvents such as Coastal AGR®, methanol, and NMP. For more information about ProMax and its ability to determine the appropriate solvent for a given set of conditions, contact Bryan Research & Engineering.



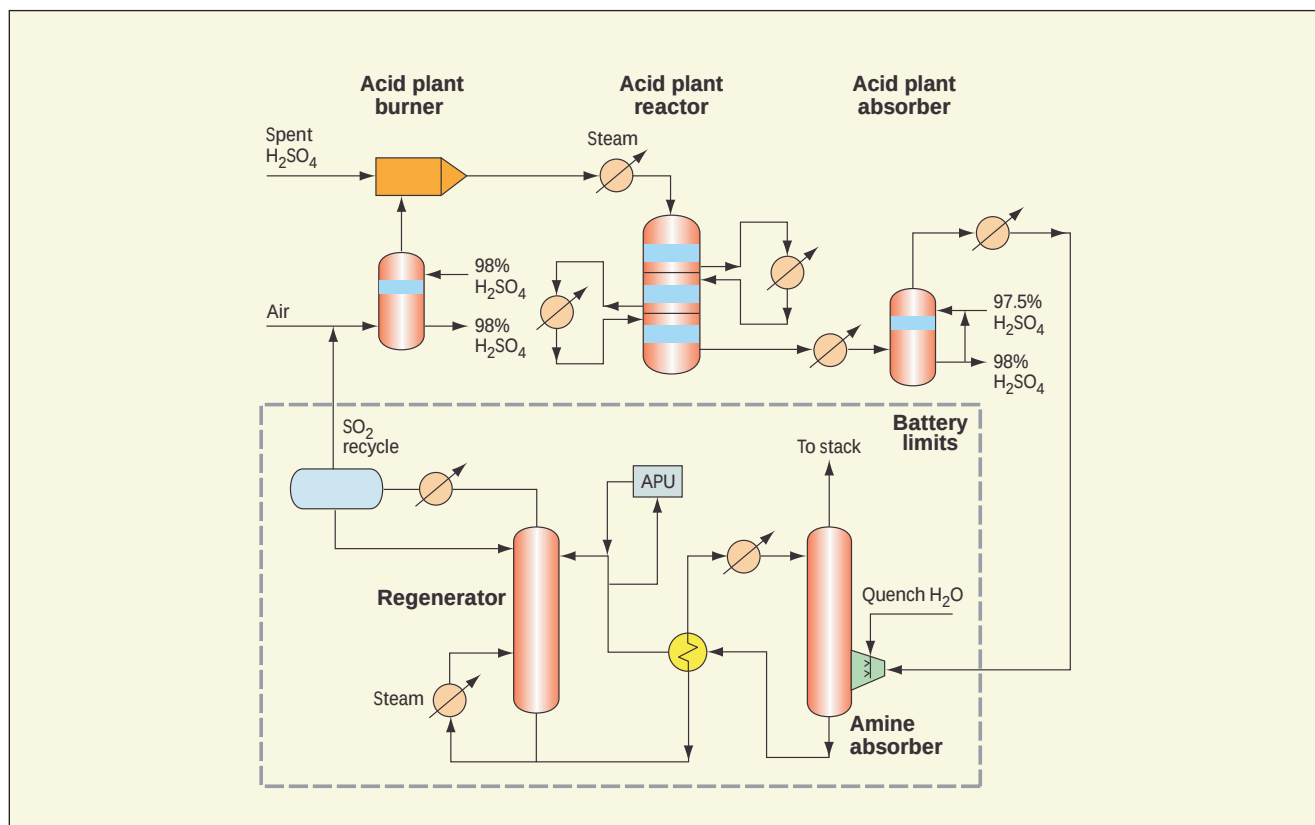


Figure 6 Spent sulphuric acid unit flow sheet

requires no external cooling in the prescrubber and is free of particulates. Furthermore, the elimination of a circulated prescrubber in this design avoids the need for a tail gas ID fan to push tail gas through the SO₂ scrubbing system.

Impact on the SRU

The transition from the 2008 hypothetical refinery processing case to the 2028 case requires that the SRU be modified to increase elemental sulphur production from 376 St/d to 600 St/d. This represents a 60% increase in SRU capacity. The SRU design is greatly defined by gas residence time and temperature considerations in the reactor, and space velocity and sulphur rundown considerations in the sulphur condensers.

When air is used to oxidise the necessary amount of H₂S to SO₂ to satisfy the sulphur reaction, the air-to-acid gas ratio needed to satisfy the O₂ demand amounts to 2.37 moles of air per mole of H₂S fed to the SRU. The introduction of air to the reaction furnace introduces 1.87 moles of inert N₂ per mole of H₂S. If 60% more capacity is required and the reaction furnace residence time must remain below a threshold level, then more than 60% of the volume of reactants must be eliminated from the reaction furnace feed. This can be accomplished by eliminating N₂ from the feed.

The primary concern in SRU design is to ensure temperatures remain above

Comparative SRU performance at 376 St/d and 600 St/d		
	376 St/day SRU	600 St/day SRU
SRU configuration	3 stage	3 stage
Conversion, 100% of equil.	98.6%	99.1%
Acid gas feed	1100 lbmol/hr H ₂ S	1254 lbmol/hr H ₂ S
Rxn furnace comb. air	3000 lbmol/hr	2000 lbmol/hr
External SO ₂ to Rxn furnace	0	190 lbmol/hr (dry)
External SO ₂ to 1st stage Claus	0	120 lbmol/hr (dry)
Combustion air	3000 lbmol/hr	2000 lbmol/hr
Rxn furnace temp	2635°F	2050°F

Table 4

2300°F, where NH₂ is a component of the SRU feed, or to keep conversion temperatures above 2000°F, where only hydrocarbons are present in the acid gas. Acid gas and air preheat can be used to increase reaction furnace temperatures, and part of the SO₂ can be bypassed to the first Claus stage to prevent flame cooling. This case was configured to ensure the reaction furnace temperature does not drop below 2000°F.

Table 4 illustrates the operating conditions of a three-stage Claus SRU, designed to produce 376 St/day of sulphur and a 600 St/day unit that is fed 310 lbmol/hr of externally sourced SO₂. For the 376 t/day case, a total of 4100 lbmol/hr of air and acid gas is fed to the SRU reaction furnace. For the 600 t/day case, a total of 3444 lbmol/hr of air and acid gas is fed to the SRU reaction furnace.

Similarly, the feed to the first-stage Claus reactor for the 376 t/day and 600

t/day cases is 3900 lbmol/hr and 3400 lbmol/hr respectively.

The conclusion to be drawn from Table 4 is that the existing SRU reaction furnace and reactors are sufficient to handle increased sulphur loads in the future refinery if NH₃ is not a feed component of the SRU. It will be important, however, that design checks of items such as sulphur condenser duties, rundown and pump-out capacities and the approach to the sulphur dew point temperature in the reactors be performed.

Case study 4 SRU tail gas scrubbing

In some cases, the upgrade of the refinery will require the addition of an SRU tail gas clean-up system. This can also be satisfied by the installation of a regenerable SO₂ scrubber as part of the SRU expansion. Figure 7 shows how the Canslov tail gas system can be integrated

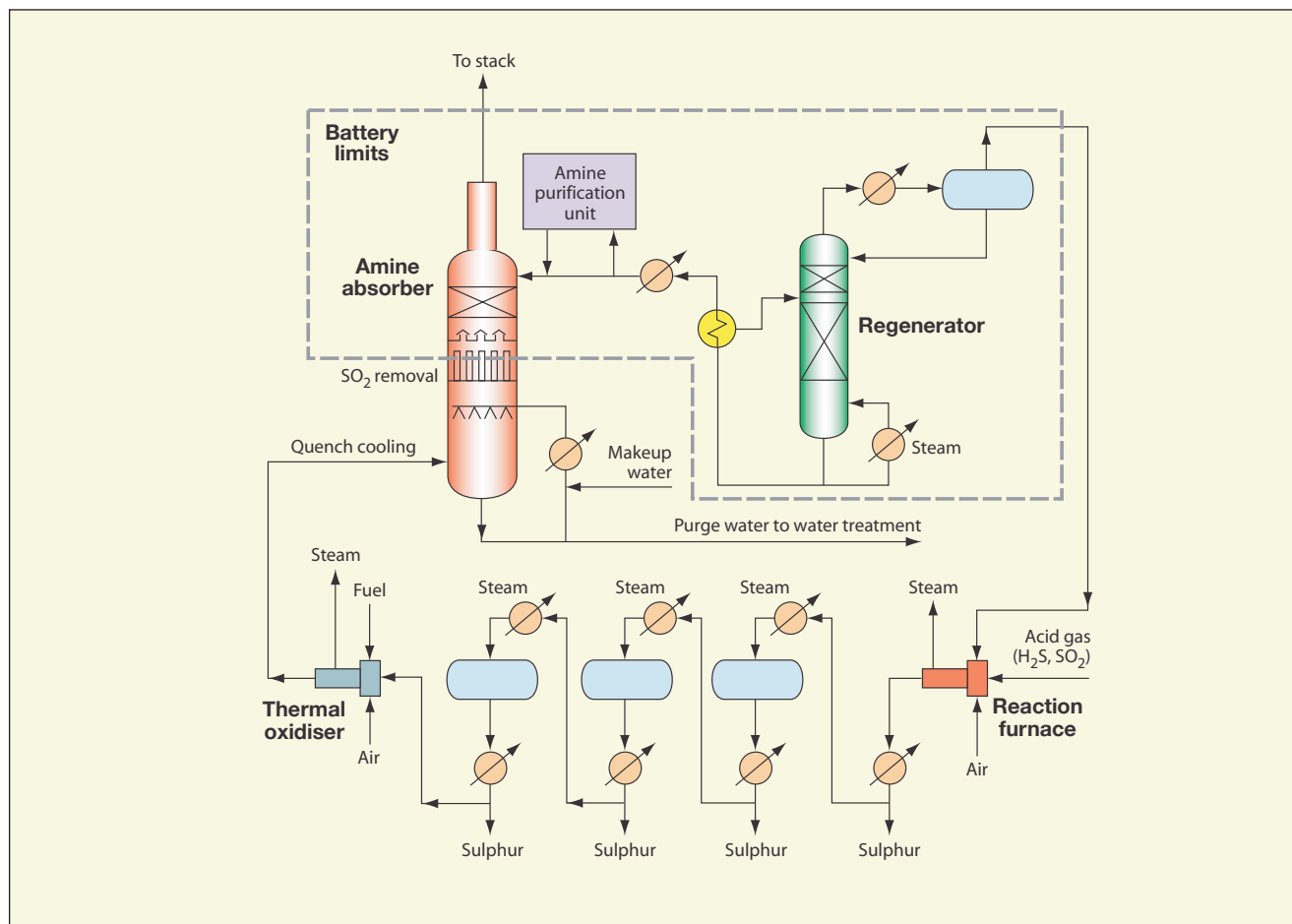


Figure 7 SRU tail gas clean-up unit

Operating parameters for the SRU unit: 97% conversion basis	
SRU production, St/day sulphur	600
SO ₂ captured, St/hr	1.5
SO ₂ captured, St/day	36.0
Annual sulphur equivalent, St/yr	6570
Flue gas flow rate, kscfm	24
Flue gas SO ₂ , vppm	13 000
Capital cost, \$MM	7.1
Annual op cost, \$MM	1.2
Utility consumption	
Power, kW-hr/t SO ₂	200
Steam, '000 lb/t SO ₂	7.3
Cooling water, '000 gal/t SO ₂	220

Table 5

into an existing three-stage SRU that is designed for a 97% conversion efficiency at end of catalyst run conditions.

Table 5 shows some of the performance characteristics of regenerable SO₂ scrubbing in a hypothetical SRU that operates at a sulphur rundown rate of 600 St/d. In this case, operating costs do not include natural gas consumption and steam production in the tail gas thermal oxidiser, which are outside of the CTI scope.

Extensive flue gas cooling is required to cool the gas to absorber conditions and to remove the water formed from the Claus reaction. The prescrubbing system must purge 44 gpm, or 7.3

Non-regenerable SO ₂ scrubbing reagent requirements			
Product	Consumption, lb reagent per lb of SO ₂	Equivalent consumption/cost (St/d; \$MM/yr) of reagent for co-gen case 185 tpd SO ₂	Equivalent of case consumption/cost (St/d; \$MM/yr) reagent for FCCU 62 tpd SO ₂
Calcium carbonate (limestone)	1.56	300/\$3.2 MM	100/\$1.2 MM
Calcium hydroxide (lime)	1.15	220/\$7.9 MM	70/\$2.6 MM
Sodium hydroxide solid	1.25	240/\$26.0 MM	80/\$8.5 MM

Table 6

Waste production/disposal			
	lb dry waste material generated (as SO ₂) per lb of SO ₂ removed	Co-gen case waste generated St/d; \$MM/yr at \$20 per tonne dry basis	FCCU case waste generated \$MM/yr at \$20 St/d; per tonne dry basis
Calcium carbonate (limestone)	2.13 (solid waste)	403/\$3.0 MM	132/\$1.0 MM
Calcium hydroxide (lime)	2.13 (solid waste)	403/\$3.0 MM	132/\$1.0 MM
Sodium hydroxide	2.22 (liquid waste)	419/\$3.0 MM	137/\$1.0 MM

Table 7

tonnes of water per tonne of SO₂ captured by the tail gas system. On an SRU basis, this translates to 0.4 tonnes of water per tonne of sulphur directed to the pit.

Comparison to non-regenerable systems

By-product management

Non-regenerable SO₂ scrubbing systems in wide use today most often employ

sodium hydroxide, lime (calcium oxide) and limestone (calcium carbonate) as reagents to remove SO_2 from flue gas streams. Prices for reagents have varied greatly. NaOH has ranged between \$200/t and \$800/t. Its supply is tied to energy prices and markets for chlorine, a by-product of NaOH. Lime has varied between \$129/t and \$170/t since 2006 and limestone has held steady at a cost of between \$10/t and \$20/t at the quarry. Delivery costs are extra. The delivered costs of NaOH, lime and limestone might average \$300/t, \$100/t and \$30/t for the purposes of this example.

Non-regenerable waste management

SO_2 is absorbed as the sulphite or bisulphite of the sodium or calcium salt. It must be oxidised to the sulphate form of the salt in an air-blown contactor and discharged to waste to minimise its chemical oxygen demand (COD). As shown in Table 7, a tonne of SO_2 generates over two tonnes of waste (dry basis) when converted to the sulphate of the salt.

Waste management costs represent a significant portion of the overall operating cost for a non-regenerable SO_2 scrubbing system.

Conclusions

Overall, regenerable SO_2 scrubbing systems installed in four locations of the refinery will capture 300 St/day of SO_2 (150 St/day sulphur equivalent) that will balance the growing load of H_2S generated by the hydrotreaters. The addition of both SO_2 and H_2S to the Claus plant feed will help avoid major additional investment in sulphur recovery facilities.

A total of nearly \$74 MM of capital is required to install four SO_2 capture and solvent regeneration systems in this hypothetical 250 000 bpd refinery. Incremental annual operating costs of \$23 MM for the SO_2 capture systems is expected, but most of this cost will be offset by a by-product revenue stream that will generate up to \$14 MM annually.

The net operating cost for regenerable vs non-regenerable solvents, inclusive of by-product revenues, is lower than that for lime and sodium hydroxide-based non-regenerable systems. It is greater than for limestone-based scrubbing systems, if the delivered price of limestone is \$30 per tonne or if the average sulphur price over the life of the project exceeds \$250/t.

Capital cost savings can be obtained in this example. This scenario has considered that four SO_2 absorbers and regenerators are required to satisfy this project and a standalone island design concept has been considered. An island concept is not essential to the design. Regenerable SO_2 absorbers can be located remotely from the regenerator and lean and rich DS piping can be run through the refinery to serve each island. A common SO_2 solvent regeneration system, located adjacent to the H_2S amine regenerator, SRU and SAR areas, will allow the SRU and SAR to back each other up as disposal points for either excess H_2S or SO_2 produced by the refinery. The maturity of the system and its use in a number of industries now allows the refinery to consider SO_2 capture as simply another utility system. It can be applied on a refinery-wide basis, much as is already done for H_2S capture systems.

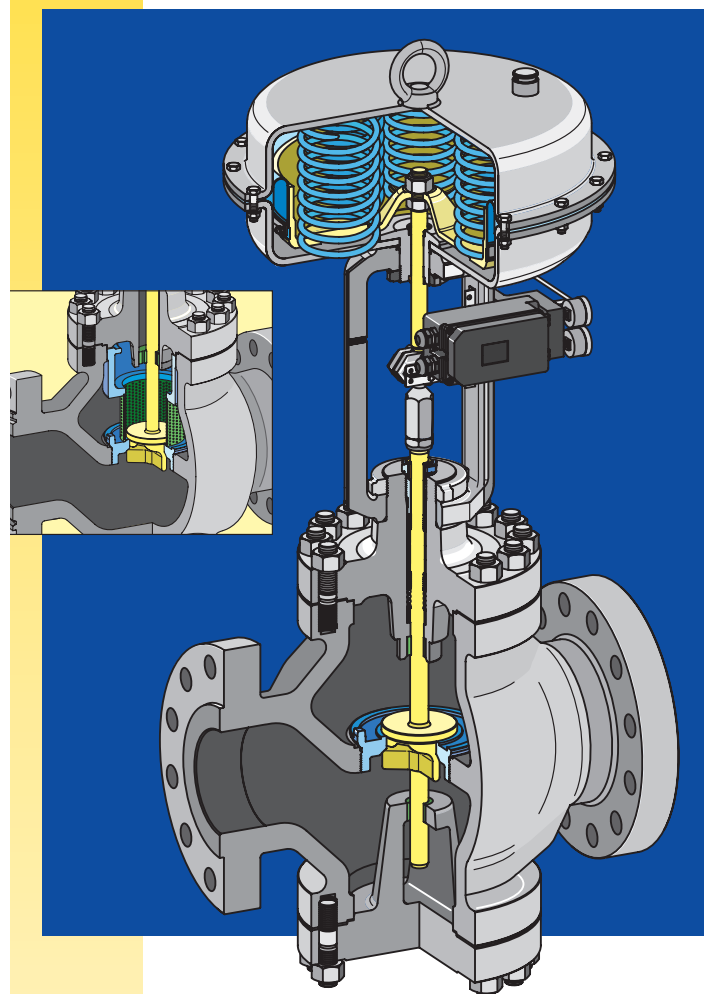
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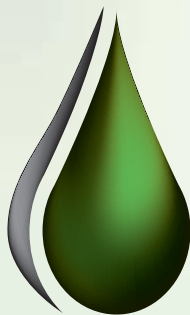
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Tough decisions for refining industry players

With the golden age of record high margins and high oil products demand behind it, the refining industry has some complicated decision-making ahead of it, said Booz & Company in a recent report. The analysis was published before oil prices swung below the psychologically important \$100/barrel mark as the September 2008 bankruptcy of Wall Street giant Lehman Brothers unleashed a global financial tsunami. It said uncertainties facing the refining sector included the effect of prices on oil demand, the extent to which new transportation technologies will displace oil-based vehicles, the cost of building new refining capacity and the future level of biofuel use amid growing concerns about food prices.

As the global economy deflates, refining margins could worsen to \$3–5/barrel, levels not seen since 2002, according to the study. Over the longer term, beyond 2013, the strength of refining margins will be dictated by demand growth in the developing world — a fundamental shift from dynamics of the recent past, when margin cycles were determined almost solely by the speed at which capacity was added, Booz & Company said. As fuel demand shrinks and refining capacity expands, refiners could find themselves in an oversupply situation. Most strikingly, the US could soon become a net exporter of gasoline — something that seemed highly unlikely just a few months ago. Asia could mop up the surplus, but the effect of such a shift, given shipping costs and specific refining economics, would be to reduce margins for both European and US refiners, Booz & Company warned.

The growing importance of biofuels, with more countries mandating spiking transportation fuels with the cleaner product, is another ingredient on the supply-side equation. However, the enduring truth for refiners globally is that they work in a cyclical industry, their investment decisions target a span of two to three decades rather than a couple of years and, irrespective of the depth and length of the looming downturn, when the world is back on its feet financially oil products demand could once again quickly outpace production capacity.

Asian refining projects

In spite of the rapid spread of the global financial crisis, Reliance Industries in India committed in late 2008 to proceed with pre-commissioning at the 580 000 bpd export-oriented refining complex.

This large project proceeded in the face of equipment shortages and cost escalations big enough to result in project cancellations for even the most profitable oil and refining companies.

With benchmark crude futures slipping from a historic high above \$147/barrel in July 2008 to below \$55/barrel in late November 2008, the refining industry is now viewed as being on the cusp of a sharp downturn after sustained high downstream margins from 2003–2007. The likely contraction in global oil demand growth in the coming months, far outpacing any increase in Chinese demand, coupled with more than half a million bpd of new capacity at the Reliance Jamnagar complex, is expected to exacerbate a drop in refining margins across Asia. Reliance was already operating an export-oriented 660 000 b/d refinery at Jamnagar.

Apparently, Reliance and other Indian refiners are continuing to proceed with new refinery projects and capacity expansions. These expansions, which would seem to contradict the current business climate, are in keeping with the Indian government's plan to make the country a refining hub, in response to the expected long-term global shortage of refining capacity. To be sure, the long-term outlook held by many planners in developing countries (including those in Africa and Venezuela) is for refined product demand to increase steadily in spite of the current surplus in refining capacity (and dramatic declines in refining margins). For example, Bharat Oman Refineries, a joint venture between state-owned refiner Bharat Petroleum Corporation Limited (BPCL) and Oman Oil Corporation, is progressing with a 120 000 bpd refinery at Bina in Madhya Pradesh and targeting completion for the end of 2009.

Hindustan Petroleum Corporation Limited has a 180 000 bpd refinery project at Bhatinda in the northern state of Punjab, aimed for completion in 2011. The largest state-owned refiner and marketer, Indian Oil Corporation (IOC), is working on a 300 000 bpd refinery at Paradip on the country's east coast. The project had been targeted for completion by fiscal 2011–2012, but is now at a crossroads over costs.

Essar Oil, the only other private refiner, has the most aggressive capacity expansion plans. It is more than tripling its relatively new 210 000 bpd refinery at Vadinar on India's west coast to 680 000 bpd by 2010. Other expansions and debottlenecking plans at existing refineries, including Mangalore Refinery

and Petrochemicals Limited, Kochi Refineries, HPCL and IOC, will together add some 286 000 b/d of capacity by 2012.

Not all projects have had a smooth start. IOC, facing a near-doubling of expenditure on its Paradip refinery from the Rupees 256.5 billion (\$5.98 billion) spending its board had approved in principle, has scrambled to look at all available options to finance the project off balance sheet. The options include scaling down the project size and implementing it in stages. The configuration currently on the drawing board is a 300 000 bpd refinery and a petrochemical complex including paraxylene and purified terephthalic acid (TPA) production facilities.

An important factor detrimental to future profitability for Indian refiners is that the Indian government will no longer extend a seven-year tax holiday ("sunset clause") to new refinery projects commissioned after March 2012. This income tax holiday to refineries will be available before March 2012 only if they are owned by a public sector company or built by companies where state-run firms have a 49% stake. These conditions have kept refineries planned by Essar Oil at Vadinar in Gujarat, Nagarjuna Oil at Cuddalore in Tamil Nadu and Cals Refineries at Haldia in West Bengal out of the tax benefit, as they have no public sector equity. Sources said even though work on private sector refineries began much before the sunset clause was introduced, the Finance Ministry has ignored their cause.

Essar, which is expanding its 10.5 million tonnes Vadinar refinery to 34 million tonnes, has written to Prime Minister Manmohan Singh, saying the move would severely affect the viability of the project and its financial interest would be jeopardised. The Vadinar expansion is to be completed before the public sector refineries come on-stream. "This will make it impossible for our refinery to compete with Paradeep, Bina or Bhatinda refineries, as well as other existing refineries, as both refineries in the past and also the upcoming refineries being built will enjoy this benefit (sunset clause), whereas Essar Oil will not be treated at par," the company wrote to the Prime Minister. "It is very unfortunate that the proposed amendment would be discriminatory to private sector refineries and will make private sector investments inviable," it said seeking a level playing field by removing the inequality. Nagarjuna Oil is building a six million tonnes refinery in Tamil Nadu, while Cals Refineries is assembling a five million tonnes unit in West Bengal.

In any event, Platts estimates that if all the current capacity expansions and new refinery projects in India proceed

without a hitch, the country's refining capacity will rise 65% from the current 3.0 million bpd to almost 4.93 million bpd by 2012, well beyond the rise in domestic demand. The surplus refining capacity, which will rely on export markets globally, will grow from about 580 000 bpd in 2008 to 2.09 million bpd by 2012, according to Platts' calculations.

Alliances between Indian refiners and Middle Eastern oil producers are being considered. For example, Saudi Aramco has not made any investments in India. Its President and CEO, Abdallah S Jum'ah, said that inter-dependence is a point of strength rather than a sign of weakness. Saudi Aramco and Saudi Arabia are continuing to work hand-in-hand with the Indian petroleum sector. Oil already accounts for more than 35% of India's primary energy consumption and is set to grow in both absolute and percentage terms, and because India's own petroleum reserves are limited that means a growing reliance on oil imports.

In fact, the IEA forecasts India's petroleum imports to triple between now and 2030, at which point India will be the world's third largest importer of petroleum, with volumes roughly equivalent to Japan's current imports. Reliance Industries' Company Chairman, Mukesh Ambani, recently noted that a stable oil pricing regime was needed to sustain investments and economic growth. He said that: "When in 1999 we started our first refinery at Jamnagar, we saw a recession globally and when we are about to start up our second refinery (at Jamnagar), history is repeating itself."

In neighbouring China, state-owned integrated giant Sinopec in mid-2008 launched operations at a 200 000 bpd greenfield refinery at Qingdao on the coast of the northern Shandong province. Two more major greenfield refineries were due to be commissioned by early 2009. China National Offshore Oil Corporation (CNOOC) will bring on-stream its 240 000 bpd Huizhou refinery at Daya Bay on the east coast of the southern Guangdong province. The state-owned upstream major is said to be planning to invest in another \$6.6 billion to expand the new Huizhou refinery to 440 000 bpd capacity by 2011.

Sinopec announced plans in 2008 to expand its Maoming refinery in Guangdong from its current 270 000 bpd capacity to 510 000 bpd, although the timeframe has not been disclosed. Sinopec and its foreign partners ExxonMobil and Saudi Aramco intend to triple the current capacity of their 240 000 bpd refinery in Quanzhou, which will process Saudi crude. PetroChina is developing a 200 000 bpd

greenfield refinery and petrochemical complex including an 800 000 mt/year ethylene plant and downstream facilities at Pengzhou in the southwestern province of Sichuan. Guangdong province alone, the economic powerhouse of China, has set a goal to raise its crude refining capacity to 2 million bpd and ethylene production capacity to more than 4 million mt/year by 2012. The province currently has a refining capacity of 670 000 bpd.

The four major state giants in China — Sinopec, PetroChina, Sinochem and CNOOC — are together expected to add some 113.8 million mt/year (about 2.276 million bpd) of refining capacity over 2006–2010, taking the country's total to around 9.4 million bpd, according to data from Sinopec. Altogether, Asia is expected to add about 1.4 million bpd of annualised new refining capacity in large projects by the end of 2009, in addition to the 700 000 bpd added in 2008. According to data provided by Credit Suisse, the large new plants in China and India will have an average distillate yield of 35–45%.

The capacity addition from new refineries in Asia alone matches the International Energy Agency's latest pared-down estimates for a 700 000 b/d growth in global oil demand for 2008 and well exceeds the 800 000 b/d figure the agency projects for increase in 2009 world consumption.

Chinese oil companies are also becoming very active overseas as they strive to keep their refineries supplied with feedstocks. The China-Russia \$25 billion loan for oil negotiation was a work in progress as of late 2008. A CNPC source close to the negotiation noted that the two sides could eventually sign a contract. According to the agreement, Russia will contract to export 300 million tonnes of crude oil to China over the next 20 years. In other overseas activities, CNOOC has been bidding \$300–\$700 million for natural gas assets in the Caribbean area, and CNPC is expected to take a 25% stake in the Pars LNG project in Iran.

Middle Eastern national oil companies have also become quite active in China, not just to secure a market for their crudes, but also to extend themselves further down the value chain. Kuwait Petroleum International and Sinopec, along with other partners, are planning a 300 000 bpd refinery that would exclusively process Kuwaiti crude and a 1 million mt/year ethylene cracker at Nansha in Guangdong. However, project costs for this venture have ballooned to an estimated \$8–9 billion in November 2008 from the \$5 billion expected in December 2007, and the start-up timeline is seen slipping to 2011 from the original 2010. KPI, in partnership with Sinochem and Shell, is building a

240 000 bpd refinery at Quanzhou on the coast of Fujian province, which is expected to be ready in 2010.

This does not take into account the possibility of further downward revisions in world oil demand growth estimates. The Paris-based energy policy adviser to the industrialised world is still waiting to see if a prolonged economic downturn in the US might signal a monumental structural shift in US oil demand and has kept its forecasts for China, India and the Middle East stable, saying statistically there is no evidence of a slowdown in these regions. However, the IEA's Executive Director Nobuo Tanaka acknowledged the biggest question mark was how the oil demand of China, India and countries in the Middle East might get affected by the global financial turmoil. At the end of the day, Asian refiners can take comfort from the fact that they are in the hub of the global centres for future oil demand growth, and their billion-dollar investments are going into facilities capable of taking in the trashiest crudes — sour, heavy, and even highly acidic — to churn out the cleanest of products. In short, they are well positioned to ride the next wave of Asian oil demand growth and attractive margins, whenever it comes.

European refiners cutting back on production

Europe's oil refiners may have to curtail production in early 2009 as profit margins sag and worsening economic conditions curtail demand, according to analysts and industry participants. While crude prices have more than halved since July this year, the rate of decline has been outpaced by drops in the prices of refined products, most noticeably for gasoline, as consumer appetites slow down and Europe tilts toward recession.

It has left refiners with the prospect of their refining margins turning negative in some instances, threatening a possible wave of discretionary run cuts and even plant closures. "We forecast that European refining margins will decline sharply in 2009, driven by a much weaker supply/demand balance, especially for diesel, the key product for European refiners," said Neil McMahon, Senior Analyst at Bernstein Research in London. Signs of reduced refinery runs have already started to emerge. Europe's largest independent refiner, Petroplus Holdings AG (PPHN.VX), has reduced run rates at its 117 000 bpd refinery in Teesside in the UK.

Meanwhile, an official from French union Confédération Générale du Travail, or CGT, said that French oil major Total SA (TOT) may pare back its gasoline production capacity in Europe amid what it sees as an irreversible

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decline in demand from the US, Europe's main export market, where the appetite for gasoline has also wilted in the tougher economic conditions.

While the demand picture is challenging enough, Europe's refiners risk having to compete against a potential surge in supplies from new facilities, particularly in Asia and the Middle East, which are likely to heap pressure on refining margins. Energy consultancy Wood Mackenzie estimates an additional 12 million bpd of refining capacity will come online by 2015.

Inventories will be increased by Reliance Industries' 580 000 bpd Jamnagar refinery in India. The refinery's diesel export capacity amounts to around 30% of current European imports. "Our analysis suggests Europe will be the most attractive destination for these cargoes," McMahon said. "If you are in Europe doing gasoline, it is not going to be pleasant," said Alan Gelder, Vice President of downstream oil at Wood Mackenzie consultancy. "It is not a particularly buoyant story for the refining sector."

European and Japanese non-integrated refiners are most vulnerable to plant closures, Fereidun Fesharaki, Chairman and Chief Executive Officer of FACTS Global Energy consultancy, said at a recent conference in London. "The global refining industry is headed towards substantial overcapacity," Fesharaki added.

Refinery utilisation in the member countries of the Organization for Economic Cooperation and Development (OECD) fell to an average of 78.9% in September, the lowest average level since October 1995, according to the group's energy watchdog, the International Energy Agency (IEA). European refinery utilisation stood at 84.1% in September, the latest month for which IEA data are available, compared with the 87.7% average since January 1995.

But the travails facing Europe's refiners could equally translate into a headache for the world's key oil producers. "Oil consumption will not grow and may even shrink," warned Petroplus Chairman Thomas O'Malley. OPEC is expected to scale back oil production to prevent oversupplying market inventory levels. "In normal market conditions, refinery cutting runs would translate into a build of crude stocks, but with the run for cash there is no strong desire to hold up stocks, so there is little choice but for OPEC to match any refinery run cuts with the corresponding production cuts," said Olivier Jakob, Managing Director of Switzerland-based consultancy Petromatrix. While restricting crude oil and refinery production should in theory lead to a recovery in prices, neither will be

achieved without a revival in consumer demand. If production cuts succeed in lifting oil prices, without a commensurate revival in product demand, refiners' already battered margins are likely to worsen further. That raises the prospect of more run cuts, more closures and, worryingly for OPEC, even less appetite for crude.

North American refiners delaying projects

Irving Oil in Canada says it will stretch out construction of its proposed second oil refinery for Saint John over an eight-year period rather than four years. Kevin Scott, Senior Executive in charge of building the refinery, said that the project, now estimated to cost \$8 billion as of late 2008, would still begin in 2011, but will take longer to build up to full planned production levels of 300 000 bpd. He says that is due to shortages of skilled labour, higher costs of capital and an expected downturn in the North American economy.

The refinery is a mainstay in the Liberal government's plans to create an energy powerhouse in Saint John, and there have been projections it will eventually create about 1100 full-time jobs. However, Energy Minister Jack Keir says he considers the announcement good news because he was fearful the company and partner BP might cancel the project entirely due to the economic downturn. Scott says the decision is partly because the oil industry is facing some exceptional challenges, such as rising capital costs and the dampening in demand for petroleum products.

A recent pullback in plans to expand or upgrade US oil refineries is an indication of the uncertainty facing refining companies after enjoying high profits for several years. The uncertainty stems from volatility in commodity and capital markets, as well as from a historic decline in gasoline usage beginning in 2008 that has raised doubts over long-term demand for petroleum-based fuels.

Marathon Oil and Valero Energy had already announced by mid-2008 they would delay or cancel refinery upgrades as part of broader cuts to capital spending programmes in 2009. And given current economic difficulties, experts warn other projects could follow. "I think it is a trend you are going to see until at least 2009, and it will continue beyond then if refining margins do not improve," said Brian Youngberg, Energy Analyst with Edward Jones in St Louis. As recently as summer of 2007, margins were near \$30 per barrel. They fell by half in summer 2008 as oil prices skyrocketed and demand weakened. A refining slowdown in the short term mostly would affect the industry and its employees, but a prolonged reversal

could send prices at the pump up again after a significant recent drop.

However, several major refinery projects are moving forward and are unlikely to be affected by the downturn. They include Marathon's 180 000 bpd expansion of its Garyville, Louisiana, plant, targeted for completion in late 2009, and Motiva's 325 000 bpd addition to its Port Arthur, Texas, refinery, to be completed in 2011. Projects in earlier stages of development or still awaiting final investment decisions may be at more risk.

In recent years, refiners announced aggressive plans to expand and upgrade refineries as profits rose and global demand for petroleum products such as gasoline and diesel fuel grew more quickly than the capacity to produce them. In the US, refineries had been running near capacity, particularly during peak summer demand periods, so additions were viewed as safe, despite the huge investment required. But the gasoline market has weakened recently because of increasing supplies and shrinking demand.

On the supply side, increased blending of ethanol with gasoline means a gallon of gas stretches to more than a gallon of motor fuel. And more imported gasoline is available because Europeans are switching to diesel vehicles. Finally, refinery upgrades boost the amount of gasoline that can be squeezed from a barrel of crude. Meanwhile, US gasoline demand has dropped 3% amid a slowing economy and \$4 gasoline prices in summer 2008. If the trend holds, it would be the first time in more than a decade that demand has not increased over the previous year.

Declining demand has been a major factor in refiner decisions to delay or cancel projects, said Cindy Schild, Refining Issues Manager at the American Petroleum Institute in Washington. But she said there is still a case to be made for more refining capacity. One reason is greater flexibility to supply the nation's fuel needs because the US now imports more crude than it has refining capacity, she said.

Today, US refining capacity stands at about 17.8 million bpd over 150 refineries, more than half of which are on the Gulf Coast. The US consumes 20 million bpd of crude oil. Expansion projects in the pipeline today will add about 900 000 bpd of crude distillation capacity by 2014, said Joanne Shore, Analyst with the US Energy Information Administration. That is roughly in line with the pace of additions over the past decade, but lower than the 1.5 million bpd or more refiners had planned to add a couple of years ago, she said. If all projects on the books now are completed, the US will no longer need to add more refining capacity, the Energy Information

Administration recently forecast. "You are basically going to have enough capacity at that point," Shore said. Even before the economic downturn began in Q3 2008, the number of refinery projects started slipping partly because of rising labour and material costs, but has accelerated recently and could fall further still, she said. For example, Houston-based Marathon Oil is delaying a \$1.9 billion upgrade of its 100 000 bpd refinery in Detroit. Marathon had already decided earlier not to pursue other projects, such as two heavy oil projects at its oil refineries in Robinson, Illinois, and Catlettsburg, Kentucky, that were deemed too costly. San Antonio-based Valero, the nation's largest refiner, is indefinitely postponing or delaying expansions and upgrades at plants in Port Arthur, Texas; Memphis, Tennessee; St Charles, Louisiana; and Quebec.

The downturn has not been limited to the US: Houston-based ConocoPhillips and the state-run Saudi Arabian Oil Co are delaying plans to build a 400 000 bpd refinery in Yanbu, Saudi Arabia, citing uncertainties in the financial and contracting markets.

LNG supply crunch

An LNG supply crunch looks inevitable around 2011/13, but what about the years beyond? Following the large increase in new LNG supply due to come on-stream by 2011 — around half in Qatar — incremental supply growth will slow drastically for at least two years, according to IEA estimates. It takes between three and four years from final investment decision (FID) to construct an export project. So, assuming projects are not unexpectedly delayed, it is a straightforward matter to project the evolution of incremental supply up to four years ahead. But only five FIDs have been taken since the start of 2006, representing just 19 million tonnes a year (t/y) of new supply.

How long this supply crunch will last will depend on how many projects are sanctioned over coming years. But while the list of proposed projects is long, those with a realistic chance of coming on-stream in the 2012–15 time frame are few, considering the current global financial crisis.

Africa's LNG export capacity — already more than a quarter of the world total — could double over the coming five years, with more to come after that if plans under discussion are realised. In addition to the current financial downturn, the main brakes on development are construction costs and, in Nigeria, security concerns. LNG Analyst, Martin Quinlan, noted that: "Algeria was the world's first LNG exporter, but it was many years before Africa's other big gas countries were in a position to join the trade. Now, however,

there is no stopping them. Africa's existing LNG export capacity of 57.5 million t/y will increase by 28% (16.1 million t/y) by 2012 from projects already going ahead, and by an additional 44.9 million t/y by 2014 from projects still subject to final investment decisions."

The five African LNG exporters — Algeria, Nigeria, Egypt, Equatorial Guinea and Libya — all have projects for new capacity either under construction or in planning. In 2012, they will be joined by Angola, which also has additional capacity planned. Mauritania and other countries are trying to prove up sufficient gas reserves to join the club.

To meet future LNG demand cost-effectively, the world's first unit employing floating liquefaction technology was ordered in September 2008. First announced in 2004, the Gulf LNG Clean Energy Project on the Pascagoula Bayou ship channel in Pascagoula, Mississippi, is estimated to cost \$1.1 billion. Technip performed the FEED work for the project. Owned by partners El Paso Corp (50%), Crest Group (30%) and Angolan national oil company Sonangol (20%), the Gulf LNG Clean Energy Project is expected to start up in November 2011. Development of the project requires the construction of an unloading dock for LNG tankers (with the option to easily add another dock in the future). Aker Kvaerner has been awarded the development contract. Current plans envision the facility welcoming a ship every three days for LNG unloading with a send-out capacity of 1.3 Bcf/d.

Peru LNG is developing an LNG project consisting of the development, construction and operation of an LNG plant. The plant consists of a 4.45 million tonnes per annum liquefaction train. The LNG will be loaded onto tankers at a marine loading terminal adjacent to the LNG plant for export to market. Ex-Im Bank approved financing for the project in early 2008.

Middle Eastern projects

As refining projects across much of the Middle East come under threat from cost inflation, Saudi Arabia seems determined to push ahead with large capacity additions. Current proposals would add some nine million bpd of refining capacity through a combination of plant expansions and new projects. But severe cost inflation means that not all of them will go ahead. Across the region, expenditure planned for refining projects dwarfs upstream spending budgets. According to estimates by Saudi Arabia-based energy finance group Apicorp, total investments in the oil downstream for the 2008–12 period amount to \$105 billion compared with \$67 billion for upstream ventures. Saudi

Arabia is tentatively planning to build two 400 000 bpd export refineries — Jubail and Yanbu — in addition to the PetroRabigh refining (368 000 bpd) and petrochemicals (2.4 million t/y).

Three refinery projects in Saudi Arabia have been delayed, according to the Middle East Economic Survey (MEES). Saudi Aramco and Dow Chemical's joint expansion of the Ras Tanura complex faces delays because the project is believed to be too large for contractor KBR and needs to be divided with another company, MEES reported. According to earlier statements by officials, it had been expected that the expansion would be operational in Q1 2012. The expected cost of the project is believed to be around \$8 billion. Bids for investment in the Jazan facility have been delayed by nearly a year to March 2009 while an incentives package is prepared, MEES said.

The start-up of a plant to be operated by Rabigh Refining & Petrochemicals will probably be pushed back to Q1 2009, MEES said. Saudi Arabia, the world's largest oil producer, is planning to raise refining capacity by 50% to provide fuel oil and gasoline for soaring local demand, and benefit from exporting high-value oil products.

2009 light olefins analysis

The massive build-up of ethylene capacity in the Middle East and Asia progressing at a rapid pace and is sending the industry into another down cycle. From 1995–2008, ethylene capacity increased by more than 22 million metric tonnes in Asia/Pacific, and by more than 13 million tonnes in the Middle East. By 2015, these regions are projected to add an additional 41 million metric tonnes of ethylene capacity. With a significant cost-advantaged feedstock base, ethylene production in the Middle East will rank as the most competitive in the world. Given that the vast majority of this production targets export markets, this surge in supply will dramatically change trade dynamics. Ethylene and derivative capacity investments in Asia are primarily driven by the region's strong desire to be more self-sufficient in petrochemical building blocks and supply the rapidly growing consumer goods manufacturing base operations. The interplay between these somewhat conflicting strategies in Asia/Pacific and the Middle East will invariably create dynamic conditions in the global ethylene and derivatives markets. CMAI experts forecast that near-term crude oil and natural gas values could help North America olefin derivative units remain competitive in the global market. From the mid-1990s to the early years of the current decade, the international market share of North American ethylene derivatives was on the decline.

NEW PRODUCTS

Calculating boiler wall thickness with wireless technology

The Smart Wireless technology from Emerson Process Management is helping to provide valuable condition monitoring information at the Total Petrochemicals plant in Carling Saint-Avold, France. The introduction of wireless transmitters provides new temperature measurement data, enabling the company to calculate changes over time in wall thickness on a boiler that provides steam to a steam cracker, enabling personnel to anticipate when it may need replacement.

By installing a wireless solution to connect the additional measurement points, Total Petrochemicals removed the need to install around 1km of new wiring. An additional benefit of the solution has been a reduction in the movement of personnel into and around at-risk areas.

Total Petrochemicals wanted to better understand the condition of the boiler and anticipate when it might need to be replaced. To achieve this aim, the company was keen to introduce a number of new temperature measurement points. By measuring the internal and external temperature of the boiler walls and identifying heat loss, it is possible to calculate the material's resistance and infer its thickness. "Our plant is more than 30 years old," said Jerome Uszes, Electricity Control & Regulation Maintenance Manager, Total Petrochemicals. "With the rising cost of copper and ageing existing wiring (corrosion, infiltration and degradation of armature), finding alternative methods to carry data throughout the plant is becoming essential."

Eight Rosemount 648 wireless temperature transmitters were installed directly onto the exterior of a boiler drum situated 50m above the ground. An Emerson Smart Wireless Gateway was positioned on the roof of a technical building around 300m from the devices. Two additional temperature gauges were installed in strategic areas between the boiler and the gateway to provide sufficient coverage to the area and to enable supplementary measuring points to be added in the future, as required.

Data from the wireless transmitters is passed from the Gateway to a third-party DCS system via Modbus. From the control room, the operators have gained visibility of the thermal status of the boiler walls, allowing them to determine how the internal (process) and external (climatic) conditions impact on the material's deterioration.

An additional wireless device, a

Rosemount 3051S pressure transmitter, is providing redundancy for an existing wired device that provides a critical measurement in the plant. This transmitter also reinforces the wireless mesh and provides an additional path back to the gateway.

The Smart Wireless' self-organising mesh technology is very reliable, and each measurement point has a redundant communication via two or three routes. With this technology, each wireless device can act as a router for other nearby devices, passing messages along until they reach their destination. If there is an obstruction, transmissions are simply rerouted along the network until a clear path to the Smart Wireless Gateway is found. As conditions change or new obstacles are encountered in a plant, such as temporary scaffolding, new equipment or a parked construction trailer, these wireless networks simply reorganise and find a way to get their signals through.

All of this happens automatically, without any involvement by the user, providing redundant communication paths and better reliability than direct, line-of-sight communications between individual devices and a receiver. This self-organising technology optimises data reliability while minimising power consumption. It also reduces the effort and infrastructure necessary to set up a successful wireless network.

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Flanges and circulation heaters

Chromalox, a manufacturer of electrical heat and control products, has introduced a new line of ANSI flange and circulation heaters with a standardised design that meets all major global certifications, eliminating the need for global organisations to deploy different designs in different parts of the world. The new line of immersion heaters also features a number of enhancements that increase product functionality and performance. The flange and circulation heaters are designed to be mounted in pipes or

"By measuring the internal and external temperature of the boiler walls and identifying heat loss, it is possible to calculate the material's resistance and infer its thickness"

vessels to efficiently and precisely heat liquids and gasses in a variety of process industries, including petrochemical, oil and gas, as well as alternative fuels.

Chromalox has redesigned the heating element layout, bussing and housing on the new line of heaters to achieve more even heat distribution, improved fluid flow, and easier installation and service. This global design also streamlines manufacturing processes to increase production flexibility and reduce turnaround times. Features of the new product line include:

— **Octobox housing design:** The Octobox design offers maximum flexibility for wiring options. It works with both NPT and Gland Plate Style connectors, has six different angles to bring conduit into the housing, and the removable plate design allows the installer to choose the exact connection size needed to match the conduit runs. The housing is fully removable, providing unrestricted access to the bussing arrangement, thermowell and circuit identification

— **Triangular element pattern:** The heating element pattern has been completely redesigned to achieve more even heat distribution, resulting in cooler elements, fewer pressure drops and a longer life for the unit

— **Element bussing/power connections:** A new style of vertical bussing is used that simplifies installation while providing more robust configuration to support higher amperage, stronger power connection points and cooler bussing temperatures

— **Fully configurable:** The new design is driven by the Chromalox Configurator, which can reduce engineering time by more than 90%. This means that, in most cases, a custom design will reach the production floor the same day it is ordered.

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Detecting LPG gas hazards

The Xgard IR LPG from Crowcon is a low-cost infrared (IR) fixed gas detector designed to detect liquid petroleum gas (LPG) hazards before concentrations reach flammable levels. Typical environments requiring LPG monitoring include petroleum refineries, petrol stations, buildings that use LPG as their main gas supply and many manufacturing processes. Conventional LPG detectors based on catalytic pellistors are susceptible to poisoning in some industrial atmospheres. This can make their readings unreliable and even destroy the sensor altogether. The Xgard IR LPG is totally immune to poisoning and will warn of LPG gas hazards in environments that are unsuitable for other types of sensors. The detection range is 0–100% of the lower explosive limit.

Infrared sensing has additional benefits over traditional sensing. Unlike catalytic pellistors, IR sensors detect flammable gas in inert backgrounds and are not damaged by high gas concentrations. The Xgard IR consumes half the power of comparable catalytic bead detectors. The new IR LPG sensor can be specified with two types of enclosures: polyester-coated aluminium or 316 stainless steel for maximum corrosion resistance in extreme environments. The sensor, which has a life expectancy of over five years, is a simple plug-in module that makes replacement quick and easy. UL approved for use in hazardous areas to detect methane, butane and propane, the Xgard IR LPG is Exd flameproof rated. The standard junction box is designed for both wall and ceiling mounting, and four cable gland options ensure compatibility on any site. The detector takes a range of accessories for harsh or wet conditions and for remote sampling.

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Separating process oils from water

The Suparator technology from Aqueous Recovery Resources effectively separates process oils and other liquids, along with suspended contaminants from water. The patented system, based on Bernoulli's Principle of physics, enables users to separate liquids differing in specific gravity, thus making significant savings in water consumption by allowing for the reuse of the water as well as other process fluids, such as separated oil. This saving of water also improves uptime, extends the use of detergents and significantly reduces the need to prepare water, thus saving on energy.

Application of this principle achieves perfect separation of any two fluids with a specific gravity differential. Unlike conventional water separation devices, it uses no moving parts or media to provide over 99% separation of polluting oils or liquid contaminants from water while it is still in the process tanks, thus saving a typical industrial user millions of gallons of water each year. This liquid-liquid separation allows for the reuse of recovered contaminants, like oil, as well providing a means of reuse for it. Plus, because separation is accomplished dynamically, Suparator is able to remove dirt and other unwanted foreign objects from the suspended oil before they can settle into the water tank and necessitate water and/or detergent changes. The technology has also been already deployed on an exploratory basis in petrochemical plant effluent pretreatment, crude washing and other applications.

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"IR sensors detect flammable gas in inert backgrounds and are not damaged by high gas concentrations"

Determination of biodiesel content

A new method that allows for the fast and accurate determination of biodiesel content in diesel from Grabner Instruments is used in IROX Diesel, a portable, fully automatic and extremely compact mid-FTIR spectrometer. The instrument's spectrometer is fine-tuned for diesel components and measures the content of total aromatics, polynuclear aromatics and biodiesel. Based on a stored number of calibration samples, it predicts such important properties as Cetane number, Cetane index or distillation properties like T85, T90 and T95.

Derived of information from the spectrum, the new method calculates biodiesel content in diesel. Two areas in the spectrum are used for the measurement: around 1745cm⁻¹ for lower and 1170cm⁻¹ for higher biodiesel content. FAME concentration is then determined by calculating the spectrum area rather than determining the height of the ester peaks compared to the baseline. The new method yields results with better accuracy than required by the biodiesel method EN 14078 and is suitable for the determination of FAME up to 40 wt%. A complete diesel measurement can be done in just three minutes, making the IROX Diesel the ideal instrument for fast and accurate testing of diesel and biodiesel blends in the laboratory or directly on-site.

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X-ray diffraction of capillary samples

Modern materials science demands sophisticated tools to perform investigations in defined environments and under controlled temperature conditions. Non-ambient X-ray diffraction (XRD) is established for a wide range of industrial and research applications. Now, a new capillary extension expands the capabilities of this already powerful combination. The novel accessory creates a two-in-one reflection and transmission high-temperature XRD system.

PANalytical's PreFIX concept allows seamless integration of the new Capillary Extension, transforming the HTK 1200N High-Temperature Oven Chamber into a high-end capillary

heater for transmission XRD between 25°C and 1000°C. Conversion between standard geometry for flat samples and the capillary setup can be carried out in minutes without removing the oven chamber from the goniometer. Temperature data are saved in XRDML format for further processing using PANalytical's X'Pert Data Collector software, which controls all measurement routines.

Studying materials in non-ambient conditions is important for many industries and areas of research. XRD of capillary samples offers an effective solution for preferred orientation problems, providing an easy and rapid method for obtaining randomly oriented powder samples. Uniform high temperature performance and excellent control characterise the HTK 1200N.

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Ultrasonic transducer for liquid levels in corrosive atmospheres

The Siemens Division Industry Automation has added a PVDF (polyvinylidene fluoride) nose cone as an option to the non-contacting ST-H ultrasonic level transducer for liquids. This new material type improves the chemical compatibility of the ST-H transducer, offering more options for chemical storage and process vessel applications. When paired with a Siemens ultrasonic controller, the ST-H transducer effectively measures the level of liquids in applications up to 10m (33ft) away in conditions from -40 to +73°C (-40 to 164°F). The transducer design includes both a 1in and 2in integral process connection. This allows easy mounting on varied vessels. When installed using the 2in mounting threads, the only wetted parts are PVDF, providing excellent chemical immunity in corrosive atmospheres. The ST-H transducer is impervious to dust, moisture, corrosion, vibration, flooding and temperature extremes. The non-contacting design virtually eliminates the nuisance, danger and expense of cleaning, adjusting and repair associated with contacting devices.

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Editor's note

PTQ would like to bring to the attention of its readership the recent acquisition by Shell Global Solutions International BV of 100% of the shares of Cansolv Technologies Inc. Cansolv offers technology for the control of sulphur dioxide (SO₂) and other contaminants as well as a carbon dioxide (CO₂) process for greenhouse gas emissions capture, and has published an article pertaining to this technology in this issue, beginning on p127, "SO₂ scrubbing in refinery applications," by Rick W Birnbaum.

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