

# Preparing for Bottom-of-the-Barrel Vessel Entry Venezuelan Coker Unit Emergency Shutdown

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## Coker Unit Turnaround - Venezuela



## Project



- ✦ Decontamination of the main fractionator coker column at a Venezuela refinery
- ✦ 4 years since last shutdown
- ✦ Main goal; eliminate delays in vessel entry by minimizing manual and mechanical cleaning activities of the tower

## Challenge

- ✦ Large amounts of coke,  $H_2S$ , and pyrophoric concerns



## Past Procedure

- ✦ Traditional chemical cleaning every 4 years with 6 different hazardous chemicals requiring full body suits
- ✦ Chemicals circulated over an average of 36 hours
- ✦ Required 12 man crew per shift and 5 days of mechanical preparation

## Past Procedure Results

- ✦ Left a tarry residue at the bottom of the tower up to 2 feet over the lower manway, completely burying bottom distributor
- ✦ Extensive mechanical cleaning was required under fresh air
- ✦ Leakage from chemical hoses required ground clean up
- ✦ Entry permits were delayed until all cleaning tasks were complete



## Options

- ✦ Available refinery materials; BTX, heavy aromatic naphtha (HAN), gas oil, kerosene
- ✦ Chlorinated solvents
- ✦ Traditional/commodity chemicals; i.e. d-limonene
- ✦ Mechanical cleaning
- ✦ Mixed approach between methods

## Results & Impacts

- ✦ Unpredictable results – often disappointing
- ✦ Removing value as feedstock (BTX)
- ✦ Long cleaning times
- ✦ High volume of waste
- ✦ Hazardous materials
- ✦ Multiple steps





**Bottoms Circulation**



**Vapour-Phase<sup>®</sup> Application**



**Continuous Monitoring**



**Water Rinse with Zyme-Ox<sup>®</sup> Plus**





## Bottoms Circulation

- ✦ Specialty Rezyd-HP chemistry added to the HVGO cutter stock
- ✦ Refinery wanted to keep their standard circulation time of 24 hours and normal flow rate
- ✦ Only change is the addition of chemistry



- ✦ Custom blend including high Kb solvent and surfactant
- ✦ Applied as an additive to common refinery cutter stocks
- ✦ Low hazard (2, 1, 0)
- ✦ Biodegradable
- ✦ Dissolves and/or fluidizes deposits
- ✦ Significantly decreases final cleaning and total cleaning time
- ✦ Low volumes required and less waste than other methods

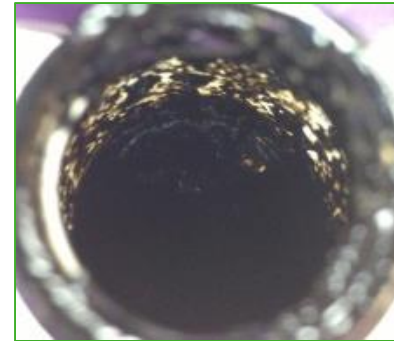


Results: loose coke for ease of removal.  
(Pictured: coker strainer basket)





- ✦ Sample comprised of 75% asphalt, 25% ground tire rubber
- ✦ Sample almost impenetrable
- ✦ Several tests tried with alternative chemistries at 6% dose with no to little effect
- ✦ Successful Results:
  - ✦ LCO 1:1
  - ✦ Rezyd-HP at 6% dose
  - ✦ 120 F
  - ✦ Slight agitation



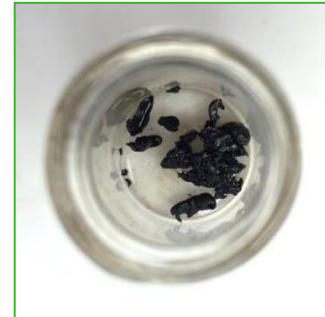
Product X



Rezyd-HP treatment:  
sample fluidized

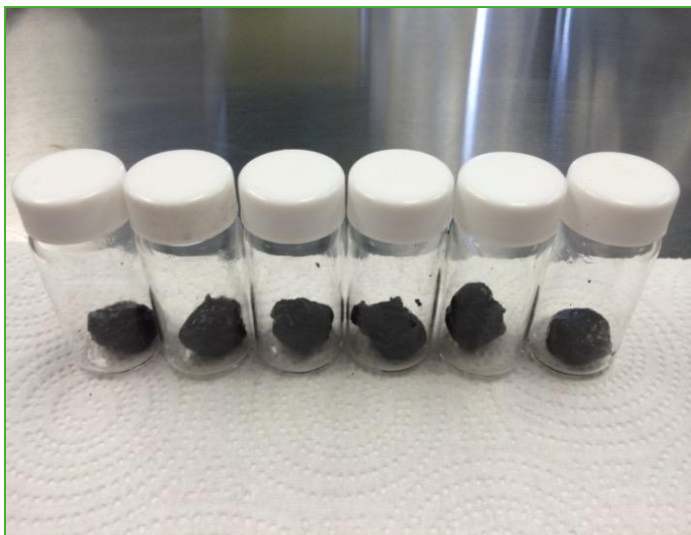


- ✦ Vacuum tower bottoms from a Texas refinery
- ✦ Successful Result:
  - ✦ After 1 hr
  - ✦ LCO 1:1
  - ✦ Rezyd-HP at 2% dose
  - ✦ Some agitation
  - ✦ 120° F
- ✦ After 4 hours all were successful but Rezyd-HP successful after 1 hour



(L to R) HP, Product X, Product Z





Quench Tower Bottoms Prior to Treatment



Product X vs Rezyd-HP in LCO @ 120F



Product X vs Rezyd-HP in HAN @ 185F





## **Bottoms Circulation**

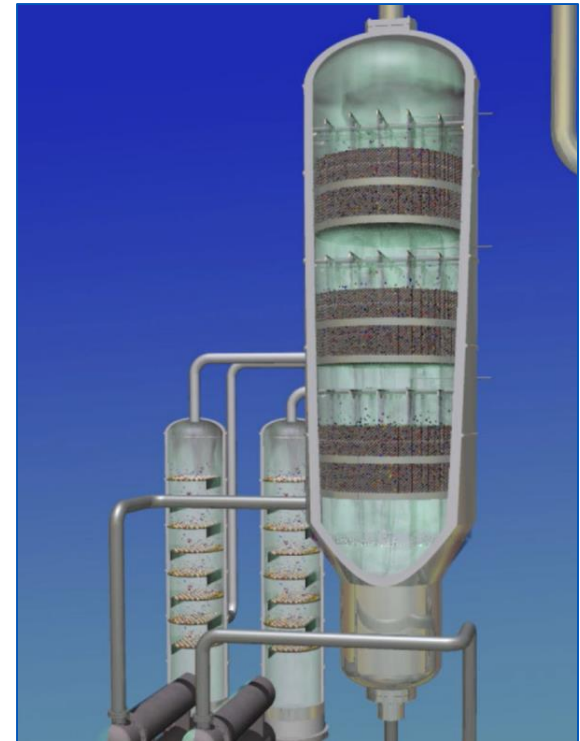


## **Vapour-Phase® Application**

- ✦ Zyme-Flow UN657 injected into steam line at base of tower (add more specifics)
- ✦ Chemistry injected over a 10 hour period
- ✦ Steam routed to the flare



- ✦ Operations shuts down and de-inventories equipment using standard procedures
- ✦ Zyme-Flow UN657 chemistry is injected into the equipment with steam
- ✦ Same boiling point as water therefore chemistry contacts all surfaces with minimum injection points



Vapour-Phase



# “True” Vapour-Phase

	ZF Vapour-Phase	Steam Dispersion
<b>Boiling Point</b>	100 C	180 C
<b>Typical # of injections</b>	Crude Unit: 1 injection	Crude Unit: 5 injections points
<b>Effluent quantity*</b>	Mostly steam condensate, minimal injections, <12 hrs (no pre steaming)	Req. post treatment/water flushing, high volume steam, long pre steaming
<b>Equipment</b>	Drum pumps	Hoses, drum pumps, frac tanks, mixed tank
<b>Ability to travel</b>	As far as steam will travel - proven multiple kilometers	Depends on steam pressure – will drop out
<b>Effluent treatment</b>	None required	Collection and post treatment (Frac tanks)

*\*some studies show 80% reduction in effluent quantity*





## **Bottoms Circulation**



## **Vapour-Phase® Application**



## **Continuous Monitoring**

- ✦ Zyme-Flow chemistry concentrations tested at vents and drains throughout process to ensure dosage – self expending chemistry
- ✦ Technicians used 4-gas meters to verify H<sub>2</sub>S, LEL, and benzene levels consistently decline until zero
- ✦ Monitored unit for cold spots







**Bottoms Circulation**



**Vapour-Phase® Application**



**Continuous Monitoring**



**Water Rinse with Zyme-Ox® Plus**

- ✦ Zyme-Ox Plus chemistry used to oxidize any additional pyrophorics
- ✦ Chemistry oxidizes on contact and does not need to be heated
- ✦ Water cools unit faster so entry could be made





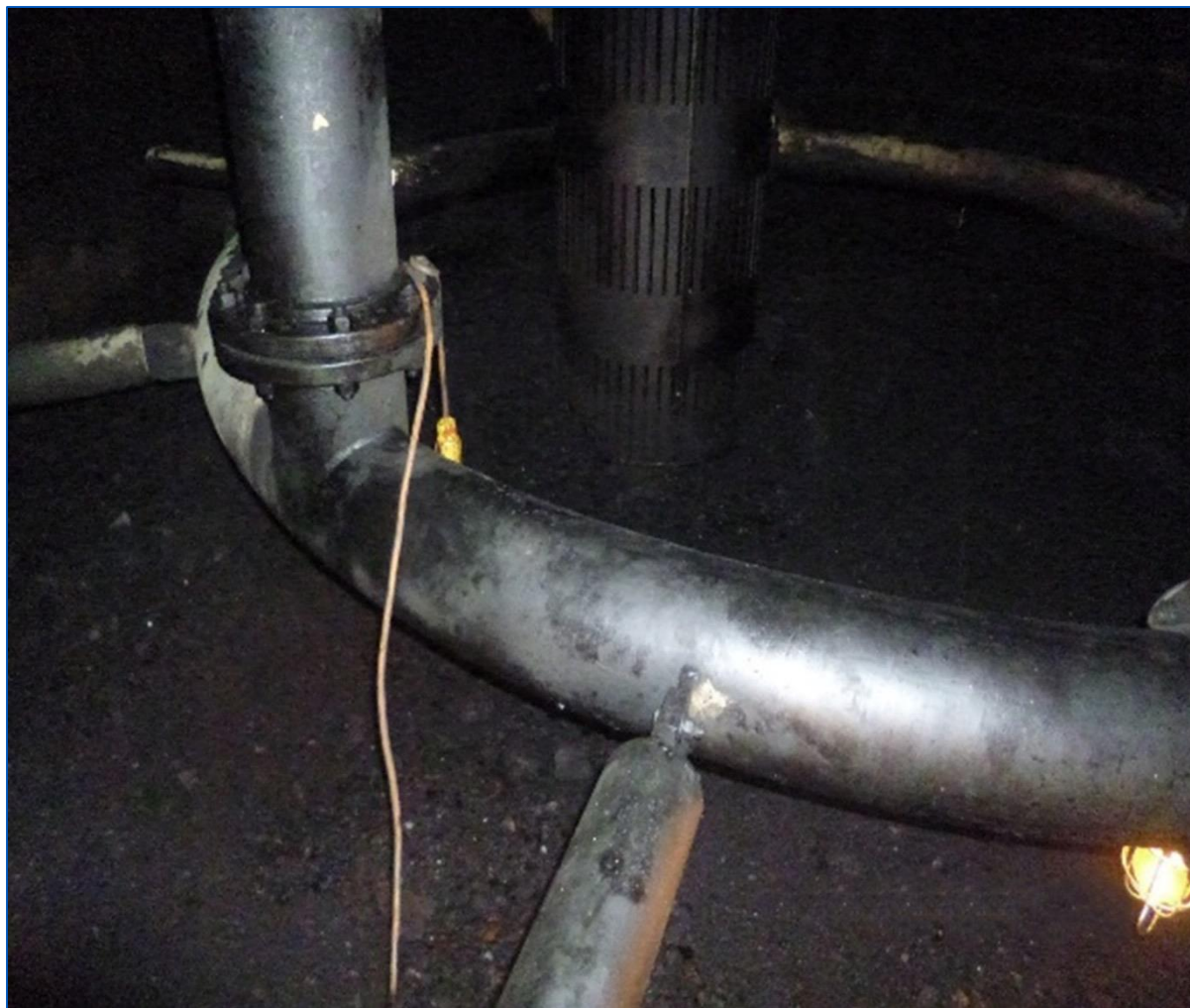
- ✦ Vessel was open and ready for inspection and hot work after 10 hours of Vapour-Phase
- ✦ Saved 7 days of mechanical preparation and cleaning
- ✦ All decontamination and maintenance work completed on schedule
- ✦ Tower free of oil with no traces of tarry hydrocarbon
- ✦ First time in vessel's history, the bottom manway was not obstructed by solids
- ✦ Easily swept out a single foot of fluff coke (hydrocarbon free)
- ✦ 84% reduction in effluent



Bottom distributor was accessible and completely unplugged



# Venezuela Coker Results



# Venezuela Coker Results



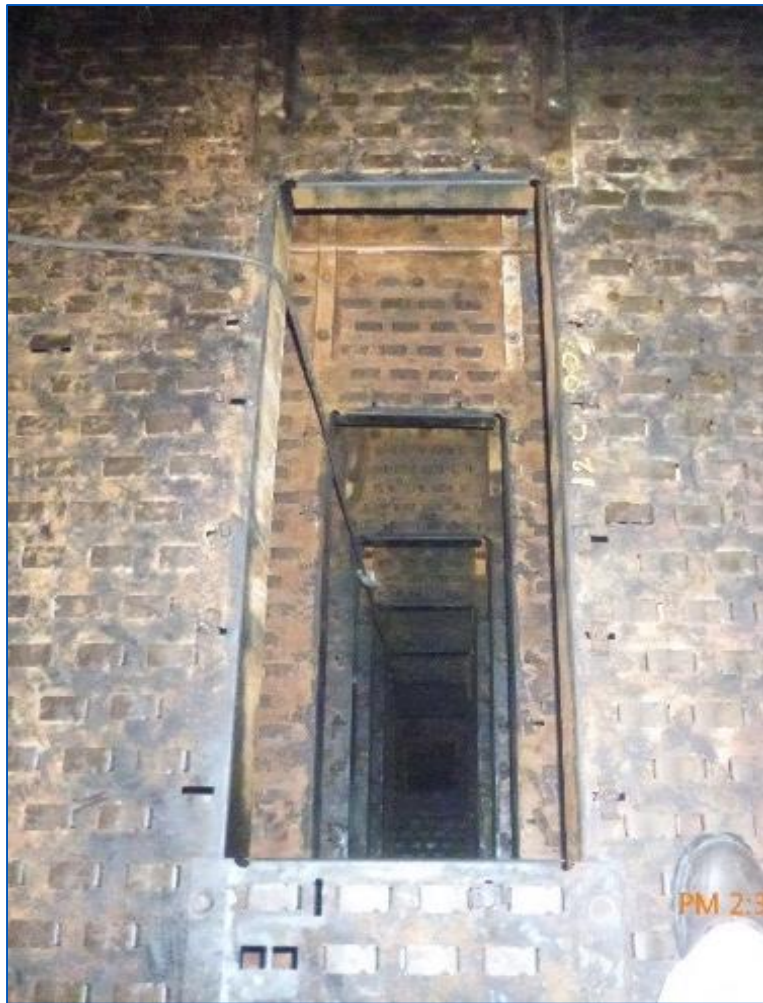


# Venezuela Coker Benefits

- ✦ Only 2 technicians per shift, 1 pneumatic pump, and 50 feet of half inch chemical hose
- ✦ Injection points connected to existing steam and process lines completed in less than one shift
- ✦ Eliminated several steps with simultaneous treatment of H<sub>2</sub>S, LEL, and oxidation of pyrophorics
- ✦ 84% reduction in effluent; 6,875 gallons versus the 43,000 gallons with previous method



# Venezuela Coker Benefits



## Background

- ✦ No treatment facility on-site
- ✦ All effluent collected per site requirements

## Oil Wash with Rezyd-HP

- ✦ Only small dose required
- ✦ After circulation, cutter stock/chemistry combination sent to slop for considerable dilution
- ✦ Chemistry does not negatively effect cutter stock

## ZymeFlow Vapour-Phase

- ✦ Large reduction in effluent (over 80% reduction) including post rinse
- ✦ Chemistry becomes part of steam – no water circulation required
- ✦ Reduced total steaming time (no pre or post steaming needed)
- ✦ Reduced cost; Non-hazardous





## Total Cost Comparison – Venezuela Coker

	<b>ZymeFlow Decon</b>	<b>Previous Chemical Contractor</b>
Chemicals Utilized	3 chemistries	6 chemicals
Application and Hours	Vapour-Phase® 10 hrs	Circulation 36+ hrs
Mechanical Prep Time	<12 hrs	120 hrs
Personnel Required	2 techs per shift	12 man crew per shift
Equipment Setup	1 pneumatic pump, 50 feet ½ in. hose	Several chemical hose circuits, stage heated frac tanks, major mechanical, fork lifts
Special Requirements	None	Haz suites, secondary containment, barricades
Remaining Coke	<1' fluff coke	Tarry coke 2' above lower manway
Mechanical Cleaning	Fluff coke easily removed, no fresh air required	Extensive under fresh air
Effluent	6,875 gallons - no issues	43,000 gallons requiring disposal



- ✦ Large differences between vessel entry methods – need to consider entire turnaround scope
- ✦ Methods are available that are faster and more efficient than mechanical-only removal of hardened deposits such as coke
- ✦ Decontamination affects not only on vessel entry but maintenance and entire turnaround schedule





- ✦ Decontamination specialists for over 25 years
- ✦ 200+ TAR and emergency outage projects/year
- ✦ Experience in over 50 countries
- ✦ Wide range of specialty blended chemistries
- ✦ Various application options including Vapour-Phase®
- ✦ Zero recordable injuries in 25 year history



[www.ZymeFlow.com](http://www.ZymeFlow.com)

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