May 4, 2017

SCAQMD Meeting
MHF Technology Discussion
Safe Harbor Statements

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Torrance Refinery

- **Economic cornerstone for the City of Torrance**
  - Continuous operation since 1929
  - 750 acres - formerly bean fields

- **600+ employees / 500+ contractors**
  - ~300 families with ties to Torrance
  - Turnaround leads to additional contractors

- **~150,000 barrels per day (mbd) crude capacity**
  - Processes crude oils primarily from California
  - Makes gasoline, jet fuel, diesel, other products

- **Supplies ~20% of SoCal’s gasoline demand**
  - ~10% of California’s gasoline demand
  - Also supplies gasoline to Nevada
  - Supplies ~25% of LAX jet fuel demand

- **Uses MHF to make “alkylate” to blend gasoline**
  - MHF requires special handling / safety equipment
Our Priorities

• Protect our workers, the community and environment through safe work practices and procedures
  o Our employees and contractors are very valuable to us
    □ They work in safe conditions and receive training
  o All refinery workers know they are accountable, responsible and have authority
    □ To stop work for any safety concern
    □ To shut equipment down for any safety concern

• Continue to improve our operational reliability to achieve safe, environmentally responsible operations
  o A safe and reliable refinery will also keep the community safe
  o About 300 families in Torrance have ties to the refinery

• Earn the right to operate in this community
  o PBF met with community groups before acquiring Torrance and continues to meet with various civic groups
  o We continue to work with city officials and regulatory agencies
  o We renewed efforts to explain to the community about what we do, our safe practices and the refinery’s local and regional socioeconomic contributions
How Modified Hydrofluoric Acid (MHF) Works
MHF Works

- Each type of acid has different characteristics and “behaviors”
  - MHF is a different type of mixture from AHF

- How MHF Works
  - Hydrogen Bonding
  - Additive forms hydrogen bonds to AHF to hold MHF in Liquid Phase
  - Water and hydrocarbons contribute to bonding AHF

- MHF CANNOT flash atomize because of hydrogen bonding

- Additive added to AHF eliminates the Flash Atomization
  - Tests show Additive works at concentrations used in Torrance

- Experiments in 1992 and 1994 showed the presence of an additive in AHF eliminates Flash Atomization of the released jets
  - At unit conditions, NO Flash Atomization was observed for compositions containing as much as 85 wt% HF up to 140°F
Acid Types: Each type of acid differs in characteristics and behaviors
Actual lab and field testing of different types of HF Acid prove the acids behave differently

- Hydrofluoric Acid (HF) type determines whether Flash Atomization occurs
  - Flash Atomization: The act of a substance disintegrating into small droplets when a pressurized liquid is released into the atmosphere

- Anhydrous Hydrofluoric Acid (AHF): 99.995 wt% HF – generic used in industry
  - Full Flash Atomization readily occurs
  - 1986 Desert Testing of AHF shown on TRAA Slide 3 was pre-MHF technology
  - HF has different characteristics - CANNOT be compared to MHF

- HF-Alky Unit Acid (HF-AUA): 90-92 wt% HF – used by most refineries
  - Partial Flash Atomization readily occurs

- Delivered MHF to the Refinery: 85 wt% HF, 15 wt% Additive
  - Flash Atomization DOES NOT occur

- MHF-AUA: 80 wt% HF, 7 wt% Additive, 3 wt% Water, 3 wt% ASO 7 wt% Hydrocarbon – used by Torrance Refinery
  - Flash Atomization DOES NOT occur

Reference
- December 2016 ARF email submission to TFD
- DAN 95M-0874 - MHF Airborne HF Reduction estimates
AHF tests conducted in the Nevada Desert in 1986 CANNOT be compared to an MHF release

• Testing in 1992 and 1994 showed the Additive in MHF eliminates Flash Atomization of HF associated with a jet release

• Actual Alkylation Unit operations with MHF additive: NO Flash Atomization was observed for compositions containing as much as 85 wt% HF up to 140°F

• Torrance Refinery’s MHF Alkylation chemical composition, process conditions, and the unit’s numerous safety systems directly contributes to Airborne Reduction Factor (ARF) and Societal Risk Index (SRI)
  o CANNOT be directly compared to an unimpeded release during desert testing

• Conclusion: Rigorous testing shows MHF DOES NOT form a dense, ground-hugging cloud

References
• Consent Decree/Safety Advisor’s Reports, May 1995 and October 1999
• DAN 95M-0874 - MHF Airborne HF Reduction estimates
• ReVAP Tutorial page 7
MHF Efficacy Depends on Four Components: Additive, Water, Acid Soluble Oil (ASO) and Hydrocarbons
MHF is delivered at 85% wt% HF and 15 wt% Additive

- The efficacy of MHF depends on four components: Additive, Water, Acid Soluble Oil, and Hydrocarbons
- Torrance Refinery MHF Alkylation unit acid concentration

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<th>December 2016</th>
<th>Average</th>
<th>Minimum</th>
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<tr>
<td>Airborne Reduction Factor % *</td>
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* ARF: Airborne Reduction Factor: Amount of MHF that remains a liquid relative to the total amount of MHF released to the atmosphere. Torrance Refinery reports ARF monthly to TFD.

Reference
- Bill of Lading from Honeywell for delivered MHF
- December 2016 monthly ARF email submission to Torrance Fire Department
Hydrogen Bonding: Holds MHF in Liquid Phase and Eliminates Flash Atomization
Allegation: “Flash vaporization will occur for MHF, like for HF”

TRAA “Case Against MHF” Jan 4, 2017 – Slide 14

MHF is 90% HF

-Plus 10% vapor suppressant additive Sulfolane-

Lower vapor pressure means a 6°F higher boiling point for MHF:

“Flash vaporization” will occur for MHF, like for HF, only 6°F higher

A dense vapor cloud, 80% aerosol and 20% vapor, WILL form.

*Note: Purple box added to TRAA’s original image/text to highlight specific points referenced/discussed
Hydrogen bonding prevents MHF from flash atomizing

- Hydrogen bonding helps resist vaporization of the HF and prevents the large-scale aerosoling of the released liquid
- HF Additive eliminates Flash Atomization even at low concentrations, promoting Rainout
- Testing in 1992 and 1994 showed inclusion of Additive eliminates Flash Atomization of HF associated with a jet release
- At actual Alkylation unit operating conditions with the Additive, NO Flash Atomization was observed for compositions containing as much as 85 wt% HF up to 140°F
- NO technical data or test data supports TRAA’s claim that the boiling point of MHF is 6°F higher than HF
- TRAA’s source - Harpole Article - is based on theoretical data versus actual testing data
  - 1995 Patent referenced in article does NOT support the theoretical assumption that Flash Atomization will occur

References
- DAN 95M-0874 - MHF Airborne HF Reduction estimates
- ReVAP Tutorial page 7
- Patent US 5,654,251
Vapor pressure is not the only fluid property of concern related to MHF
Allegation: “Vapor pressure is the only fluid property related to the claimed relative safety of MHF.”

TRAA “Case Against MHF” Jan 4, 2017 – Slide 11

Vapor Pressure of 10% MHF is close to HF’s

Vapor pressure is the only fluid property related to the claimed relative safety of MHF.

Temperature 86°F.
Phillips Petroleum Company, 1992,
European Patent EP 0796657 B1,
“Alkylation catalyst containing HF and a sulfone,”

Temperature 76°F.
Phillips Petroleum Company, 1995
US Patent 5534657,
Isoparaffin-olefin alkylation,
Vapor pressure is **NOT** the only fluid property of concern related to MHF

- Additive’s primary effectiveness results from formation of hydrogen bonds that hold MHF in liquid phase, which has nothing to do with vapor pressure
  - Additive is a heavy liquid with very low vapor pressure that does not evaporate
  - Very difficult for the Additive to get into vapor phase

- Hydrogen bonding helps MHF resist vaporizing and prevents large-scale aerosoling of the released liquid

- The Additive is only one component that impacts vapor pressure and aerosoling
  - Water and Acid Soluble Oil (ASO) also have significant effects

- Water is a more effective vapor suppressant than the Additive due to strong hydrogen bonding. However, water content is limited to 3 wt% due to corrosion concerns

- Patent US 5,654,251 states the following in support of low concentrations of MHF Additive being effective in depressing vapor pressure:
  “One important function of the presence of the [additive] component in the composition is its vapor pressure depressant effect upon the overall catalyst composition. Therefore, to take advantage of the vapor pressure depressant effects of the [additive] compound, it is desirable to utilize the [additive] in the catalyst mixture in an amount in the range of from about 2.5 weight percent to about 50 weight percent. In the situation where both vapor pressure depression and improved catalytic activity and selectivity are desired, the composition that works best in the alkylation of olefins has less than 30 weight percent [additive].” [Emphasis added.]

**References**
- DAN 95M-0874 - MHF Airborne HF Reduction estimates
- ReVAP Tutorial page 7
Torrance Refinery MHF Unit, with its safety systems, is the most sophisticated in the nation.
Redundant emergency systems, routinely tested, validated, and work as designed

- Torrance MHF alkylation unit features redundant, active mitigation systems
  - Water systems
    - Nine water cannons are tested weekly
    - Acid service pumps deluge systems are tested monthly
    - Fixed water sprays on vessels are tested annually
  - Acid sensitive paint maintained on unit flanges and connections in HF service
  - Detailed inspection of barriers completed weekly
  - Automatic Evacuation System tested monthly
  - Risk Management Prevention Plan (RMPP) interlocks are tested monthly
  - MHF sensors tested monthly
  - Acid off-loading system tested prior to every truck delivery
  - Active routine and preventive maintenance Inspection program
  - TFD is invited to witness all testing
  - Operator physically present in unit at all times – two rounds per shift

- Testing shows that using MHF catalyst with barriers provides 89% ARF at Torrance
  - Mitigation water systems provide additional 11% ARF to contain release on site

- There have been NO offsite releases since MHF alkylation was introduced in 1997

Reference
- Actual unit configuration, performance and testing
Managing Risk: Quantitative Risk Analysis used to compare and determine safety of competing technologies
Quantitative Risk Assessment is an effective tool and industry risk management standard

• Risk assessment is used by most industries to improve safety and reliability of equipment/processes
  o Methodology follows Center for Chemical Process Safety (CCPS) guidelines and considered a global scientific standard
  o Torrance Refinery also follows American Petroleum Institute “Recommended Practice 751 - Safe Operation of Hydrofluoric Acid Alkylation Units”
    □ Includes periodic third-party audits and other safety requirements

• Applied Quantitative Risk Assessment (QRA) for MHF
  o Provides quantitative estimates of risks
  o Considers broad range of scenarios
  o Applies appropriate allowances for likelihood of occurrence
  o Facilitates comparison of different processes - i.e., MHF vs. Sulfuric Acid
  o Highlights most effective risk mitigation options - provides layers of protection

• Leak size and frequency was derived from industry data modeled on the MHF QRA, which includes a range of release sizes

References
• CCPS CPQRA published guideline book
• American Petroleum Institute Recommend Practice 751
Results of 1998 Quantitative Risk Assessment shows that mitigation systems favor MHF alkylation

- 1998 QRA demonstrated that the Torrance MHF Alkylation Unit has safety mitigation systems that provide an SRI 24x lower than a sulfuric acid unit of comparable capacity
  - Excluded transportation, regeneration, and incineration of spent Sulfuric Acid
    - When added to QRA, risk from sulfuric acid increases significantly
  - Post-1998: MHF-sensitive flange paint and perimeter HF laser were added
    - Additions would increase SRI

- QRA results show toxic risks associated with sulfuric acid alkylation are higher than for comparable MHF alkylation unit
  - Both processes were shown to represent very low risk
  - Number of people potentially exposed and evacuation zone area were higher for sulfuric acid alkylation than MHF alkylation

Reference
- MHF Alkylation Risk Assessment, October 1994
- Safety Advisor Presentation TOR 510.10 - MHF vs Sulfuric Acid Alkylation Risk Assessment 1998
Airborne Reduction Factor
Airborne Reduction Factor (ARF) is **NOT** a function of Vapor Pressure

- ARF is a function of four components: Additive, Water, Acid Strength, and Reactor Temperature
  - Process Chemistry Safety of MHF is measured by ARF, a “release behavior” property of MHF

- ARF represents the amount of HF that remains a liquid relative to the amount of HF potentially released to the atmosphere after a release
  - The larger the ARF, the less potential for HF to become airborne

**References**
- Consent Decree Safety Advisor’s Report, October 1999, p 1B.A-34
- DAN 96M-0144 - Small Scale HF/Additive Tests at MHF Design Conditions
Barriers greatly enhance the Additive’s effectiveness and improve ARF
Testing showed barriers were effective and confirmed ARF data

- Left: Shows barrier effectiveness over distances less than one foot is greater than 90% ARF
- Right: Shows close agreement of modeled vs tested ARF data

**Figure 3**
HF Reduction vs. Barrier Distance

**Model Evaluation Using Experimental Data**

**References**
- *DAN 98M-0166 - Effects of Active and Passive Mitigation on AHF, AUA & MHF Releases*
MHF at <20% wt% was extensively tested - ARF was NOT extrapolated

- ARF was determined based on MHF testing at various concentrations and temperatures
- Figure 5 shows ARF tested at different concentrations at the same temperature
- Figure 4 shows ARF tested at different temperatures and concentrations

References
- Dan96M-0144 - Small Scale HF/Additive Tests at MHF Design Conditions
MHF at <20% wt% was extensively tested - ARF was NOT extrapolated

- Additive range of concentrations \(<20\) wt% were tested in 1992, 1994, 1996 and 2000
  - Left: Tests confirmed the Additive increases ARF even at low concentrations
- ARF calculated as a function of acid strength, Additive, water, reactor temperature
  - Right: Shows model has good agreement with ARF test results

References
- DAN 96M-0144 - Small Scale HF/Additive Tests at MHF Design Conditions
- DAN 95M-0874 - MHF Airborne HF Reduction estimates
- DAN 98M-0166 - Effects of Active and Passive Mitigation on AHF, AUA, and MHF Releases
- DAN 93M-0408 - HF/Additive Release Tests at Quest
89% ARF based on actual testing with barriers

- Barriers on the Unit settlers are 3” from potential leak source
  - Model predicts 95.8% ARF for these conditions
  - Conservative 89% ARF was used - adjusted for shorter travel distance of 3” vs 8”
- ARF was conservatively adjusted to 89% for pipe flange covers at <1” distance
  - Same ARF as settler barriers - also adjusted because collected liquid that drops to ground will experience small amount of vaporization
- Acid circulation pump seals at 89% ARF are also conservatively estimated

References
• DAN 98M-0166 - Effects of Active and Passive Mitigation on AHF, AUA & MHF Releases
Sulfuric Acid Alkylation
No HF/MHF Alkylation Unit has ever been converted to a Sulfuric Acid Alkylation Unit

• There are many technical reasons conversion has never been done
  o Processing equipment and metallurgy differ between unit types
    □ Vessels, piping, and equipment are not interchangeable
    □ New grass roots Sulfuric Acid Alkylation unit would be required

• April 1, 2017 SCAQMD testimony on conversions:
  o Bay Area: Units originally built as Sulfuric Acid - never converted from HF
  o UK: 4 of 6 refineries are HF Alkylation - 2 others have no Alkylation Units
  o Europe: No Alkylation Units have ever been converted to Sulfuric Acid

• SCAQMD’s Norton Engineering Study cost conversion estimate too low
  o Failed to consider the cost of acid regeneration and incineration
  o Estimate was based on replacement of reaction section only
  o Failed to consider regulatory and construction costs in Southern California
  o New 30 kbd grass roots units third-party cost estimate is significantly higher

• Cost estimates from the 1990’s and early 2000’s are irrelevant to today’s costs

References
• DuPont Design Basis for a new plant in Torrance
• Norton Engineering Study and presentation at American Fuel & Petrochemical Manufacturers meeting February 2016
• Burns and McDonnell / Dupont / Stratco
A modular approach is unfeasible for a Sulfuric Acid Alkylation unit at Torrance

- Equipment required for a processing unit is very different from the Torrance Refinery’s FCC ESP, which is an emissions control device

- Processing equipment for a Sulfuric Acid Alkylation unit cannot be manufactured and constructed modularly like the ESP
  - Consists of towers, heat exchangers, other pressure vessels, pumps, piping networks, instrumentation, and many other types of equipment

- Construction of a new Sulfuric Acid Alkylation unit would require shutting the refinery down to demolish and replace the existing MHF Alkylation unit
  - Refinery would be unable to produce alkylate for cleaner-burning CARB gasoline

References
- *Construction Fundamentals*
Have been unable to verify sulfuric acid pipeline from Carson to Torrance

- Building a sulfuric acid pipeline would take many years
  - Requires acquisition of appropriate rights-of-way and permits through various municipalities and regulatory agencies

- Transportation of spent and fresh sulfuric acid offsite poses additional safety risks to the community
  - Spent sulfuric acid contains dissolved sulfur dioxide and hydrocarbons
    - Spent solution is corrosive and can be potentially unstable and reactive
  - Trucks and railcars have over-pressured to atmosphere in the past
    - Releasing a vapor/liquid mixture can form a hazardous aerosol
    - There would be ~1440 trucks shipments per month if regeneration offsite

- Process hazard analysis for an MHF vs. Sulfuric Acid unit siting decision must consider transportation risks along with regeneration risks
  - Combined risk may result in a different risk management decision than considering the process risk alone

Reference(s)
- EcoServices Plant Representative
Valero announced its new Sulfuric Acid Plant project in January 2016, with completion expected in 1H2019

- **Valero is building a new $300 million (MM), 13MBD Sulfuric Acid Alkylation Plant in Texas**
  - Estimate excludes added cost of spent sulfuric acid regeneration and incineration plants
    - Regeneration and incineration keep acid supply constant

- **Basic project design and permitting process nominally takes two years**

- **Valero project entered detailed engineering, procurement and construction phase**
  - Expected to take longer than three years to complete

- **Torrance MHF Alkylation Unit is ~30MBD, more than 2x larger than Valero’s**
  - Regulatory, construction and operating costs are significantly higher in California

- **Replacement cost estimates for building a Sulfuric Acid Alky unit at Torrance Refinery**
  - Burns & McDonnell: New grass roots unit ranges from $500MM to $600MM
  - Cost of Sulfuric Acid Regeneration and Incineration plants would be an additional cost

References
- **Valero First Quarter 2016 Results**
- **Burns and McDonnell study**
- **Public Company Records on Refinery Sale and Purchase**
Sulfuric Acid Alkylation **DOES NOT** eliminate toxic airborne risk - the risk increases

- With a Sulfuric Acid Alkylation unit, the sulfuric acid mixed with hydrocarbons can become and remain airborne
  - Quest sulfuric acid experiments convincingly demonstrate this phenomenon
- **Criteria pollutant emissions - \( \text{SO}_2 \) & \( \text{SO}_3 \) - are produced from combusting spent sulfuric acid in an incinerator during the regeneration process**
  - MHF Alkylation does **NOT** produce \( \text{SO}_2 \) or \( \text{SO}_3 \)
- **Sulfuric Acid Alkylation consumes \( \sim 2x \) utilities as MHF Alkylation**
  - Results in increased GHG emissions and larger carbon footprint
  - Each new piece of equipment is a potential source of VOC fugitive emissions
- **Spent sulfuric acid is highly corrosive, reactive, flammable**
  - Produces a carcinogenic mist that is more toxic than HF mist per the International Agency on Research for Cancer
  - Spent sulfuric acid is listed in the same hazardous material category as M/HF
- **Motiva Delaware City \( \text{H}_2\text{SO}_4 \) release cited by TRAA occurred in 2001, not 2011**
  - Caused one onsite fatality, eight injuries, and offsite fish kill in local river

**Reference**
- **CSB Investigation Report (October 2002), Motiva Delaware City Refinery Spent Sulfuric Acid storage tank explosion and fire on July 17, 2001**
Other Alternative Alkylation Technologies
Currently, none of the alternatives are commercially viable for Torrance, including Sulfuric Acid

- **Solid Acid Catalyst (SAC):** One small unit in a chemical plant in China - 2,700 BPD
  - Norton Engineering Study: Too early to be considered commercially viable technology
  - Issues with catalyst regeneration cause the plant to shut down
  - **NO** commercial plant in the United States
  - Testimony at April 1st SCAQMD Hearing about European refinery to SAC:
    - Have inquired about this technology through various refining, governmental, and technology licensing sources
    - Have not been able to obtain any information about this conversion
    - Request the AQMD to provide the information regarding this conversion so that this can be evaluated and verified

- **Liquid Ionic Catalyst:** nascent technology is only in initial test phase
  - Only one ~200 gallon per day demonstration unit running today
  - Norton Engineering Study: Too early to be considered commercially viable technology
  - Chevron plans to install small 4,500 bpd unit in Salt Lake City

- A QRA has not been performed on ILA or SAC, so their societal benefit cannot be/has not been determined

**References**
- DuPont Design Basis for a new plant in Torrance
- Norton Engineering Study and presentation at American Fuel & Petrochemical Manufacturers meeting February 2016
PBF continues to evaluate alternative technologies

• PBF has been evaluating alternative alkylation technologies since we announced the acquisition of the Torrance Refinery in September 2015
  o We have met with experts from Honeywell/UOP, Stratco, DuPont and Burns & McDonnell, as well as independent alkylation experts to explore alternatives
  o Sulfuric Acid Alkylation is the only commercially viable alternative
    □ Presents unique challenges
    □ Solid catalyst and liquid ionic alkylation have been in development for decades
    □ There are no commercially viable units running in the U.S.

• Through the Court-ordered Consent Decree process, MHF Alkylation was determined to be “…as safe as or safer than Sulfuric Acid technology”
  o Converting to or building a grass roots Sulfuric Acid Alkylation unit would be in contradiction to the Consent Decree and does NOT make sense

• Before transitioning from MHF Alkylation to a catalyst other than Sulfuric Acid at the Torrance Refinery, the new technology has to be proven
  o Must be inherently safer than MHF alkylation
  o Must be commercially viable in scope and scale to our existing unit

• We are confident the safety systems on the MHF Alkylation Unit protect our employees and the community while reliably producing CARB gasoline
Transition and Impacts
Torrance Refinery becomes uncompetitive if the Alkylation Unit outage lasts more than 30 days

• Seeking Alpha: ExxonMobil estimated daily gross revenue losses of ~$1 million to $1.5 million a day due to the closure of the FCC and Alkylation Unit starting in Feb 2015
  o When the MHF Alkylation unit is down, FCC throughput must be reduced to minimum
  o Will be limited to one month of operation due to railcar logistics

• MHF unit makes alkylate for producing cleaner-burning CARB gasoline
  o Alkylate availability is limited due to high global demand and transport costs

• The Torrance MHF Alkylation unit produces a critical blending component for making cleaner-burning CARB gasoline for Southern California and the State of California
  o Alkylate is required to meet stringent state-mandated gasoline specifications
  o Torrance Refinery supplies ~20% of daily regional demand and ~10% statewide

• Refinery projects take many years to complete
  o From design to construction and then startup, each stage is critical to long-term, safe, reliable operations
  o If steps are skipped or rushed, then mistakes can happen

Reference
• Seeking Alpha: “Exxon Mobil: About The Torrance Refinery,” April 4, 2016; ExxonMobil Oil Corporation Stipulated Abatement Order (Case No. 1183-494)
Summary
Summary: Torrance Refinery's use of MHF is safe

- Mobil, Phillips & Quest Engineers developed MHF Alkylation technology
  - 1990 to 1999: Used rigorous testing and pilot plant testing
  - Additive is a vapor depressant that forms a hydrogen bond that prevents Flash Atomization of MHF at operating conditions
  - Current MHF chemistry results in an airborne reduction factor (ARF) of 50%

- Combination of catalyst and barrier technology increases ARF to 89%

- Additional layers of protection further increase ARF and prevent potential offsite release including Automatic Evacuation, water cannons/deluge systems, etc.

- Torrance MHF Unit product yield and quality are comparable to HF alkylation

- The Quantitative Risk Analysis showed the Torrance MHF Unit is as safe as or safer than a similarly-sized sulfuric acid unit based on (SRI)

- Since using MHF in the alkylation unit starting in 1997, there has not been an HF offsite release of HF at the Torrance Refinery

*Note: Prior slides provided supporting statements and references*