Appendix A:
Concept Paper for Rule 6-5: Fluidized Catalytic Cracking Units (FCCU)

Rules to Be Amended or Drafted

Regulation of emissions from fluidized catalytic cracking units requires drafting a new regulation: Regulation 6, Rule 5, *Direct and indirect Particulate Emissions from Refinery Fluidized Catalytic Cracking Units*.

Goals

The goal of this rulemaking is to achieve technically feasible and cost-effective emission reductions of $PM_{2.5}$ and $PM_{2.5}$ precursors from fluidized catalytic cracking units (FCCUs) at Bay Area refineries. The Air District plans to do this in two actions as described in the Initial Report for the Refinery Strategy. The first action will propose a new regulation that will address ammonia emissions (a $PM_{2.5}$ precursor) at those FCCU that use ammonia or urea injection. The second action will amend Regulation 6, Rule 5 to address direct $PM_{2.5}$ emissions and emissions of other $PM_{2.5}$ precursors.

Background

Fluidized catalytic cracking units are complex processing units at refineries that convert heavy components of crude oil into light, high-octane products that are required in the production of gasoline.

The FCCU gets its name because the catalyst comes in such small particles that it flows like a fluid. During the reaction phase, the catalyst becomes coated with petroleum coke, which must be burned off in the presence of air so that the catalyst can be regenerated and reused. The catalyst regenerator exhaust contains particulate matter (PM), sulfur dioxide (SO_2), ammonia, carbon monoxide (CO), oxides of nitrogen (NO_x), and volatile organic compounds (VOC).

The Bay Area has five petroleum refineries. Four of these, Chevron, Shell, Tesoro and Valero, operate FCCUs. The Valero refinery has recently retrofitted its FCCU with a wet scrubber and has lower $PM_{2.5}$ and SO_2 emissions from its FCCUs than the other refineries as a result. The Chevron and Tesoro FCCUs use ammonia to control filterable particulate matter emissions, resulting in unreacted ammonia being emitted to the atmosphere (*ammonia slip)*. The Shell FCCU uses ammonia or urea injection to control NO_x emissions, resulting in unreacted ammonia being emitted to the atmosphere.

Process and Source Description

The FCCU (see the figure below) consists of two vessels. In the reactor vessel, the conversion reaction occurs in the presence of a fine, powdered catalyst and steam, during which the catalyst becomes coated with petroleum coke. In the regenerator vessel, this coke is removed from the surface of the spent catalyst by burning it off in the presence of air so that the catalyst can be reused. The cracked products from the reactor vessel are separated in a fractionator column into intermediate streams for further processing.

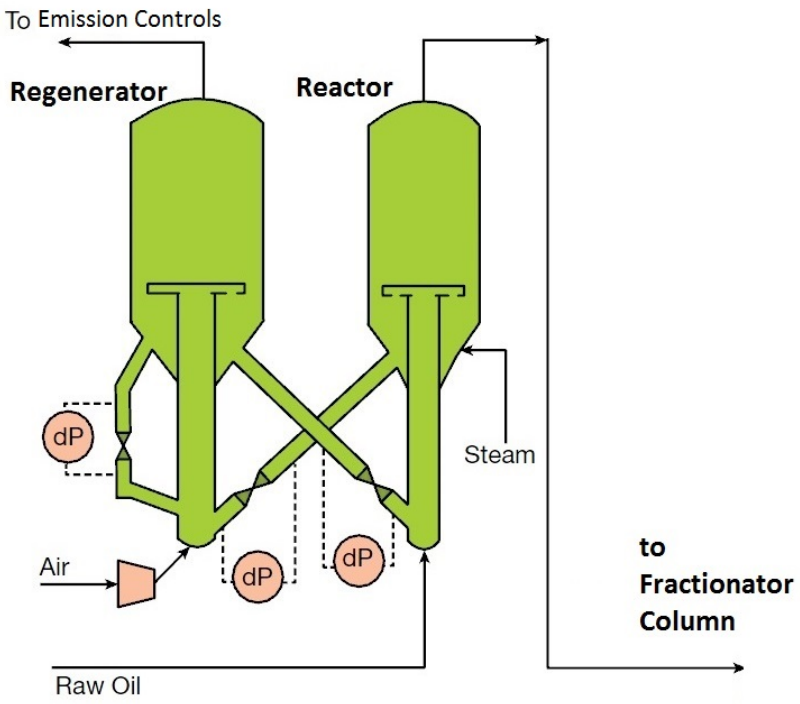

Figure 1 - FCCU Process

The catalyst regenerator exhaust is the main emission point for the FCCU, which can emit high levels of PM, SO_2, ammonia, CO, NO_x and VOC.

FCCU PM emissions can be classified as direct or indirect PM emissions. Indirect PM emissions are not particulate matter when emitted, but are precursors to the atmospheric formation of $PM_{2.5}$. Direct emissions may be further classified as material that is a liquid or solid at the emissions point to the atmosphere ("filterable" particulate), or as material that is a gas at the emission point, but that immediately condenses in the atmosphere to a liquid or solid form ("condensable" particulate). This distinction is important because, until recently, particulate emissions from FCCUs were measured in the exhaust stack by collecting a sample from the exhaust stream at the stack – thus ignoring the condensable emission fraction. The most recent particulate test method now accurately incorporates a condensation step to quantify condensable emissions. Limited source testing using this test method suggests that the amount of condensable particulate may be greater than the filterable amount in some FCCUs.

SO_2, ammonia, NO_x and VOC can react in the atmosphere to form secondary $PM_{2.5}$. Most of the secondary $PM_{2.5}$ formed in the Bay Area consists of ammonium sulfate and ammonium nitrate particles, formed by reactions between ammonia with NO_x and SO_2 in humid air.

Because the FCCU exhaust contains so many pollutant species, FCCUs often utilize a combination of emission control techniques – typically flue gas additives to control NO_x and SO_2, and an electrostatic

precipitator (ESP) to control PM. Bay Area refineries also use selective catalytic reduction (SCR) for NO_x control and wet scrubbers for control of multiple pollutants.

Regulatory History and Context

There are currently no Air District regulations that apply to ammonia emissions from FCCUs. There are two federal standards in part 60 that may apply to FCCUs, depending on the year of construction, reconstruction, or modification, but neither one applies limits to ammonia emissions.[1]

Emissions

Based on recent source tests, ammonia concentrations at the FCCU catalyst regeneration outlet (post-control) are 29 parts per million by volume (ppmv) at the Chevron refinery and 23 ppmv at the Shell refinery. Test data are not available for the Tesoro refinery, but Tesoro is permitted to inject twice as much ammonia as the Chevron refinery actually uses.

Regulatory Concepts and Proposed Regulations

In 2003, South Coast AQMD adopted an ammonia emission limit of 10 ppmv, corrected to 3 percent oxygen, for FCCUs in their Rule 1105.1. Air District staff is proposing the same limit in Regulation 6, Rule 5. Staff is also proposing a continuous emission monitoring system (CEMS), whereas the South Coast AQMD requires annual source tests. An emission limit of 10 ppmv was recently imposed at the Bay Area Valero refinery FCCU in an Air District permit and this appears to be the most stringent emission limit imposed on refinery FCCUs.

Although District staff is proposing a stringent ammonia emission limit, they recognize that ammonia and urea injection are used to promote PM control at FCCUs with electrostatic precipitators (ESPs) and that these ESPs are subject to District and federal PM emission limits. Therefore, while District staff intends to impose the lowest possible ammonia emission limit for existing FCCUs, they will consider existing PM emission limits at the FCCU ESPs and the possible impact on ESP efficiency before proposing a final ammonia emission limit that will result in the greatest overall public health benefit.

Staff is proposing a limited exemption from the ammonia slip limits during periods of "startup," "shutdown," "bypass," or "emergency bypass." Because these definitions are always contentious, the draft rule only allows this exemption when a Permit to Operate explicitly provides it. This puts the burden on the refineries to apply for an amended permit.

The proposed FCCU ammonia slip limit is 10 parts per million by volume, dry (ppmvd), corrected to 3 percent O_2, on a rolling seven-day average. This time basis (rather than an hourly limit) is possible because a CEMS will also be required. The value of the limit (10 ppmvd) is the same that appears in the recently-amended Valero refinery FCCU permit and in South Coast Rule 1105.1 ("PM_{10} and Ammonia Emissions from FCCUs," 2003). Based on source test data, Chevron operates significantly higher than this limit (because of high ammonia injection upstream of the FCCU ESP), as does Shell because of urea injection to control NO_x emissions from the CO boilers that operate downstream of the FCCU. No

[1] 40 CFR part 60, subpart J, *Standards of Performance for Petroleum Refineries* and 40 CFR part 60, subpart Ja, *Standards of Performance for Petroleum Refineries for which Construction, Reconstruction, or Modification Commenced after May 14, 2007*

ammonia source test data are available for Tesoro; but Tesoro is permitted to inject twice as much ammonia as the Chevron refinery actually uses.

Control Mechanisms

Staff do not believe that the proposed regulations will require any additional controls. We expect that the refineries that use ammonia or urea injection will be able to meet the proposed limits by optimizing injection locations and rates.

Costs and Emissions Reductions

Although there will be one-time optimization costs, reduced use of ammonia and urea should result in long-term cost savings.

Emission reductions are based on current emission rates of 29 ppmv (Chevron) and 23 ppmv (Shell) being reduced to 10 ppmv, then applying the resulting percentage reduction to the associated mass emissions of ammonia at each refinery. Because of a lack of test data, the Tesoro emission reduction is assumed to be the same as at Shell.

Facility	Ammonia Reduction (tpy)	Capital Cost ($ M)	Total Annualized Cost ($ M)
Chevron	58	NA	NA
Shell	15	NA	NA
Tesoro	15*	NA	NA

*Assumed to be the same as Shell refinery from reduced use of ammonia injection.

REGULATION 6
PARTICULATE MATTER
RULE 5
CONDENSABLE AND INDIRECT PARTICULATE EMISSIONS FROM REFINERY FLUIDIZED CATALYTIC CRACKING UNITS

INDEX

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CONDENSABLE AND INDIRECT PARTICULATE EMISSIONS FROM REFINERY FLUIDIZED CATALYTIC CRACKING UNITS

(Adopted [Adoption Date])

6-5-100 GENERAL

6-5-101 Description: This rule limits the emissions of condensable and indirect particulate matter emissions from petroleum refinery fluidized catalytic cracking units (FCCUs). Regulation 6, Rule 1 addresses filterable particulate emissions from FCCUs. For the purposes of this rule, commingled emissions from an FCCU and one or more other sources from a single exhaust point shall all be considered to be FCCU emissions.

6-5-110 EXEMPTIONS

6-5-111 Limited Exemption, Emissions during Startup, Shutdown, Bypass and Emergency Bypass: The requirements of Section 6-5-301 shall not apply to FCCU emissions during a startup, shutdown, bypass or emergency bypass period as specifically defined and allowed in a District Permit to Operate. This exemption shall apply only to the pollutants specified in the District Permit to Operate.

6-5-112 Limited Exemption, Installation of Wet Scrubber: The emission limit effective date for ammonia in Section 6-5-301 may be extended to a later date specified in a District Authority to Construct for an existing FCCU to be controlled with a new wet scrubber, but may not be extended by more than 36 months.

6-5-200 DEFINITIONS

6-5-201 7-day Rolling Average: The arithmetic mean of the ammonia emissions described in Section 6-5-301 in the most recent 7 calendar days of operation of the FCCU. Each calendar day initiates a new rolling average period.

6-5-202 Ammonia Slip: Ammonia slip is the amount of unreacted ammonia emitted to the atmosphere from the FCCU, regardless of the source of the ammonia.

6-5-203 Catalyst Regeneration Unit (CRU): A catalyst regeneration unit regenerates spent FCCU catalyst by burning off the coke that has deposited on the catalyst surface. The resulting CRU flue gas is the primary emission source addressed by this rule.

6-5-204 Condensable Particulate Matter: Material emitted to the atmosphere in a gaseous form that condenses and/or reacts to form a solid or liquid at testing conditions.

6-5-205 Fluidized Catalytic Cracking Unit (FCCU): A fluidized catalytic cracking unit (FCCU) is a processing unit that converts heavy petroleum fractions, typically from crude oil distillation units into lighter fuel intermediates by using a fine, powdered catalyst to promote a chemical reaction in which the heavy petroleum molecules are broken into smaller molecules. In addition to the cracking reactor, an FCCU includes a catalyst regeneration unit (CRU), ancillary equipment including blowers and all equipment for controlling air pollutant emissions and recovering heat.

6-5-206 Indirect Particulate Matter: Material emitted to the atmosphere in a gaseous form that will not condense to a solid or liquid form at atmospheric temperature and pressure, but that may chemically react in the atmosphere into a solid or liquid form. For the purposes of this rule, indirect particulate shall include only sulfur dioxide (SO_2) and ammonia.

6-5-207 Petroleum Refinery: An establishment that is located on one or more contiguous or adjacent properties, and under common control, and that processes crude oil to produce more usable products such as gasoline, diesel fuel, aviation fuel, lubricating oils, asphalt or petrochemical feedstocks. Petroleum refinery processes include separation processes (e.g., atmospheric or vacuum distillation, and light ends

recovery), petroleum conversion processes (e.g., cracking, reforming, alkylation, polymerization, isomerization, coking, and visbreaking) petroleum treating processes (e.g., hydrodesulurization, hydrotreating, chemical sweetening, acid gas removal, and deasphalting), feedstock and product handling (e.g., storage, blending, loading, and unloading), and auxiliary facilities (e.g., boilers, waste water treatment, hydrogen production, sulfur recovery plant, cooling towers, blowdown systems, compressor engines, and power plants).

6-5-208 Wet Scrubber: A device that removes air pollutants from gas streams by contacting the gas stream with a scrubbing liquid.

6-5-300 STANDARDS

6-5-301 Fluidized Catalytic Cracking Unit (FCCU) Emission Limits: A person operating an FCCU shall not cause emissions to the atmosphere from the FCCU that exceed the limits in Table 1 on or after the indicated effectiveness date:

Table 1 – FCCU Emission Limits

Pollutant	Emission Limit	Effective Date
Ammonia	10 ppmvd at 3% O_2 as 7-day rolling average	January 1, 2018
Condensable Particulate Matter	[future]	[future]
Sulfur Dioxide (SO_2)	[future]	[future]

6-5-400 ADMINISTRATIVE REQUIREMENTS

6-5-401 Ammonia Control Plan and Permit Applications: No later than January 1, 2017, a person subject to the ammonia emission limit in Section 6-5-301 shall submit to the APCO a control plan detailing the measures, if any, to be taken in order to meet the requirements of Section 6-5-301, and also applications for all Authorities to Construct necessary for compliance with Section 6-5-301.

6-5-402 Ammonia Parametric Monitoring Plan: No later than January 1, 2017, submit to the APCO a plan for the installation of an ammonia parametric monitoring system to perform monitoring as required by Section 6-5-501. This plan shall identify the proposed monitoring technique, monitoring equipment, installation details and installation schedule.

6-5-500 MONITORING AND RECORDS

6-5-501 Ammonia Monitoring: A person who operates an FCCU subject to the ammonia emission limit in Section 6-5-301 shall operate the following;

501.1 Parametric monitors that comply with District Regulation 1, Section 523 to continuously measure emissions (ppmvd at 3% O_2) of ammonia from the FCCU.

501.2 Parametric monitors that comply with District Regulation 1, Section 523 to continuously measure the injection or addition rate (pounds per hour) of ammonia, urea or any other nitrogen-based reducing agent into the CRU flue gas.

6-5-502 Ammonia Records: A person who operates an FCCU subject to the ammonia emission limit in Section 6-5-301 shall maintain records of the data required to be measured in Section 6-5-501. These records shall be kept for a period of at least five years and shall make them available to the APCO on request.

6-5-600 MANUAL OF PROCEDURES

6-5-601 Compliance Determination: All compliance determinations shall be made in the as-found operating condition. No compliance determinations shall be made during periods subject to the exemption in Section 6-5-111.