March 1991

Louisiana Division

LOUISIANA DIVISION GUIDELINES FOR REACTIVE CHEMICALS REVIEW

The enclosed package contains guidelines to assist you in preparing for a productive and comprehensive Reactive Chemicals Review. It is important to realize that Reactive Chemicals considerations are YOUR responsibility. The Reactive Chemicals Committee is made up of people experienced in this area and helping you fulfill your reactive chemicals responsibility is our primary goal.

Evaluation of past incidents shows that inadequate operating procedures, lack of positive raw material identification, critical instrument problems, and material of construction incompatibility cause serious concerns. Consider these items carefully.

Attached is a Reactive Chemicals Review checklist which will guide you in preparing for your review. Please complete this checklist and include as the cover sheet for your review package. Attachments are also provided for updating Reactive Chemicals data and to assist you in developing "Worst Case" scenarios. A list of resources to help you prepare is included.

The final attachment is a self evaluation questionnaire which we encourage you to fill out to help you recognize strengths and weaknesses of your program. We think this questionnaire will be an asset to you in further development of your Reactive Chemicals Program. The results of the self evaluation should be a topic of discussion at your review.

Make every attempt to limit your review presentation to chemical reactivity. The Reactive Chemicals Committee does not deal with other problems unless they bear on chemical hazards. Do not review markets, costs, strategy, etc.

The Plant should send one copy of the completed Questionnaire to the LAD Audit Facilitator 10 calendar days before the audit. Send 10 copies of the presentation packet to Cindy Gum (Reactive Chemicals Office Professional, Building 2510, Ext. 1601) at least 1 week prior to the review.

Gerald Wagener, Chairman
Reactive Chemicals Committee
Building 2511, Ext. 1828

DOW U.S.A.

LOUISIANA DIVISION

Reactive Chemicals

Consolidated Audits

6/93

REACTIVE CHEMICALS REVIEW AGENDA

The reactive chemicals review meeting will comprise the major steps, described below. The emphasis level and attention placed on each step will vary for each type of review. Prepare a presentation to cover the package submitted to the Review Team four weeks prior to the review meeting. A general outline of the presentation is given below; the exact nature of the presentation will depend on input from the plant's RC committee consultant as to what areas of the Reactive Chemicals program should be emphasized. Remember, the audit team will have already reviewed the package and does not need to have a verbatim presentation of it at the audit meeting.

A. PROCESS CHEMISTRY: Summarize the contents of the package pertaining to the process.

B. LETTER OF RECOMMENDATIONS: Review status from the previous review (or audit), thereby completing that correspondence.

C. SCENARIOS & LINES OF DEFENSE: Review past incidents in the technology (brief descriptions only); present at least two worst case reactive chemicals scenarios derived from HAZOP or other hazard identification procedures for your process; present your lines of defense as reviewed in the package.

D. CONTINUOUS IMPROVEMENT ITEMS: Discuss items and/or areas for improvement that have emerged during the preparation for the review.

E. CHEMICAL CONCERNS: Discuss the results of your review of the process using the "Review of Reactive Chemicals Concerns". This is not a question and answer session, but a forum for discussing your thoughts on plant reactive chemicals concerns stimulated by this document.

F. PRE-REVIEW RESPONSES: Discuss the responses from the Committee arising from the pre-audit review of your package. Cover those items that have not been referred to in A through E, as requested by the Committee during the review.

THE REACTIVE CHEMICALS THOUGHT PROCESS

The thought process, shown below, addresses areas that need to be examined in preparation for the Process Review. The focus of reactive chemicals concerns can be quite different for the various functions. Therefore, it is necessary that each group participating in a review, consider the impact of potential hazardous reactive chemicals situations. This thought process is appropriate for process changes, project reviews, mini reviews, consolidated audits, and all aspects of the management of reactive chemicals.

The significance of the twelve areas outlined below will vary from one operation to another. Use these areas as a checklist; they will provoke questions about your process. Include in your package your responses to these issues.

The thought process is one of stimulation: it should assist your group's continuous improvement of its reactive chemicals awareness.

1. Review the Louisiana Division Reactive Chemicals Program Manual.

2. Review and address status of action items from the prior audit or review.

3. Describe the PROCESS CHEMISTRY; the following areas should be addressed:

   HEATS OF REACTION: [Calculate maximum temperature rise(s) from reactive chemicals data.] Even though this represents an important part of process knowledge, they are often left out, incorrect, or not known. Heats of reaction are basic data required for worst case scenarios. Include the data for delta $H_{reaction}$ in the process flow sheet display of RC data and in the chemistry for the principle reactions. Use consistent units throughout; do not mix joules/gm, BTU/lb mole, BTU/lb, kcal/mole.

   INDEX FLOW SHEETS WITH TEST DATA: Develop a schematic or block diagram (an index flow sheet works well here) showing flows of chemicals and key process steps. Show the points where reactive chemicals testing has been done. List the tests and the data as a summary, giving T_{onset}, T_{max}, and exotherm total energy. The operating and maximum temperatures should also be shown on the diagram so that they may be compared with the reactive chemicals data. Not all tests will be shown on the process flow sheet, e.g., sawdust and chemicals.

   RAW MATERIAL IDENTIFICATION: Describe how confirmation of chemical identity is accomplished, such as lab chemical analysis procedures used. Consider the source of materials and likelihood of receiving 'look-alike' chemicals from supplier.

MATERIAL BALANCE: The index flow sheet will yield sufficient detail. This information is used to determine areas of need for reactive chemicals information.

WASTE DISPOSAL: Describe the fate of waste generated during the process. Include here absorbents used to handle spills, the testing performed to determine suitability, and procedures used to dispose of all waste materials, including temporary in-block storage procedures. Describe the venting and header system(s) that connect the process overheads to the Throx system.

MATERIALS OF CONSTRUCTION: Outline procedures for maintaining integrity of materials of construction supplies. Describe confirmation of identity, if appropriate.

4. Describe the PROCESS CONDITIONS, highlighting the main process(es). Pay particular attention to the following areas of concern:

    Side reactions, including impact of water, ambient temperature extremes
    Catalysts, desired and undesired
    Inhibitors
    Relief devices
    Raw materials storage

    Compare the reactive chemicals test results with the unit's process conditions, i.e. compare operating temperatures and extremes to T_{onset} of the thermal event. A definition of T_{onset} is given in Appendix A in the Thermal Stability section under Reactive Chemicals Testing. Are any potential reactive chemicals scenarios apparent? Be prepared to discuss.

5. Review the RAW MATERIALS and PRODUCTS for Reactive Chemicals data on storage of these materials. Describe any information, relating to storage needs of the product, that the customer should be made aware. Have ARC data been obtained for product made in commercial quantities?

6. Review status of the COMPATIBILITY CHART; revise to reflect changes in the process. Existing charts will be audited for completeness and relevance of the data. If a new chart is needed, contact Reactive Chemicals Testing for assistance. Use the computer program CHEMPAT to generate the compatibility chart.

7. Describe the PROCESS CHANGE MANAGEMENT system in place for the process under review.

8. Review the TRAINING programs for Reactive Chemicals that are used in the block. Describe the IPT modules and the worst case scenarios drills used to train personnel.

9. The HAZOP (Hazard and Operability) study is a flexible technique for process safety and reliability analysis. Describe any HAZOP analyses, or other hazard evaluation processes, that have been performed, or are planned.

10. Review, and include in the package, WORST CASE SCENARIOS for the process. Consider the plant's INCIDENT HISTORY. Use the HAZOP approach, where appropriate, to review the following areas:

    CHEMICALS - process and those not directly involved in manufacture. In particular, review the presence of heels, the impact of low/high flow rates and backflow, the presence and/or absence of catalyst and inhibitors, the potential for peroxide formation.

    EQUIPMENT - performance deviations. In particular, review the impact of failure in weigh cells, relief systems, agitators, static mixers, exchangers, pumps, scrubbers, critical instruments. Review the possibilities of too high or too low pressure, temperature, and/or flow.

    UTILITIES - total and partial loss; include pipeline sources of raw materials.

    STARTUP/SHUTDOWN/TURNAROUND - Review special concerns and scenarios. Show calculations to support your worst case scenarios, for example adiabatic temperature rise.

    Review your AREAS OF CONCERN; be prepared to discuss these as an integral part of the review process.

11. Review LINES OF DEFENSE in light of the worst case scenarios described in the previous section. Lines of defense are provided by integration of the following types of activities into the plant's operations:

    Training
    Monitoring equipment
    Alternate strategies in the program code
    Instrumentation, such as on-line analytical or critical instruments
    Raw material analysis and confirmation
    Material handling procedures

Include in the package WORST CASE SCENARIOS and describe the LINES OF DEFENSE set up to handle the situation. Stress the interpretation of your answer(s). Use HAZOP and/or incident histories as a source of scenarios.

12. Use the "Review of Reactive Chemicals Concerns" to think through the state of the plant's program in the areas addressed in the document. **That section is not a questionnaire to be answered in a 'yes/no' mode.** Rather, the intention of it is to stimulate (re-)examination of areas of the process that have the potential for an incident. It is also a tool to assist in review preparation. Include your written comments and observations to "Review of Reactive Chemicals Concerns" in the review package.

LHC II REVIEW OF REACTIVE CHEMICALS CONCERNS QUESTIONNAIRE/CHECKLIST

This section provides a detailed format within which to conduct a self-audit of the process(es) under review. There are 23 sections that cover various aspects of plant operations that have Reactive Chemicals concerns and/or issues. With each section there are one or more places for you to add notes that are pertinent to your process. This questionnaire also serves as a Reactive Chemicals checklist for new processes and process changes. Answer the questions only as they apply to Reactive Chemical concerns.

A. EVALUATION OF REACTIVE CHEMICALS DATA

The objective of these questions is to determine if the appropriate test data have been obtained and appropriate safeguards provided. Refer to the Process Flow Sheet and Test Summary Data.

a. Have Reactive Chemicals test data been gathered and evaluated for the following:

Yes No

[X] [ ] Process materials and mixtures that are normal to the operation;
[X] [ ] Mixtures that may result from abnormal conditions;
[X] [ ] Materials of construction throughout the process;
NA Potential sources of flammable dusts tested/explosive range known; rate of pressure rise data;
[X] [ ] Accelerating Rate Calorimetry (ARC) test on reactive mixtures and formulations that are handled in drums or larger volumes;
[X] [ ] Auxiliary materials, e.g., cooling tower chemicals that are normal to the operation;

Additional Comments: Dusts are not handled. Mixtures that result from abnormal conditions are only tested if these conditions are predictable and/or expected to result from a process change.

Are changes in the following entities tested:
[X] [ ] Chemical components
[X] [ ] Significant changes in concentrations, in formulations
[X] [ ] Materials of construction?
[ ] [X] Vent Sizing Package (VSP) run on reactors/tanks containing reactive materials.

Additional Comments: Any changes to materials, chemicals, or operational limits are administered through the Management of Change process. VSP does not apply. A copy of the LHC II MOC Policy is attached.

b. Do all individuals involved with reactive chemicals evaluation understand the information on the data sheets and know the limitations for extrapolating operating parameters from the data? What kind of training have they had?

Response(s): All data is interpreted with the help of LAD reactive chemicals personnel. Extrapolations are not used unless approved through Management of Change, with the appropriate reviews. All LHC II employees have had reactive chemicals training, as it relates to their job. This does not include data evaluation.

c. Have existing reactive chemicals data been reviewed to ensure that they are still appropriate to the process under consideration. In particular, consider the following:

Does it thoroughly define hazardous bounds? **Yes**
Has the process been checked out with a material balance flow diagram? **Yes-Ongoing**

DO A 031184
CONFIDENTIAL

Do data include total potential energy available in case a runaway reaction occurs? **This is currently being evaluated for the reactor area.**

Have test data been reviewed with Reactive Chemicals Testing and updated? **Yes**
When? **1992** Who? **Alex Guidry**

Does your system have the capability to adequately remove heat in a worst case situation?

Response(s): This is a consideration in the reactor area. As this project evolves this is being addressed, and will be reviewed prior to the project being started up.

B. CONFIRMING ANALYSIS OF RAW MATERIALS
a. Is there a program in place for chemically confirming all raw materials; are you comfortable with a Certificate of Analysis being required and received for those raw materials difficult to test? Do your suppliers manufacture look-alike chemicals that are different and could possibly be put in a mislabeled container by mistake?

Response(s): All raw materials are received via pipeline through Dow or Exxon lines. None are received in bulk storage. These materials are analyzed either continuously or by grab samples. The materials are normally directly off of plant production (LHC 3 ethane recycle, Chem Grade Propylene), or from large storage well systems (Mount Belview, Napoleonville). The materials are normally not analyzed for materials that are considered to be reactive unless they are suspected to be present.

b. Are inhibitor levels tested on in-coming raw materials that require an inhibitor? Have you worked with your suppliers of raw materials on specifications and potential contaminants?

Response(s): We have no incoming raw material that requires an inhibitor. There aredetailed pipeline specifications for all raw materials.

c. What level of training do analysts receive; are the analytical data for raw materials unambiguous; are there materials that could give similar analytical data?

Response(s): All LHC II Dow employees receive formal training and are tested for comprehension on Reactive Chemical concerns, as it relates to LHC II. All persons with analytical job requirements are trained on proper techniques and are required to use procedures when performing tests.

C. MATERIALS OF CONSTRUCTION
a. Has the process been reviewed for appropriate materials of construction with respect to operating conditions? Does the Tech Center provide information and/or recommendations for materials of construction? Is information sought from suppliers of raw materials?

Response(s): All materials of construction have been evaluated for the service for which they are used. The Tech Center has provided recommendations as to the proper material of construction to use in certain services. All raw materials are received via pipeline and carbon steel is appropriate.

b. Is testing required just prior to installing parts to assure the correct material of construction? Are materials used such as lubricants, thread compound, instrument filling fluids, etc., compatible with the process?

DO A 031185
CONFIDENTIAL

Response(s): Due to the non reactive nature of the process, materials of construction are not tested just prior to use. Any new materials that enter the block are tested for compatibility and required to be evaluated through the Management of Change process, which includes a New Chemical/Product Evaluation procedure. (Attached)

c. Are undesirable materials of construction identified(YES), controlled (by **THE MANAGEMENT OF CHANGE PROCESS**), and communicated (TO ALL EMPLOYEES)?

Response(s):From a reactive chemical's point of view, the only materials of construction which are unsuitable in the plant are those, such as aluminum, which are incompatible with caustic/amines. Employees are trained on this and tested. There are issues concerning materials of construction that are related to thermal strength properties, rather than reactivity.

d. Are materials monitored for corrosion in the process? Are conditions that can cause corrosion in the system well known?

Response(s): Vessels and pipes are inspected for wall lost due to corrosion. Those areas in the plant which are prone to internal corrosion are inspected on a routine basis. These areas are the amine system and caustic feed systems.

D. SIDE REACTIONS

Have side reactions in your process been adequately researched and identified? **Yes, the chemistry is well known and changes are fully evaluated prior to implementation.**

Have conditions for unwanted reactions been identified such as

pH Yes
water Yes
contaminants Yes
H2 evolution Yes
unusually lengthy temperature excursions? Yes
Is any part of your process or storage subject to peroxide No
acetylide Yes
azide formation? No

If so, are the sources known and a program in place to keep this under control?

Response(s):Hydrogen evolution is possible in the caustic area. Acetylides are formed in the pyrolysis process and has the potential to build up in the C3 Splitters. All employees are trained on these possibilities and tested for comprehension. It is possible, and has been mentioned in several reports, to form copper acetylides in the process. Based on these reports it does seem to be a remote possibility. Acetylide formation requires 50% copper or more, a moderate to high level of acteylene. A Dow Study also "indicated that copper may be saftely used in light hydrocarbon systems containing up to fractional percentage concentrations of acetylenes." * LHC II aceteylene reactor inlet concentration is 1% or less, but copper is not allowed in this area.

** Dow R&D Report LAD 587 : "Potential Acetylide Formation In Copper Sample Lines", Manuel Bonds, December 31, 1980*

E. SCRUBBERS [ ] N/A **The only scrubber which exists is 2RS-1, the reactor regen quench water scrubber.**

DO A 031186
CONFIDENTIAL

a. Is backflow of the scrubber into the process possible? **No, since the operation of the scrubber is only associated with an off-line reactor being regenerated and the low operating pressure of the scrubber. This pressure is protected by a safety valve.**

Is it possible to create an unwanted vacuum on the process from the operation of the scrubber? **No**
Are two or more process vessels relieved to a common scrubber? **Yes, but not at the same time.**

b. Can flammable or reactive materials accumulate in the scrubber medium or vapor space? **Yes - Flammable. there have been incidents associated with similar vessels within Dow. The Technology Center has recognized this and appointed a team of plant engineers to evaluate scrubber modifications. This team is expected to complete this project by year end 1995.**

Can the vent stream overcome the scrubber on very high flow? **Yes - The safety valve will relieve.**

c. How is the scrubber medium monitored to assure its effectiveness?

Response(s): There is no monitoring since once through quench water is used.

F. CATALYSTS [ ] N/A
a. Where does the catalyst in the process end up? Can it become a hazard? Is it in the Material Balance? Can catalytic activity be lost, poisoned or inhibited such that reactants could be charged without reacting. Are all potential reactions known for improper flows or conditions across the catalyst bed?

Response(s): The only catalyst used is palladium on diatomaceous earth. The catalyst remains in the fixed bed reactor, but could presumably be carried through the process and either terminate in the waste water filter system or on the reactor dehydrator mole sieve. There is an authorized project to replace this catalyst with a low palladium/silver catalyst commercially available. The catalyst has high crush strength and low attrition. This coupled with low palladium should reduce potential.

b. Is the catalyst checked before loading a new batch? Does a new or fresh catalyst bed require a special procedure?

Response(s): **Yes to both questions**

c. What are the procedures for starting up a catalyst bed or molecular sieve bed? Do they prevent a plug-flow type temperature front?

Response(s): LHC II uses detailed procedures that have evolved over time based on our experience and that of other Dow plants. Plug flow type temperature fronts are not specifically protected against.

d. Can the material of construction cause a catalytic effect with the product? Are there any components in the product that can react with the material of construction and cause catalytic problems? Can iron enter the process causing a hazardous catalytic effect or stop the reaction; can $FeCl_3$ be made by an acid condition? Can rust from carbon steel vessels become a potential source of unwanted catalyst?

Response(s): There is data which suggests that iron oxide with hydrogen / acetylene or ethylene under an elevated pressure and temperature can initiate unwanted hydrogenation. This is considered to be a low risk, but is covered in the LHC II training material. A common material found in hydrocarbon pipelines is iron sulfide. This can autoignite when exposed to air. This also is covered by training.

DO A 031187
CONFIDENTIAL

G. INHIBITORS [ ] N/A

a. Are inhibitor levels monitored? How are they monitored? Is the inhibitor affected by materials of construction or vice versa?

Response(s):The only inhibitor used is BETZ 20Y8, which is used as a chain terminator in the deethanizer and depropanizer towers. It is not required to prevent a reactive chemicals incident, but is used, rather, to extend run lengths on process equipment. Residual quantities are monitored by analysis weekly.

b. Is inhibitor effectiveness temperature dependent or can cold temperatures cause separation of the inhibitor from the product? **(NO)** Does the inhibitor require a small amount of oxygen to be effective? **(NO)** If so, is it monitored so as to avoid being eliminated by nitrogen padding? **(NO)**

H. ENVIRONMENTAL CONTROLS

a. How are the mixing of waste streams monitored for unwanted reactivity?

Response(s): There is no monitoring , however the only mixing which takes place is a virtually pure water stream with slight hydrocarbon contamination, and a virtually pure water stream with slight amine concentration. Waste which is stored in packs is separated according to waste characterization number.

b. How are carbon adsorption beds, pressure swing absorption units (PSA's), etc. monitored for correct operation?

Response(s): **N/A**

I. LAB CHEMICAL STORAGE

a. Is there a policy governing ownership responsibility, and date of receipt, for chemicals being stored; is a log or chemical inventory kept; is disposal or transfer of ownership of chemicals and samples required when the current owner is transferred?

Response(s): The C-9 checklist is used to insure that an inventory on all lab chemicals is performed semi-annually. This also serves as a log of these chemicals. No transfer of ownership is required at this time. Chemical inventory is kept at a minimum to prevent expiration of chemicals.

b. Are unstable chemicals given special storage provisions; is moisture a problem with some chemicals you store? Are your chemicals stored by compatibility or alphabetically?

Response(s): Chemicals are stored in approved chemical cabinets according to the following procedures. Corrosives are stored only with corrosives, flammables with flammables, others that have no concerns are stored in a cabinet in the lab. All outside cabinets are grounded with vent caps open. Moisture can present a quality problem.

J. HAZARDOUS MATERIAL HANDLING - POTENTIAL CONSEQUENCES

a. Is the material you handle subject to heat of compression hazard? If so, what procedures are in place to prevent explosions when opening valves/starting pipeline flows?

Response(s): YES - Lines are nitrogen purged, and slowly padded with process. This is done slowly and according to established procedures. We also rely heavily on training and relaying actual experiences on to plant operations.

DO A 031188
CONFIDENTIAL

b. Can material be concentrated or built up in a recycle stream to the point of instability? Can polymer or other materials in the process build up and become pyrophoric when exposed to air; is oxygen monitored in process systems where a component can be easily oxidized; are any peroxide-forming materials and conditions present in your process? If so, how is this controlled?

Response(s): Recycle streams pose no hazard of instability. Polymers of butadiene can build up and become pyrophoric when exposed to air. This is well known within the hydrocarbon industry. The 3 places where LHC II is the most vulnerable is 2E-52 A/B (Deethanizer preheaters), 2RE-52 A/B (Deethanizer reboilers), and 2C-55 A/B (Depropanizer towers). 2RE-52 A/B and 2C-55 A/B are campaigned until the online tower or exchanger fouls and then a clean one is put on line. The most crucial point is during the maintenance procedures when the polymer is exposed to air. Another area that polymers pose a certain risk is in the spent cell effluent stripping towers. The polymer is formed via Aldol-Condensation. We have trained all employees on these circumstances and procedures govern all operations. LHC II has 3 flare header systems, the wet, the dry, and the stainless headers. The stainless header is used for either cryogenic gasses, or those liquids which will auto-refrigerate when vaporized (as when a safety valve is relieving). The wet and dry headers have one continuous paramagnetic analyzer which is common to them which monitors for O2. This is displayed on the Vax 1 graphics. The stainless header has its' own continuous paramagnetic O2 analyzer. This is displayed on the PDP-11 graphics. The alarms on these headers are set at 3.0 % O2. Normal operation is at 0.25-0.5% O2. Operator action when an alarm is received is to increase nitrogen purge flow on the headers and to investigate potential sources.All refrigeration machines are sampled routinely for inerts, this is especially important since 2 of the machines operate at mild vacuum conditions.

c. Can any of the materials, when contacted with a high surface area substrate, result in a lowering of the auto ignition temperature to a hazardous range?

Response(s) : Yes, almost any of the heavier hydrocarbons can have their autoignition temperature lowered when this occurs. The most typical example of this would be hydrocarbons dripping on a hot insulation blanket. These blankets were recently audited and work orders have been entered to replace those with hydrocarbons on them. This can also occur on filter (sock or carbon beds) media that may have polymers, iron oxide, or hydrocarbons on them.

d. Can prolonged storage of any material lead to a hazardous situation?

Response(s): This is not normally considered a problem, however an incident resulting in the overpressure of isopentane stored in drums did occur. The material has a high vapor pressure at normal ambient temperatures.

K. WASTE HANDLING

a. Are the absorbents used in your area selected on the basis of test data? Are procedures in place to prevent spontaneous ignition with absorbents and filters? Any prohibited absorbents? Has everyone been trained on this?

Response(s) : KSORB is the only absorbent acceptable for use within the LHC II plant.

b. Are different waste chemicals collected in a common container? If so, what are the controls over what is put into the container? Does control of waste include materials of construction; time limit of storage; written procedure for disposal.

Response(s): No, this is not allowed. Materials are stored based on waste characterization numbers.

L. HEELS IN TANK CARS, TRAILERS, LINES, VESSELS, AND BARGES [ ] N/A
Are heels, resulting from cleaning, a hazard with your products? Are procedures in place to analytically test all heels before making transfers? Are vapors in pressurized vessels/trailers analyzed if no liquid sample can be obtained? Are dedicated transport vessels used without confirming heel identity? If so, how do customer and vessel handling procedures ensure the contents of the returned vessel?

Response(s) : LHC II does no loading, we only receive materials in tank trucks

M. EXCHANGERS [ ]

Yes No
a. [ ] [X] Does the failure of any heat transfer system result in an uncontrollable condition? Have you evaluated the effects of recirculation or cooling failure?

b. Is the exchanger medium compatible with the process material? Will cross-contamination with the process be hazardous; is monitoring provided to detect a leak?

Response(s): All heat exchangers utilize either plant produced hydrocarbons, steam, or river water. The possibility of contamination does create a quality problem but is not hazardous.

c. Is temperature monitoring provided around the exchanger? Has the reboiler's maximum temperature been evaluated with respect to time/temperature exposure to the material being vaporized?

Response(s): N/A

N AGITATORS [X] N/A
a. Has agitator failure (power failure) been evaluated during the step with the most available energy to determine if a runaway can occur? Is monitoring provided to detect agitator failure? Are reactive feed flows interlocked to stop on agitator failure?

Response(s):____
____

0. STATIC MIXERS [X] N/A
Can overheating occur within the static mixer if flow of reactants is suddenly stopped without purge-out? Are temperatures before and after the mixer monitored?

Response(s):____
____

P. PUMPS
a. How are all pumps protected from deadheading? Does the monitoring scheme assure detection and alarm/SD on pump cavitation? If not, how is this detected and controlled? Are feed pumps interlocked with shutdown trips?

Response(s): Pumps are not normally protected against deadheading. There are some pumps which have recirculation HIC valves, but these are manual, and an exception rather than the rule. Those pumps which contain conjugated dienes do have alarms on low flow which activate in the control room.

b. Have recycle streams been evaluated for loss of recycle? Can extended time agitation lead to an unacceptable temperature rise? Is a reaction controlled by pumping through a heat exchanger?

Response(s): No

c. Are pump seals monitored for flow of seal fluid and seal loss; would a seal fluid leak into the process be a reactive chemicals hazard?

Response(s) : Pump seals are monitored for loss of primary seal. All barrier fluids are compatible with the process.

d. Are there installations in the process where pumps are used for mixing? If so, has there been an evaluation of the effectiveness of mixing? Can unreacted materials be forwarded to undesirable places due to poor mixing?

Response(s): N/A

Q. BACKFLOW

Have potential backflow scenarios been evaluated; has process backflow been effectively prevented in feed lines, nitrogen connections, condensate, gas cylinders? Is redundancy of protection provided?

Response(s): Yes, but protection is not redundant in most cases.

Describe your backflow protection: Feed lines are protected by check valves, low flow alarms, and low pressure trips. Nitrogen protection is basically check valves on paymeter and at drops and operating discipline. LHC II is a net exporter of condensate and therefore normally has excess to supply all its own needs. There is an on-line analyzer which monitors hydrocarbons in the line to power. There are no gas cylinder tie ins to the process, with the exception of calibration gas tie ins at analyzers. These are protected with check valves and sample switching systems.

R. FLOW RATE, DISTILLATION

a. Have low and high flow rates been evaluated for their effects on reaction stability and heat removal? If the control valve is fully open will this flow rate result in a hazardous situation?

Response(s): N/A

b. Has total reflux of your distillation columns or reactor systems been evaluated for loss of overheads through leaking overhead valves? Concentration of unstable components in certain trays?

Response(s} : Loss of overheads on all towers would not result in a reactive chemicals concern. Unstable components can concentrate up on certain trays. This is a concern in 2C-54, the C-3 splitter. The materials which could present a problem are Methyl Acetylene (MA) and/or Propadiene (PD). Simulations of this occurrence show that both the MA and PD, under total reflux conditions, should concentrate up in the column bottoms. The conditions near equilibrium are approximately 0.70% MA, 0.70 % PD, at 255 PSIA and 130 Fahrenheit. Although these conditions seem unlikely to pose a risk, it is credible with leakby of lights in the overhead, that they could concentrate up further.

S. RELIEF DEVICES AND VENT SYSTEMS

Have relief devices been calculated for worst case reactive chemicals runaway; two-phase flow? Are relief device vent systems common to more than one system? If so, has the system been sized for back pressure when one or more than one reactor overpressures?

Response(s): The documentation on the relief system is out of date. All hydrocarbon safety valves relieve to a flare header system.

T. COMPATIBILITY CHART

Has a current cross-compatibility chart been developed for chemicals used in the block that may be mixed unintentionally **(YES-for the most part)**; are self-reactive materials and materials of construction, included in the data? **(NO)** Is the compatibility chart posted where all block employees can use it? **(YES, accessible on the Training PC)** Are employees trained in its use? **(YES)** Is there a policy for keeping the cross-compatibility chart up to date? **(Yes, associated with the MOC process.)**

U. REACTIVE CHEMICALS TRAINING AND SCENARIOS

a. Is a training module developed for Reactive Chemicals in the department? Is reactive chemicals training conducted/tested/documented? Is attendance checked for those needing training?

Response(s): Yes, LHC II does have a Reactive Chemicals training program in place. Known incidents inside and outside of Dow are covered. This is attended by all personnel. The testing is performed on the training PC, with a required score of 100%. All training is documented. Documentation is available at the plant.

b. Does reactive chemicals training include materials specific to the block; have hazard envelopes of chemical mixtures that are reactive, flammable, or explosive been developed and included in the training program; are case histories of past incidents in your unit, the Dow world, and the chemical industry, related to your process, included in the training program; have potentially wrong mixtures or procedures been emphasized.

Response(s): All of these issues and areas are covered in detail.

c. Are important parameters, such as pH, water, contaminants, similar analyzer peaks, assurance of exotherm onset, side reactions, etc. included in periodic training; are employees trained on the ways instruments and control devices
are prone to fail?

Response(s): All are covered with the exception of the way an instrument is prone to fail. Each shift does, however have personnel with instrument training.

d. Are employees drilled on scenarios covering reactive chemicals concerns with written corrective procedures and/or responses for process upsets? If so, how often and which shifts?

Response(s): LHC II does have a progressive emergency drill system, however reactive chemical scenarios have not been tested recently. This will be included in the list of potential future drills.

V. CUSTOMER INFORMATION/PRODUCT STEWARDSHIP

a. Are customers informed of potential reactive chemicals hazards of products/formulations? Is the customer information current; are changes in formulations or concentrations communicated to the customers?

Response(s): With the primary raw materials we generate being ethylene and propylene, all of the customers are aware of the hazards as it relates to their process.

b. Is assistance offered to the customer to pursue reactive chemicals concerns; do you assure yourself that the customers understand the data provided; are materials of construction concerns communicated to the customer?

Response(s): Upon request, LHC II will provide this information. Global specs will address the material of construction concern.

DO A 031192
CONFIDENTIAL

W. REACTIVE CHEMICALS REVIEWS

a. Are all processes reviewed by line supervision and engineers, technology center, Safety Director and the LAD Reactive Chemicals Committee within approximately 90 days of a new superintendent or at scheduled Consolidated Audits, not to exceed two years?

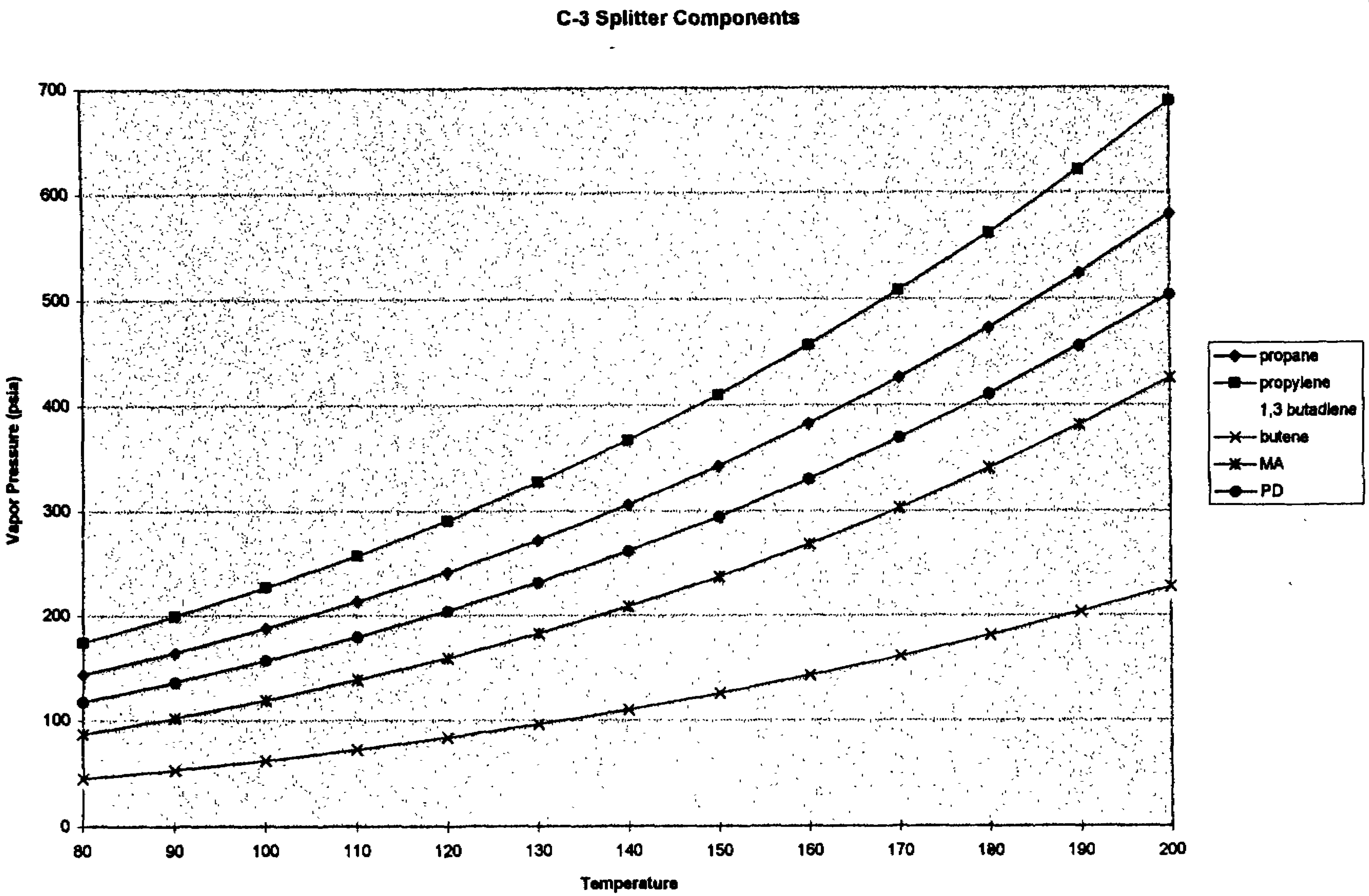
Response(s): YES

b. Are appropriate process changes reviewed by the Reactive Chemicals Committee before they are installed; are pre-startup reviews held for process changes and recommissioning equipment; are pre-startup reviews held for appropriate processes that are infrequently operated (> 6 mos.)?

Response(s): YES

c. Are formulation changes reviewed by the Reactive Chemicals Committee before they are established?

Response(s): YES



DO A 031194
CONFIDENTIAl

LHC 2 Plant Personnel Interview Questions

KY

..hat are the lines of defense to prevent an excessive furnace firing rate?

JP

M....imum fuel gas header pressure,
Fuel gas pressure indications in control room,
Several temperature points monitored in furnace,
Stack temperatures monitored and alarmed on high temperatures,
Computer control of excess oxygen and combustibles

"D"

Both SOS's correct, 1 out of 2 OS's correct

A - yes
B - yes

What are the lines of defense to prevent spent molecular sieve from smoldering and catching fire when it is dumped?

C - yes

Regenerate and water flush the dehydòator before dumping

D - yes

Both SOS's correct, both OS's correct

What are the lines of defense to prevent to prevent a run away reaction in the acetylene convertors?

"B" Shift
B R.P.B.
F.L.

Inlet feed temperature control,
Inlet, outlet, and six bed temperatures are monitored,
High temperature alarms on all temperatures,
Hydrogen to feed ratio control,
Alarms on low CO concentration,
Differential hydrogen analysis

BARBAY (VAC)

Both SOS's correct, both OS's correct

4. What are the lines of defense to prevent an ethylene decomposition when an ethylene line is pressured up?

Ethylene pipelines are inerted, padded close to process pressure with nitrogen, then <u>*slowly*</u> *padded with ethylene*

Both SOS's correct, both OS's correct

JGS 7/95

'e the lines of defense to prevent autoignition of polymer during cleaning of the anizer column and deethanizer reboiler?

De, panizer column and deethanizer reboiler steamed for several days before opening,
Depropanizer is kept wet while open,
Waste polymer is saturated with water for disposal

Both SOS's correct, both OS's correct

/hat are some of the Reactive Chemical concerns to consider when using caustic?

It reacts with aluminum to form hydrogen and aluminum hydroxide,
Above 140 degrees F, it reacts with carbon steel, thus causing hydrogen embrittlement,
Heat of solution when diluting concentrated caustic can be significant

Both SOS's correct, 1 out of 2 OS's correct

LPG pipelines often contain iron sulfide. This is produced when hydrogen sulfide and/or other sulfur containing materials react with the carbon steel pipe. What is the Reactive Cl nical concern with iron sulfide?

It is pyrophoric, that is, it auto ignites when exposed to air.

Both SOS's correct, 1 out of 2 OS's correct

3. Why should a distillation column which contains acetylenic compounds never be put on total reflux?

The explosive compounds could concentrate up in the tower

Both SOS's correct, 1 out of 2 OS's correct

JGS 7/95

DO A 031197
CONFIDENTIAL

9. Loss of the LHC 2 turbo expanders or the ethylene refrigeration system will result in high ethylene concentration in the hydrogen off gas. Why should such an event be reported to the Benzene plant immediately?

The hydrogen is fed into a methanator reactor (at the Benzene plant) which can thermally run-away with high ethylene (olefin content) in the feed

Both SOS's correct, 1 out of 2 OS's correct

10. One of the most significant reactive chemical concerns in the reactor area occurs during the regeneration step. During the burn off stage, the reactor is heated up to 550-600 degrees F. Then air is added to allow burn off of the green oil on the catalyst. Why is it important that the temperatures of the reactor be monitored closely and NEVER be allowed to exceed 1300 degrees F?

At this temperature, carbon steel can lose its integrity

Both SOS's correct, 1 out of 2 OS's correct

11. Are Reactive Chemical incidents at Dow Light Hydrocarbon plants discussed with you?

Yes - by VAX mail, bulletin board postings, safety meetings

12. What type of Reactive Chemical training have you had?

IPT Reactive Chemicals module and test

13. Have you seen the packets from Reactive Chemical reviews (new superintendent review, Consolidated Audit, process changes) held at the LHC 2 plant or the main Reactive Chemical concerns, worst case scenarios, and lines of defense presented at the reviews? Where can this information and the LHC 2 Reactive Chemicals Handbook be found?

2 SOS's - yes, Reactive Chemicals info kept in file room in B-4801T
2 OS's - no, did not know where it was kept

14. Who is the Reactive Chemicals contact at the LHC 2 plant?

Steve Milligan

Both SOS's correct
1 out of 2 OS's correct

Results of Interviews

- SOS's have excellent knowledge of Reactive Chemical concerns (100% correct)
OS's have less knowledge of Reactive Chemical concerns (70% correct)
- OS's have not seen Reactive Chemical concerns, worst case scenarios, and lines of defense from Reactive Chemical reviews, and did not know where Reactive Chemical information and LHC 2 Reactive Chemicals Handbook are kept.
- Both SOS's and one OS knew who LHC 2's Reactive Chemicals contact is.

Reactive Chemical Review 7/13/95

Presented By:

Steve Milligan, Michelle Kelley, Orlando Quintero and Shu Rau

LHC II Reactive Chemicals Incident Report

- *Glowing Embers Fire in Vacuum Truck Hopper - 5/81*
- *Light Hydrocarbons Filter Pot Fire - 7/83*
- *Explosion and Flame while Loading Tank with Caustic - 2/87*
- *LHC II Plant Molecular Sieve Column Fire - 8/88*
- *Autoignition on Fiberglass Filter with Molecular Sieve, Iron and Hydrocarbons - 4/94*

Summary 2/87

- *An operator opened a valve on a two inch 50% caustic line to fill a day tank at the LHC II plant. After a flow was started, the operator turned away and walked a few steps before he heard a moderate explosion.*

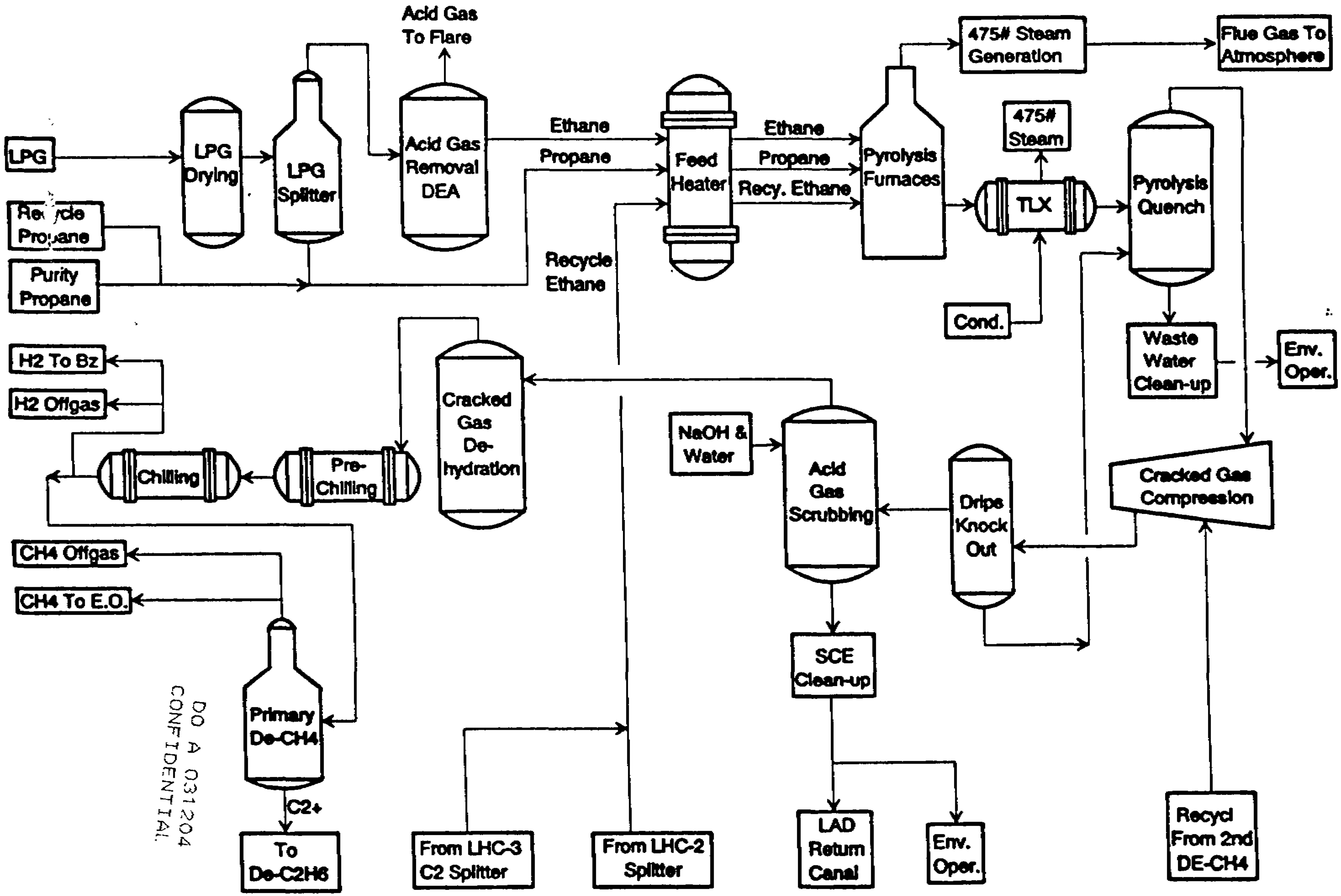
- *Severity - Learning Experience*

Summary 4/94

- A fiberglass filter element was removed from service and began to smoke after several minutes of exposure to the air. The filter had on it, significant levels of molecular sieve and iron, as well as hydrocarbons.

- Severity - Significant

LHC-2 Process Flow



DO A 031204
CONFIDENTIAL

Incoming Feed Preparation Additives

- Incoming feed not analyzed for additives
- Betz 6A9 Antifoam added to the DEA
  - monitored by Betz technical representative weekly
  - positive identification test when delivered

Incoming Feed Preparation
Worst Case Scenario

- *Molecular sieve is decontaminated and dumped from the vessel as part of a maintenance activity. The sieve is not saturated with water in the vessel before dumping. Iron sulfide particles are present from the incoming feed pipelines. The sieve has not been fully decontaminated, so hydrocarbon residual is present. When the sieve is dumped, it is raining. Water is absorbed by the sieve, causing an exotherm. The iron sulfide contacts oxygen in the air and starts to exotherm. The hydrocarbon residual begins to smolder, then burn. Water must be quickly added to the sieve both inside and outside the vessel to extinguish the fire and deactivate the sieve.*

Furnace Area Additives

- Dimethylsulfide (DMS)
  - Supplier provides Certificate of Analysis
  - Trailers are dedicated to DMS transport
  - Distinctive odor

Furnace Area
Worst Case Scenario

A furnace is warmed and put on line. The decoke air blind is not installed per procedure. The furnace next to it is taken down for decoke. Air is inadvertently opened on the on line furnace rather than the off line furnace. An explosive mixture develops in the on line furnace, causing a catastrophic explosion in the furnace tubes.

Quench and Compression Concerns and Prevention

- *Air entering system*
  - *equipment is inerted before being put back into service*

- *Butadiene polymer present when lines or equipment are opened*
  - *equipment is decontaminated by steaming or flushing*
  - *equipment is kept wet when open to air if polymer is present*

Cracked Gas Dehydrator Area Concerns and Prevention

- *Molecular Sieve exotherm upon contact with wet air**
  - *sieve is saturated with water before dumping to deactivate*

- *Butadiene polymer present when lines or equipment are opened*
  - *equipment is decontaminated by steaming*
  - *equipment is kept wet when open to air if polymer is present*

- *Iron Sulfide in pipelines, filters, vessels exotherm upon contact with air**
  - *procedures specify to keep wet when exposed to air*

**if hydrocarbons are present, the heat generated could cause autoignition of the hydrocarbons*

Utilities
Additives

- **Boiler feedwater chemicals (Betz)**
  - *vendor supplies Certificate of Analysis*
  - *positive identification test before offloading*
  - *monitored weekly by Betz technical representative*

- **Lube oil**
  - *vendor supplies Certificate of Analysis*
  - *positive identification test before offloading*
  - *monitored periodically by MTS*

Utilities
Worst Case Scenario

- *Air enters flare header through leaking valve on the suction end of a compressor that is under a vacuum. Oxygen analyzer detects high level and alarms. Hydrocarbons are also present in the flare header. Before the operator can increase the nitrogen purges, the oxygen builds up to the flammable limit. An explosion occurs in the flare header.*

Cracked Gas Chilling and Cold Train Function

- *Condense the cracked gas for introduction into the Demethanizer.*
- *Make the first cut by venting off the hydrogen rich offgas.*
- *Utilizes refrigerated propylene and ethylene as well as process ethylene, ethane, methane and hydrogen for cooling.*

Cracked Gas Chilling and Cold Train Worst Case Scenario

- *While in the process of hydrogenating the off-line acetylene reactor, the plant experiences a plant upset that causes the ethylene refrigeration compressor to trip. The ethylene concentration on the hydrogen off-gas exceeds 30%. Due to the confusion during the upset, no one calls Benzene to inform them of the incident nor does anyone shutdown the reactor hydrogenation. The Benzene plant is alerted of the problem by an alarm on a key cold train temperature wired to their plant, and they take steps to avoid an incident in their plant. However, the temperature rise in the acetylene reactor goes undetected until the recorder and PDP-11 both alarm at 650°F; hydrogen flow is automatically tripped off at 750°F.*

Primary Demethanizer Concerns and Prevention

- *Swapping methane stream to Glycol II from LHC III's methane to LHC II's methane.*
  - *Glycol II must place their hydrogenation reactor in service before allowing LHC II to provide methane.*
  - *Glycol II is to be called before swapping methane sources.*
  - *Glycol II's reactor will trip on high temperature.*

- *Off-line washing of the column with TX from the Benzene plant.*
  - *This practice has been successful in clearing the column of unknown foreign material responsible for creating flooding and hydraulic distribution problems in the column.*
  - *TX is from the Benzene plant.*

De-Ethanizer Function

- *Performs the split between the ethane and lighter overhead stream fed into the ethylene purification area and the propylene and heavier bottoms stream that is fed to the propylene purification area.*

- *Utilizes refrigerated propylene in the condenser and 60 PSI steam in the reboiler.*

De-Ethanizer Concerns and Prevention

- *Butadiene polymer present when reboiler and column are opened.*
  - *Reboiler is decontaminated by steaming.*
  - *Column has never been opened.*
- *Passing ethylene in the bottoms stream and sending contaminated propylene to Glycol I.*
  - *Analysis control of the bottoms along with alarming on ethane and ethylene in the bottoms stream.*
  - *Alarming on ethane in crude C3 from LHC III.*
  - *Procedure for dealing with ethylene contamination.*

Acetylene Reactor Area Chemistry

- Preferred Reaction
  - $C2H2 + H2 + Heat + Catalyst \longrightarrow C2H4$
- Side Reactions
  - $C2H4 + H2 + Heat + Catalyst \longrightarrow C2H6$
  - $C2H4 + H2 + Heat + Catalyst \longrightarrow$ Green-oil (C4 to C24)

Acetylene Reactor Area Concerns and Prevention

- Reactor stack vapor space containing hydrocarbons and oxygen.
  - Initiating a study of this problem along with LHC-6.

- Acetylene break will contaminate ethylene product.
  - Procedurally, all user plants that are adversely affected by acetylene are isolated from our product until samples show acceptable levels of acetylene.

Ethylene Purification Function

- Remove contaminates from the ethylene product.
  - Dehydration of the stream to prevent hydrates forming in downstream vessels.
  - Methane removal; recycled back to cracked gas compressor.
  - Ethane removal; recycled back to furnaces.

- Utilizes refrigerated propylene in the columns' condensers, and first extraction propylene from the refrigeration compressor in the reboilers.

Ethylene Purification
Worst Case Scenario

- *A hydrate develops in the C2-Splitter column which will be promptly attacked with an alcohol flush through the reflux line. While still feeding the clean ethylene storage drums, the alcohol fills the discharge line of the off-line reflux pump and begins spilling over into the reflux stream. Under normal conditions, no appreciable quantity of alcohol will come overhead even if introduced at the reflux. However, the column experiences a large pressure drop due to changes in ethylene supply to the vinyl header. Overhead flow surges drawing as much as 5 ppm of alcohol into the storage drums. Poly A and Poly B have reactive chemicals incidents due to the high alcohol content of their feedstock ethylene.*

Propylene Purification Concerns and Prevention

- Methylacetylene/propadiene decomposition.
  - Situation could arise were all feed to the C3-Splitter is from LHC III and Exxon; MAPD content unknown.
  - Avoid total reflux of C3-Splitter.
  - Little concern during normal operation.

- Butadiene polymer present in the depropanizer and its reboiler.
  - Procedurally, the column and reboiler are maintained soaked with water when opened and before cleaning.
  - Steps have been taken to lengthen run times to reduce risk of incident.

- Dead-heading butadiene pump.
  - Alarm on low flow and high pressure.
  - The depropanizer and 2D-88 level controllers are clamped at 5% output when in automatic.

Ethylene/Propylene Distribution Function

- *Prepare and deliver product ethylene and propylene from LHC II and/or storage ethylene and propylene from the wells to user plants.*
- *Dehydration*
- *Pressure regulation*

Ethylene/Propylene Distribution Worst Case Scenario

- *The EBV on the ethylene from the well has lost air pressure and slams closed. While the instrument folks work on the problem the pressure downstream of the valve drifts down to the Poly A header pressure; from over 1000 psi to 450 psi. The instrument folks corrected the problem which causes the 8 inch EBV to open fully. The heat of compression initiates the decomposition of ethylene. An ethylene decomposition wave propagates down the line until it finds a weak point in the line. The line ruptures releasing ethylene to atmosphere resulting in a fire. Property damage is suffered due to the decomposition and fire; injury to personnel is likely.*

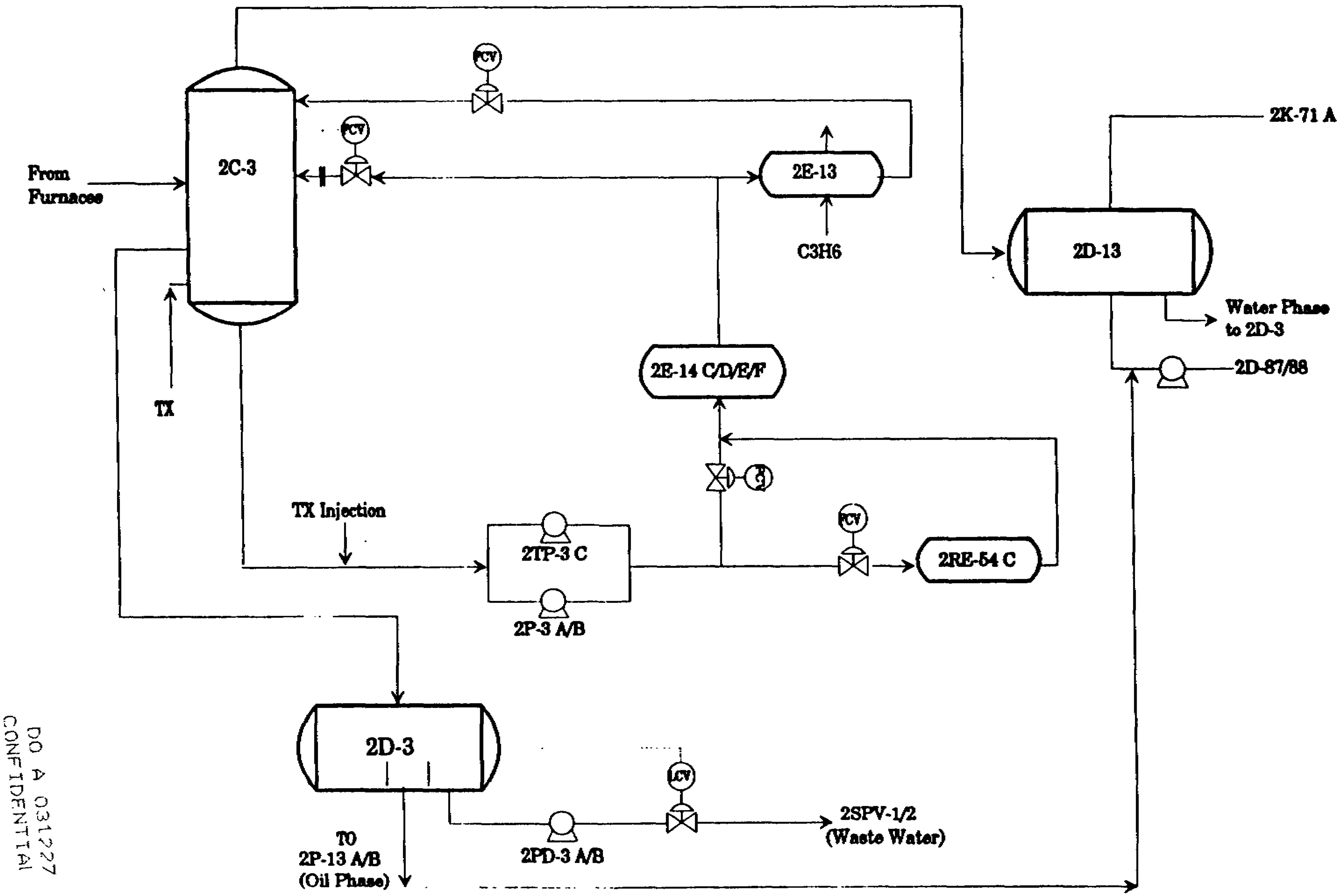
Ethylene/Propylene Refrigeration Systems Concerns and Prevention

- Air in systems
  - *weekly analytical testing for inerts in system.*
- Isopentane washing of the ethylene refrigerated exchangers.
  - *Relying on the Certificate of Analysis for positive identification.*
  - *Installation of dry gas seals on the ethylene compressor will eliminate this practice.*

Wastewater, Caustic and Spent Cell Effluent Areas

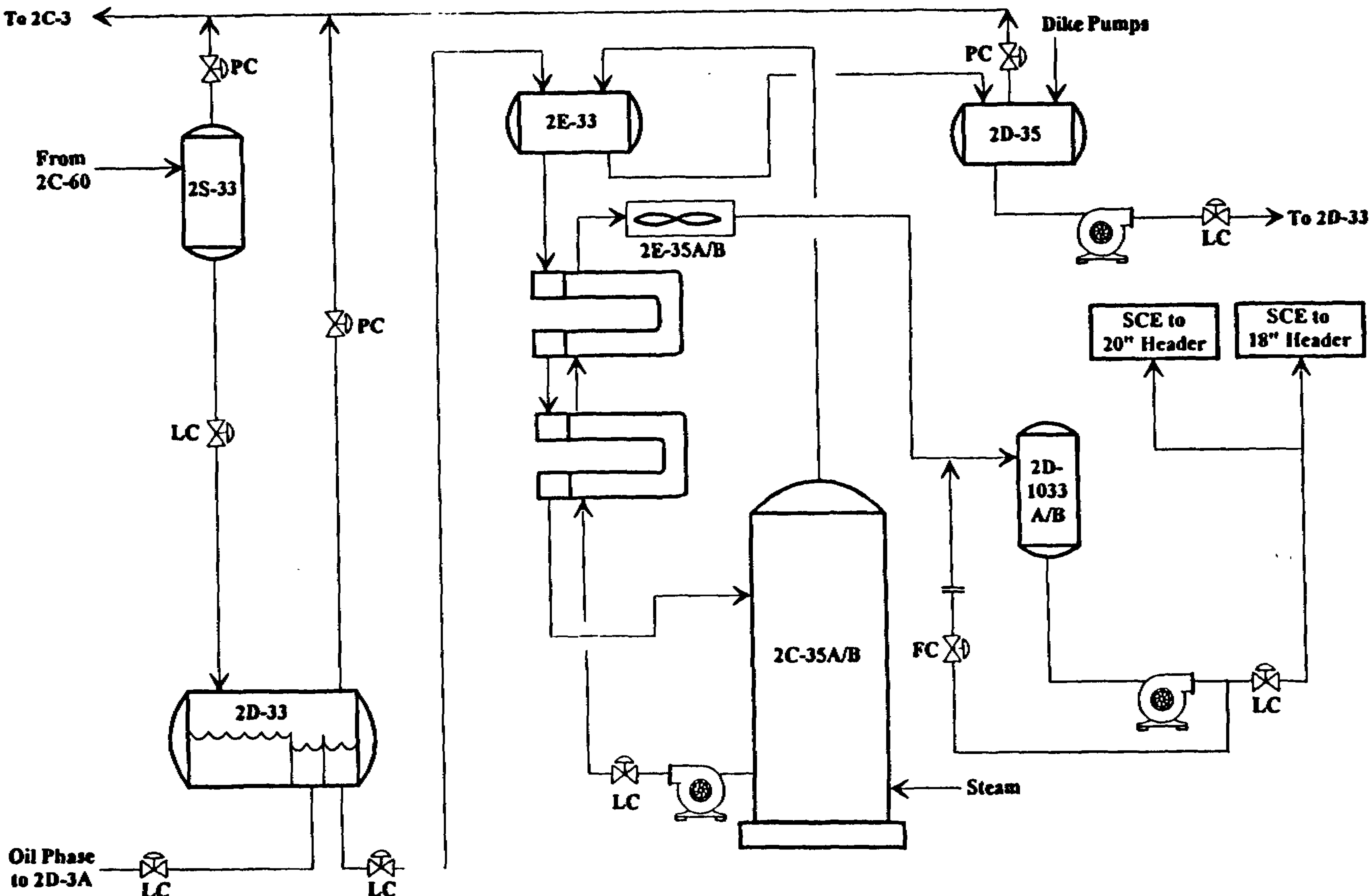
- Area Descriptions
- Chemical Reactions
- Process Additives
- Worst Case Scenario

2C-3



2C-3
From Furnaces
TX
TX Injection
FCV
FCV
2E-13
C3H6
2E-14 C/D/E/F
FCV
2TP-3 C
2P-3 A/B
2RE-54 C
2K-71 A
2D-13
Water Phase to 2D-3
2D-87/88
2D-3
TO 2P-13 A/B (Oil Phase)
2PD-3 A/B
LCV
2SPV-1/2 (Waste Water)

Spent Cell Effluent Cleanup



N:\RAU\SCEC.DS4
Revised: 7/5/93

Chemical Reactions:
2C-60 A/B

Cell effluent is used to react with acid gases to remove them from the cracked gas stream.

- *Carbon Dioxide Removal:*
  - $CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$
- *Hydrogen Sulfide Removal:*
  - $H_2S + 2NaOH \longrightarrow Na_2S + 2H_2O$
- *Excess caustic is maintained to keep the Na_2CO_3 in solution.*
- *The reactions are exothermic but occur only in small quantities.*

Process Additives

- TX (Toluene / Xylene) Wash
  - *Solvent used to dissolve heavy organics in process lines and equipment*
  - *Received in dedicated line from LHC III*

- *Antifoam - Oceanol*
  - *Prevent foaming in 2C-60 A/B*
  - *Used in minute quantities*
  - *Certificate of Analysis on current supply*

Worst Case Scenario: Caustic / Spent Cell Effluent

- Rupture on vessel or line in caustic service
  - Hydrogen Embrittlement - welding
  - Wrong material of construction (Al, Zn)

- Procedures are in place to prevent such incidents from occurring.