CONSTRUCTION PERMIT
OFFICE OF AIR MANAGEMENT

Eli Lilly and Company
10500 S. State Road 63
Clinton, IN 47842

is hereby authorized to construct the three antibiotic intermediate processes L, I, and E, or other pharmaceutical products of equivalent or lower PTE at the above location consisting of the equipment and operations listed in pages 3 through 6 of this permit.

This permit is issued to the above mentioned company (herein known as the Permittee) under the provisions of 326 IAC 2-1 and 40 CFR 52.780, with conditions listed on the attached pages.

Construction Permit No.: CP-165-9135-00009	
Issued by: Paul Dubenetzky, Branch Chief Office of Air Management	Issuance Date:

Process L process tanks (C2-TK-2), (C2TK24), (C2TK23), (C2TK22), (C2RVF4), (C2TK23A); fluid bed dryers (C2FBD5), and (C2FBD6); and tote bag/drum filling station (C2TBFS001) will no longer be covered by Operation Permit No. 83-09-91-0078.

Process E process tanks (C12TK01); holding tank (C12TK20); crystallizers (C12TK25), (C12TK26), and (C12TK27); filtrate tanks (C12TK28), and (C12TK36); toluene pretreatment tank (C12TK34); NAOH and H2O makeup tank (C12TK37); primary tank (C12TK38); separating tanks (C12TK34B), and (C12TK34C); hot well on C12TK26 (C12TK38A); will no longer be covered by Operation Permit No. 83-09-91-0079.

Rosemund filters (C12RF175), and (C12RF176); and HCl charge pot (C12TK17C) will no longer be covered by Registration No. CP 165-3055.

Solvent storage tanks (C64BTK163), (C64BTK165), and (C64BTK169) will no longer be covered by Operation Permit No. PC (83) 1837.

Solvent storage tanks (C64ETK158), (C64ETK160), (C64ETK162), (C64ETK164), (C64BTK167), and (C64ETK174) will no longer be covered by Registration dated 10/11/90.

Solvent storage tank (C64FTK203) will no longer be covered by Construction Permit No. CP 165-3801.

Solvent storage tank (C64HTK255) will no longer be covered by Construction Permit No. CP 165-1951.

(a) Process L

(1) one (1) process tank (C2-TK-2), nominal capacity of 2,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control

equipment;

(2) one (1) process tank (C2TK24), nominal capacity of 2,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(3) one (1) process tank (C2TK23), nominal capacity of 2,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(4) one (1) process tank (C2TK22), nominal capacity of 2,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(5) one (1) rotary vacuum filter (C2RVF4), controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(6) one (1) fluid bed dryer (C2FBD5), controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(7) one (1) fluid bed dryer (C2FBD6), controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(8) one (1) process tank (C2TK23A), nominal capacity of 150 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(9) one (1) tote bag/drum filling station (C2TBFS001);

(b) Process I

(1) one (1) process tank (C13TK29), nominal capacity of 4,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(2) one (1) filter (C13FLT1), controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(3) one (1) filter (C13FLT2), controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(4) one (1) hopper (C13H1), nominal capacity of 42 cubic feet, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(5) one (1) hopper (C13H2), nominal capacity of 42 cubic feet, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(6) one (1) hopper (C13H3), nominal capacity of 42 cubic feet, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(c) Process E

(1) one (1) process tank (C12TK01), nominal capacity of 500 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(2) one (1) process tank (C12TK12), nominal capacity of 4,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(3) one (1) holding tank (C12TK20), nominal capacity of 2,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(4) one (1) crystallizer (C12TK25), nominal capacity of 4,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(5) one (1) crystallizer (C12TK26), nominal capacity of 4,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(6) one (1) evaporator (C12TK27), nominal capacity of 4,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(7) one (1) filtrate tank (C12TK28), nominal capacity of 4,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(8) one (1) toluene pretreatment tank (C12TK34), nominal capacity of 2,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(9) one (1) filtrate tank (C12TK36), nominal capacity of 2,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control

equipment;

(10) one (1) NAOH and H2O makeup tank (C12TK37), nominal capacity of 2,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(11) one (1) primary tank (C12TK38), nominal capacity of 1,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(12) one (1) hot well (C12TK34B), nominal capacity of 50 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(13) one (1) separating tank (C12TK34C), nominal capacity of 220 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(14) one (1) hot well on C12TK26 (C12TK38A), nominal capacity of 30 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(15) one (1) Rosemund filter (C12RF175), nominal capacity of 4 square meter, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(16) one (1) Rosemund filter (C12RF176), nominal capacity of 4 square meter, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(17) one (1) HCl charge pot (C12TK17C), nominal capacity of 100 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(18) one (1) basket centrifuge (C12CENT3A), size 24 inch x 48 inch, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(19) one (1) basket centrifuge (C12CENT3B), size 24 inch x 48 inch, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(d) Solvent Recovery

(1) one (1) neutralization tank (C63TK207), nominal capacity of 8,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(e) Solvent Storage

(1) one (1) solvent storage tank (C64BTK163), nominal capacity of 19,494 gallons, controlled by a vent condenser;

(2) one (1) solvent storage tank (C64BTK165), nominal capacity of 19,494 gallons, controlled by a vent condenser;

(3) one (1) solvent storage tank (C64BTK167), nominal capacity of 19,494 gallons;

(4) one (1) solvent storage tank (C64BTK169), nominal capacity of 19,494 gallons;

(5) one (1) solvent storage tank (C64ETK158), nominal capacity of 38,551 gallons, controlled by a vent condenser;

(6) one (1) solvent storage tank (C64ETK160), nominal capacity of 38,551 gallons, controlled by a vent condenser;

(7) one (1) solvent storage tank (C64ETK162), nominal capacity of 38,551 gallons, controlled by a vent condenser;

(8) one (1) solvent storage tank (C64ETK164), nominal capacity of 38,551 gallons, controlled by a vent condenser;

(9) one (1) solvent storage tank (C64ETK174), nominal capacity of 38,551 gallons, controlled by a vent condenser;

(10) one (1) solvent storage tank (C64FTK203), nominal capacity of 19,494 gallons, controlled by the vent condenser;

Construction Conditions

General Construction Conditions

1. That the data and information supplied with the application shall be considered part of this permit. Prior to any proposed change in construction which may increase allowable emissions, the change must be approved by the Office of Air Management (OAM).

2. That this permit to construct does not relieve the permittee of the responsibility to comply with the provisions of the Indiana Environmental Management Law (IC 13-11 through 13-20; 13-22 through 13-25; and 13-30), the Air Pollution Control Law (IC 13-17) and the rules promulgated thereunder, as well as other applicable local, state, and federal requirements.

Effective Date of the Permit

3. That pursuant to IC 13-15-5-3, this permit becomes effective upon its issuance.

4. That pursuant to 326 IAC 2-1-9(b)(Revocation of Permits), the Commissioner may revoke this permit if construction is not commenced within eighteen (18) months after receipt of this approval or if construction is suspended for a continuous period of one (1) year or more.

5. That notwithstanding Construction Condition No. 6, all requirements and conditions of this construction permit shall remain in effect unless modified in a manner consistent with procedures established for modifications of construction permits pursuant to 326 IAC 2 (Permit Review Rules).

First Time Operation Permit

6. That this document shall also become a first-time operation permit pursuant to 326 IAC 2-1-4 (Operating Permits) when, prior to start of operation, the following requirements are met:

    (a) The attached affidavit of construction shall be submitted to the Office of Air Management (OAM), Permit Administration & Development Section, verifying that the facilities were constructed as proposed in the application. The facilities covered in the Construction Permit may begin operating on the date the Affidavit of Construction is postmarked or hand delivered to IDEM.

    (b) If construction is completed in phases; i.e., the entire construction is not done continuously, a separate affidavit must be submitted for each phase of construction. Any permit conditions associated with operation start up dates such as stack testing for New Source Performance Standards (NSPS) shall be applicable to each individual phase.

    (c) Permittee shall receive an Operation Permit Validation Letter from the Chief of the Permit Administration & Development Section and attach it to this document.

    (d) The operation permit will be subject to annual operating permit fees pursuant to 326 IAC 2-7-19 (Fees).

    (e) The Permittee has submitted their Part 70 application (T-165-6462-00009) on August 21, 1996 for the existing source. The equipment being reviewed under this permit shall be incorporated in the submitted Part 70 application.

7. That when the facility is constructed and placed into operation the following operation conditions shall be met:

Operation Conditions

General Operation Conditions

1. That the data and information supplied in the application shall be considered part of this permit. Prior to any change in the operation which may result in an increase in allowable emissions exceeding those specified in 326 IAC 2-1-1 (Construction and Operating Permit Requirements), the change must be approved by the Office of Air Management (OAM).

2. That the permittee shall comply with the provisions of the Indiana Environmental Management Law (IC 13-11 through 13-20; 13-22 through 13-25; and 13-30), the Air Pollution Control Law (IC 13-17) and the rules promulgated thereunder.

Preventive Maintenance Plan

3. That pursuant to 326 IAC 1-6-3 (Preventive Maintenance Plans), the Permittee shall prepare and maintain a preventive maintenance plan, including the following information:

   (a) Identification of the individual(s) responsible for inspecting, maintaining, and repairing emission control devices.

   (b) A description of the items or conditions that will be inspected and the inspection schedule for said items or conditions.

   (c) Identification of the replacement parts which will be maintained in inventory for quick replacement.

   The preventive maintenance plan shall be submitted to IDEM, OAM upon request and shall be subject to review and approval.

Transfer of Permit

4. That pursuant to 326 IAC 2-1-6 (Transfer of Permits):

   (a) In the event that ownership of the equipment performing processes L, I, and E, or processes with equivalent PTE or less, identified in this permit is changed, the Permittee shall notify OAM, Permit Branch, within thirty (30) days of the change. Notification shall include the date or proposed date of said change.

   (b) The written notification shall be sufficient to transfer the permit from the current owner to the new owner.

   (c) The OAM shall reserve the right to issue a new permit.

Permit Revocation

5. That pursuant to 326 IAC 2-1-9(a)(Revocation of Permits), this permit to construct and operate may be revoked for any of the following causes:

(a) Violation of any conditions of this permit.

(b) Failure to disclose all the relevant facts, or misrepresentation in obtaining this permit.

(c) Changes in regulatory requirements that mandate either a temporary or permanent reduction of discharge of contaminants. However, the amendment of appropriate sections of this permit shall not require revocation of this permit.

(d) Noncompliance with orders issued pursuant to 326 IAC 1-5 (Episode Alert Levels) to reduce emissions during an air pollution episode.

(e) For any cause which establishes in the judgment of IDEM, the fact that continuance of this permit is not consistent with purposes of 326 IAC 2-1 (Permit Review Rules).

Availability of Permit

6. That pursuant to 326 IAC 2-1-3(l), the Permittee shall maintain the applicable permit on the premises of this source and shall make this permit available for inspection by the IDEM or other public official having jurisdiction.

Control Equipment Requirements

7. That

(a) the regenerative thermal oxidizers or condensers (when Eli Lilly and Company elects to control VOC by condensers) operate at all times, except during safety testing, the following equipment is in operation and emitting VOCs:

Process L

(1) process tank (C2-TK-2)

(2) process tank (C2TK24)

(3) process tank (C2TK23)

(4) process tank (C2TK22)

(5) rotary vacuum filter (C2RVF4)

(6) fluid bed dryer (C2FBD5)

(7) fluid bed dryer (C2FBD6)

(8) process tank (C2TK23A)

Process I

(1) process tank (C13TK29)

(2) filter (C13FLT1)

(3) filter (C13FLT2)

(4) centrifuge hopper (C13H1)

(5) centrifuge hopper (C13H2)

(6) centrifuge hopper (C13H3)

Process E

(1) process tank (C12TK01)

(2) process tank (C12TK12)

(3) holding tank (C12TK20)

(4) crystallizer (C12TK25)

(5) crystallizer (C12TK26)

(6) evaporator (C12TK27)

(7) filtrate tank (C12TK28)

(8) toluene pretreatment tank (C12TK34);

(9) filtrate tank (C12TK36)

(10) NAOH and H2O makeup tank (C12TK37)

(11) primary tank (C12TK38)

(12) hot well (C12TK34B)

(13) separating tank (C12TK34C)

(14) hot well on C12TK26 (C12TK38A)

(15) Rosemund filter (C12RF175)

(16) Rosemund filter (C12RF176)

(17) HCl charge pot (C12TK17C)

(18) basket centrifuge (C12CENT3A)

(19) basket centrifuge (C12CENT3B)

Solvent Recovery

(1) solvent recovery tank (C63TK207);

(b) the operating temperature of the RTO shall be monitored continuously;

(c) when the VOC emissions from the equipment covered in 7(a) above are controlled by the condensers, the outlet gas temperature shall be equal to or less than that will have a control efficiency of 93.1%;

(d) when the VOC emissions from the equipment listed in 7(a) are controlled by RTOs, the RTO combustion chamber shall maintain a minimum operating temperature of 1600^{0}F determined by the performance test for Construction permit No. CP 165-5344. The performance test determined that at least 93.1% destruction of the volatile organic compounds is achieved at this temperature;

(e) the VOC emissions from the solvent storage tanks shall be controlled by the vent condensers that will achieve VOC control efficiencies as described below:

Tank ID	VOC control efficiency (%)	Coolant supply temperature (^{0}C)
C64ETK158	49.4	5
C64ETK160	49.4	5
C64ETK162	86.6	5
C64BTK163	99.5	-40
C64ETK164	56.9	5

C64BTK165	99.5	-40
C64BTK167	N/A	-40
C64BTK169	N/A	-40
C64ETK174	54.4	5
C64BTK203	93.3	-40

; and

(f) the fugitive VOC emissions from pumps, valves, flanges, and other sources of fugitive emissions shall be reduced through the use of Eli Lilly and Company LDAR program most recently approved by the IDEM, OAM.

These conditions are necessary to, and will make the potential to emit (PTE) of the VOC emissions from this modification to 39 tons per year. Therefore, these conditions shall make the Prevention of Significant Deterioration (PSD), 326 IAC 2-2 and 40 CFR 52.21 rules not applicable to this modification.

<u>Compliance with 326 IAC 8-5-3</u>

8. That pursuant to 326 IAC 8-5-3 Eli Lilly and Company shall cover the process tank C12TK12, containing a volatile organic compound at any time. These covers must remain closed, unless production, sampling, maintenance, or inspection procedures require operator access.

<u>Record Keeping of Operating Parameters</u>

9. That pursuant to 326 IAC 2-1-3(i)(8) Eli Lilly and Company shall record the following during the times the volatile organic compounds are being emitted:

(a) the operating temperature of the RTO;

(b) the coolant supply temperatures of the condensers, when the VOC emissions from the equipment covered in 7(a), and 7(e) are controlled by the condensers;

<u>Malfunction Condition</u>

10. That pursuant to 326 IAC 1-6-2 (Records; Notice of Malfunction):

(a) A record of all malfunctions, including startups or shutdowns of any facility or emission control equipment, which result in violations of applicable air pollution control regulations or applicable emission limitations shall be kept and retained for a period of three (3) years and shall be made available to the Indiana Department of Environmental Management (IDEM), Office of Air Management (OAM) or appointed representative upon request.

(b) When a malfunction of any facility or emission control equipment occurs which lasts more than one (1) hour, said condition shall be reported to OAM, using the Malfunction Report Forms (2 pages). Notification shall be made by telephone or facsimile, as soon as practicable, but in no event later than four (4) daytime business hours after the beginning of said occurrence.

(c) Failure to report a malfunction of any emission control equipment shall constitute a violation of 326 IAC 1-6, and any other applicable rules. Information of the scope and expected duration of the malfunction shall be provided, including the items specified in 326 IAC 1-6-2(a)(1) through (6).

(d) Malfunction is defined as any sudden, unavoidable failure of any air pollution control equipment, process, or combustion or process equipment to operate in a normal and usual manner. [326 IAC 1-2-39]

SOCMI HON, 40 CFR 63 Subparts I, and H (Pharmaceutical Processes Using Methylene Chloride)

11. The permittee shall comply with National Emission Standards for Organic Hazardous Air Pollutants for Equipment Leaks, 40 CFR part 63, Subpart H, as required by the National Emission Standards for Organic Hazardous Air Pollutants for Certain Processes Subject to the Netoriated Regulation for Equipment Leaks, 40 CFR part 63, subpart I.

Pursuant to that rule, the Lilly Leak and Repair (LDAR) procedure, most recently approved by the Office of Air Management, shall be implemented to reduce fugitive VOC emissions for processes that use methylene chloride from the process equipment listed in the permit application. If it is not feasible to either pressure test a group of fugitive sources or monitor a specific compound, then a written justification will be required for each source or compound exempted from testing. Any necessary adjustments to the procedures shall be submitted to the Office of Air Management for approval prior to implementation.

Compliance with 326 IAC12, and 40 CFR Part 60.116b(b), (d), and (f)

12. Pursuant to 326 IAC 12, and 40 CFR 60.116b, the following shall apply.

(a) The Permittee shall keep readily accessible records showing the dimension and analysis showing the capacity of the following storage vessels: C64BTK163, C64BTK165, C64BTK167, C64BTK169, C64ETK158, C64ETK160, C64ETK162, C64ETK164, C64ETK174, and C64FTK203.

(b) The Permittee shall notify the IDEM, OAM, in the event of vapor pressure of the solvent stored in the tanks C64ETK158, C64ETK160, C64ETK162, C64ETK164, and C64ETK174, exceeds the respective maximum true vapor pressure values for each volume range

(c) The Permittee shall measure the vapor pressure if the vapor pressure can not be otherwise determined.

Limit on the production of the compounds

13. The Permittee shall limit the production of the compounds currently made in the permitted equipment to the products or processes listed in the application. The permittee shall reevaluate its potential emissions or Potential To Emit (PTE) estimate of VOC, and obtain NSR approval before manufacturing any product other than the products currently being produced, which results in higher PTE than specified in 326 IAC 2-1-1 or 326 IAC 2-2.

Reporting Requirements

14. That a log of information necessary to document compliance with operation permit condition nos. 3, 4, 7, 8, 9, 10, 11, and 12 shall be maintained. These records shall be kept for at least the past 36 month period except for Condition no.12(a), which shall be kept for the life of the storage tanks; and made available upon request to the Office of Air Management (OAM).

Emergency Reduction Plans

15. Pursuant to 326 IAC 1-5-2 (Emergency Reduction Plans; Submission):

(a) The Permittee shall submit an amendment to the Emergency Reduction Plan only if this permit results in changes to the Plan, or a letter stating no amendment is necessary.

(b) These amendment to the ERPs shall be submitted for approval to:

Indiana Department of Environmental Management
Compliance Branch, Office of Air Management
100 North Senate Avenue, P.O. Box 6015
Indianapolis, Indiana 46206-6015

within 180 calendar days from the issuance date of this permit.

Annual Emission Reporting

16. That pursuant to 326 IAC 2-6 (Emission Reporting), the owner/operator of Eli Lilly and Company must annually submit an emission statement for the source. This statement must be received by July 1 of each year and must comply with the minimum requirements specified in 326 IAC 2-6-4. A copy of this rule is enclosed. The annual statement must be submitted to:

Technical Support and Modeling Section, Office of Air Management
100 North Senate Avenue, P. O. Box 6015
Indianapolis, Indiana 46206-6015

The annual emission statement covers the twelve (12) consecutive month time period starting January 1 and ending December 31.

MALFUNCTION REPORT

INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
OFFICE OF AIR MANAGEMENT

FAX NUMBER - 317 233-5967

This form should only be used to report malfunctions applicable to Rule 326 IAC 1-6 and to qualify for the exemption under 326 IAC 1-6-4.

THIS FACILITY MEETS THE APPLICABILITY REQUIREMENTS BECAUSE: IT HAS POTENTIAL TO EMIT 25 LBS/HR PARTICULATES ?_____, 100 LBS/HR VOC ?_____, 100 LBS/HR SULFUR DIOXIDE ?_____ OR 2000 LBS/HR OF ANY OTHER POLLUTANT ?_____ EMISSIONS FROM MALFUNCTIONING CONTROL EQUIPMENT OR PROCESS EQUIPMENT CAUSED EMISSIONS IN EXCESS OF APPLICABLE LIMITATION ________.

THIS MALFUNCTION RESULTED IN A VIOLATION OF: 326 IAC _______ OR, PERMIT CONDITION # _______ AND/OR PERMIT LIMIT OF _______________
THIS INCIDENT MEETS THE DEFINITION OF 'MALFUNCTION' AS LISTED ON REVERSE SIDE ? Y N
THIS MALFUNCTION IS OR WILL BE LONGER THAN THE ONE (1) HOUR REPORTING REQUIREMENT ? Y N

COMPANY: Eli Lilly and Company PHONE NO. (765) 832-4607
LOCATION: Clinton, Indiana
PERMIT NO. CP 165-9135 AFS PLANT ID: 165-00009 AFS POINT ID: _________________ INSP: _____________________
CONTROL/PROCESS DEVICE WHICH MALFUNCTIONED AND REASON:
____
____
DATE/TIME MALFUNCTION STARTED: _____/_____/ 19____ ___________________AM / PM
ESTIMATED HOURS OF OPERATION WITH MALFUNCTION CONDITION:____

DATE/TIME CONTROL EQUIPMENT BACK-IN SERVICE______/______/ 19____ _______________ AM/PM

TYPE OF POLLUTANTS EMITTED: TSP, PM-10, SO2, VOC, OTHER: ____________________________________
ESTIMATED AMOUNT OF POLLUTANT EMITTED DURING MALFUNCTION: _________________________________
MEASURES TAKEN TO MINIMIZE EMISSIONS: ____

____

REASONS WHY FACILITY CANNOT BE SHUTDOWN DURING REPAIRS:

CONTINUED OPERATION REQUIRED TO PROVIDE ESSENTIAL* SERVICES:
____
CONTINUED OPERATION NECESSARY TO PREVENT INJURY TO PERSONS:____
CONTINUED OPERATION NECESSARY TO PREVENT SEVERE DAMAGE TO EQUIPMENT:____
INTERIM CONTROL MEASURES: (IF APPLICABLE)
____
____

MALFUNCTION REPORTED BY: __________________________________TITLE:______________________________
(SIGNATURE IF FAXED)

MALFUNCTION RECORDED BY: ______________________DATE:________________TIME:_________________

Please note - This form should only be used to report malfunctions applicable to Rule 326 IAC 1-6 and to qualify for the exemption under 326 IAC 1-6-4.

326 IAC 1-6-1 Applicability of rule

Sec. 1. The requirements of this rule (326 IAC 1-6) shall apply to the owner or operator of any facility which has the potential to emit twenty-five (25) pounds per hour of particulate, one hundred (100) pounds per hour of volatile organic compounds or SO2, or two thousand (2,000) pounds per hour of any other pollutant; or to the owner or operator of any facility with emission control equipment which suffers a malfunction that causes emissions in excess of the applicable limitation.

326 IAC 1-2-39 “Malfunction” definition

Sec. 39. Any sudden, unavoidable failure of any air pollution control equipment, process, or combustion or process equipment to operate in a normal and usual manner. (Air Pollution Control Board; 326 IAC 1-2-39; filed Mar 10, 1988, 1:20 p.m. : 11 IR 2373)

***Essential services** are interpreted to mean those operations, such as, the providing of electricity by power plants. Continued operation solely for the economic benefit of the owner or operator shall not be sufficient reason why a facility cannot be shutdown during a control equipment shutdown.

If this item is checked on the front, please explain rationale:

____

____

Indiana Department of Environmental Management
Office of Air Management

Technical Support Document (TSD) for New Construction and Operation

Source Background and Description

Source Name:	Eli Lilly and Company
Source Location:	10500 S. St. Rd. 63, Clinton, IN 47842
County:	Vermillion
Construction Permit No.:	CP 165-9135
SIC Code:	2833
Permit Reviewer:	Dr. T. P. Sinha

The Office of Air Management (OAM) has reviewed an application from Eli Lilly and Company relating to the construction and operation of three intermediate processes of the Cefaclor production process consisting of the following equipment:

(a) Process L

(1) one (1) process tank (C2-TK-2), maximum capacity of 2,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(2) one (1) process tank (C2TK24), maximum capacity of 2,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(3) one (1) process tank (C2TK23), maximum capacity of 2,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(4) one (1) process tank (C2TK22), maximum capacity of 2,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(5) one (1) rotary vacuum filter (C2RVF4), controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(6) one (1) fluid bed dryer (C2FBD5), controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(7) one (1) fluid bed dryer (C2FBD6), controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(8) one (1) process tank (C2TK23A), maximum capacity of 150 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(9) one (1) tote bag/drum filling station (C2TBFS001), maximum capacity of 2,000

gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(b) Process I

(1) one (1) process tank (C13TK29), maximum capacity of 4,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(2) one (1) filter (C13FLT1), controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(3) one (1) filter (C13FLT2), controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(4) one (1) hopper (C13H1), nominal capacity of 42 cubic feet, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(5) one (1) hopper (C13H2), nominal capacity of 42 cubic feet, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(6) one (1) hopper (C13H3), nominal capacity of 42 cubic feet, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(c) Process E

(1) one (1) process tank (C12TK01), maximum capacity of 500 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(2) one (1) process tank (C12TK12), maximum capacity of 4,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(3) one (1) holding tank (C12TK20), maximum capacity of 2,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(4) one (1) crystallizer (C12TK25), maximum capacity of 4,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control

equipment;

(5) one (1) crystallizer (C12TK26), maximum capacity of 4,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(6) one (1) crystallizer (C12TK27), maximum capacity of 4,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(7) one (1) filtrate tank (C12TK28), maximum capacity of 4,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(8) one (1) toluene pretreatment tank (C12TK34), maximum capacity of 2,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(9) one (1) filtrate tank (C12TK36), maximum capacity of 2,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(10) one (1) NAOH and H2O makeup tank (C12TK37), maximum capacity of 2,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(11) one (1) primary tank (C12TK38), maximum capacity of 1,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(12) one (1) separating tank (C12TK34B), maximum capacity of 50 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(13) one (1) separating tank (C12TK34C), maximum capacity of 220 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(14) one (1) hot well on C12TK26 (C12TK38A), maximum capacity of 30 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(15) one (1) Rosemund filter (C12RF175), maximum capacity of 4 square meter, controlled by the existing regenerative thermal oxidizers, condensers, or

equivalent control equipment;

(16) one (1) Rosemund filter (C12RF176), maximum capacity of 4 square meter, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(17) one (1) HCl charge pot (C12TK17C), maximum capacity of 100 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(18) one (1) basket centrifuge (C12CENT3A), size 24 inch x 48 inch, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(19) one (1) basket centrifuge (C12CENT3B), size 24 inch x 48 inch, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(d) Solvent Recovery

(1) one (1) solvent recovery tank (C63TK207), maximum capacity of 8,000 gallons, controlled by the existing regenerative thermal oxidizers, condensers, or equivalent control equipment;

(e) Solvent Storage

(1) one (1) solvent storage tank (C64BTK163), maximum capacity of 19,494 gallons, controlled by a vent condenser;

(2) one (1) solvent storage tank (C64BTK165), maximum capacity of 19,494 gallons, controlled by a vent condenser;

(3) one (1) solvent storage tank (C64BTK167), maximum capacity of 19,494 gallons;

(4) one (1) solvent storage tank (C64BTK169), maximum capacity of 19,494 gallons;

(5) one (1) solvent storage tank (C64ETK158), maximum capacity of 38,551 gallons, controlled by a vent condenser;

(6) one (1) solvent storage tank (C64ETK160), maximum capacity of 38,551 gallons, controlled by a vent condenser;

(7) one (1) solvent storage tank (C64ETK162), maximum capacity of 38,551 gallons, controlled by a vent condenser;

(8) one (1) solvent storage tank (C64ETK164), maximum capacity of 38,551 gallons, controlled by a vent condenser;

(9) one (1) solvent storage tank (C64ETK174), maximum capacity of 38,551 gallons, controlled by a vent condenser;

(10) one (1) solvent storage tank (C64FTK203), maximum capacity of 19,494 gallons, controlled by the vent condenser;

Stack Summary

Stack ID	Operation	Height (feet)	Diameter (feet)	Flow Rate (acfm)	Temperature (^{0}F)
PVC70-ASCBR 1	Chemical Operations	100	9	129,000	130
PVC70-ASCBR 2	Chemical Operations	100	9	129,000	130

Recommendation

The staff recommends to the Commissioner that the construction and operation be approved. This recommendation is based on the following facts and conditions:

Information, unless otherwise stated, used in this review was derived from the application and additional information submitted by the applicant.

A complete application for the purposes of this review was received on October 21, 1997.

Emissions Calculations

See Appendix A (Emissions Calculation Section) for detailed calculations (70 pages).

Total Potential and Allowable Emissions

Indiana Permit Allowable Emissions Definition (after compliance with applicable rules, based on 8,760 hours of operation per year at rated capacity):

Pollutant	Allowable Emissions (tons/year)	Potential Emissions (tons/year)

Particulate Matter (PM)		< 0.1
Particulate Matter (PM10)		< 0.1
Sulfur Dioxide (SO_2)		0.0
Volatile Organic Compounds (VOC)	450	450
Carbon Monoxide (CO)		0.0
Nitrogen Oxides (NO_x)		0.0
Single Hazardous Air Pollutant (HAP)		101
Combination of HAPs		101

(a) Allowable VOC emissions are determined from the applicability of rule 326 IAC 8-5-3. See appendix A for detailed calculations.

(b) The allowable VOC emissions based on the rules cited are equal to the potential emissions, therefore, the potential emissions are used for the permitting determination.

(c) Allowable emissions (as defined in the Indiana Rule) of VOC are greater than 25 tons per year. Therefore, pursuant to 326 IAC 2-1, Sections 1 and 3, a construction permit is required.

County Attainment Status

(a) Volatile organic compounds (VOC) are precursors for the formation of ozone. Therefore, VOC emissions are considered when evaluating the rule applicability relating to the ozone standards. Vermillion County has been designated as attainment or unclassifiable for ozone. Therefore, VOC emissions were reviewed pursuant to the requirements for Prevention of Significant Deterioration (PSD), 326 IAC 2-2 and 40 CFR 52.21.

(b) Vermillion County has been classified as attainment or unclassifiable for total suspended particles, particulate matter 10 microns, and nitrogen oxides. Therefore, these emissions were reviewed pursuant to the requirements for Prevention of Significant Deterioration (PSD), 326 IAC 2-2 and 40 CFR 52.21.

Source Status

Existing Source PSD (emissions after controls, based on 8,760 hours of operation per year at rated capacity):

Pollutant	Emissions (ton/yr)
VOC	> 250

(a) This existing source is a major stationary source because it is in one of the 28 listed source categories and at least one regulated pollutant is emitted at a rate of 100 tons per year or more.

Proposed Modification

PTE from the proposed modification (based on 8,760 hours of operation per year at rated capacity including enforceable emission control and production limit):

Pollutant	PM (ton/yr)	PM10 (ton/yr)	SO_2 (ton/yr)	VOC* (ton/yr)	CO (ton/yr)	NO_x (ton/yr)
Proposed Modification	Neg.	Neg.	0.0	39	0.0	0.0
PSD Significant Level	25	15	40	40	100	40

* The applicant has taken a VOC limit of 39 tons per year from the above equipment.

(a) This modification to an existing major stationary source is not major because the emissions increases are less than the PSD significant levels. Therefore, pursuant to 326 IAC 2-2, and 40 CFR 52.21, the PSD requirements do not apply.

Part 70 Permit Determination

326 IAC 2-7 (Part 70 Permit Program)

This existing source has submitted their Part 70 permit application (T-165-6462-00009) on August 21, 1996. The equipment being reviewed under this permit shall be incorporated in the submitted Part 70 application.

Federal Rule Applicability

40 CFR Part 60, Subpart Kb

All solvent storage tanks are subject to New Source Performance Standard, 326 IAC 12, (40 CFR Part 60.110b, Subpart Kb - Standards of Performance for Volatile Organic Liquid Storage Vessels). Pursuant to this rule the owner or operator of each storage vessel shall keep readily accessible records showing the dimension of the storage vessel and an analysis showing the capacity of the storage vessel.

The following solvent storage tanks are subject to 40 CFR 60.116b(d), and 116b(f): C64ETK158, C64ETK160, C64ETK162, C64ETK164, and C64ETK174. 40 CFR 60.116b(d) requires the owner or operator of the storage tanks to notify IDEM, OAM in the event of the vapor pressure of the solvent stored in the tank increases above the specified vapor pressure. 40 CFR Part 60.116b(f) requires the owner or operator of the storage tanks to measure the vapor pressure if the vapor pressure can not be otherwise determined.

All the solvent storage tanks have been constructed and used prior to the submittal of this application (under previously issued permits CP 165-3801, PC (83) 1837and registration dated 10/11/90). None of the tanks are modified, as defined by the NSPS general provisions. Therefore, no new NSPS provisions are applicable to the solvent storage tanks.

40 CFR Part 60, Subpart VV

The part of the source including the new facilities has the design capacity to produce less than 1000 Mg/year, hence it is exempt from the New Source Performance Standard, 326 IAC 12, (40 CFR Part 60.480), Subpart VV, Standards of Performance for Equipment Leaks of VOC in the Synthetic Organic Chemical Manufacturing Industry (SOCMI).

40 CFR Part 60, Subpart III

The New Source Performance Standard, 326 IAC 12, (40 CFR Part 60.610, Subpart III - Standards of Performance for Volatile Organic Compounds (VOC) Emissions From Synthetic Organic Chemical Manufacturing Industry (SOCMI)) Air Oxidation Unit Processes, does not apply to the process tanks, because these tanks are not air oxidation units.

40 CFR Part 60, Subpart NNN

The New Source Performance Standard, 326 IAC 12,(40 CFR Part 60.660, Subpart NNN - Standards of Performance for Volatile Organic Compounds (VOC) Emissions From Synthetic Organic Chemical Manufacturing Industry (SOCMI)) Distillation Operations, does not apply to the process tanks, because these process tanks are not distillation units.

40 CFR Part 60, Subpart RRR

The New Source Performance Standard, 326 IAC 12, (40 CFR Part 60.700, Subpart RRR - Standards of Performance for Volatile Organic Compounds (VOC) Emissions From Synthetic Organic Chemical Manufacturing Industry (SOCMI)) Reactor Processes, does not apply to the tanks, because these tanks are operated as batch reactors.

40 CFR 63, Subparts H and I

The SOCMI HON, 40 CFR 63.190(b)(5) Subparts H and I rules apply to the process tanks because it involves a pharmaceutical production process. Lilly will comply with the requirements of Subparts H and I for pharmaceutical production processes that use methylene chloride as a solvent.

40 CFR Part 61

The tanks under this modification are not subject to Emission Standard For Hazardous Air Pollutants, 326 IAC 14 and 40 CFR Part 61, as no hazardous air pollutants covered under these rules are emitted from the tanks.

State Rule Applicability

326 IAC 2-6 (Emission Reporting)

This source is subject to 326 IAC 2-6 (Emission Reporting), because the source has the potential to emit more than 100 tons/yr of VOC. Pursuant to this rule, the owner/operator of this source must annually submit an emission statement of the facility. The annual statement must be received by July 1 of each year and must contain the minimum requirements as specified in 326 IAC 2-6-4.

New Equipment

326 IAC 8-5-3 (Synthesized Pharmaceutical Manufacturing Operations)

The process tank, C13TK29; the filters C13FLT1, and C13FLT2; the centrifuge hoppers, C13H1, C13H2, and C13H3; the centrifuges, C12CENT3A , and C13CENT3B; and the extractor waste tank, C63SRTK207 have potential emissions of less than 15 pounds per day. Therefore, this equipment is not subject to 326 IAC 8-5-3 (Synthesized Pharmaceutical Manufacturing Operations) rule.

The tank, C12TK12, is subject to 326 IAC 8-5-3, because its potential uncontrolled VOC emissions are more than 15 lbs/day, and are used in pharmaceutical manufacturing by chemical synthesis. The VOC emitted by this tank is toluene. The vapor pressure of toluene is below the threshold in 326 IAC 8-5-3(b)(1), which would require controls.

The process tank is equipped with a tight fitting cover. As indicated by the applicant, the cover is closed at all times unless the production, sampling, inspection, or maintenance activities require access to the tank. Hence, it meets the rule 326 IAC 8-5-3(b)(5).

Building T27 standard operating procedure as indicated by the applicant is to repair all the visible equipment leaks as soon as possible. During the operation, process operators inspect vessels and equipment (valves, flanges, etc.) for visible indications of leaks. Any leaks are repaired as soon as the leaking component is off-line for a period of time long enough to complete the repair. Hence it meets the rule 326 IAC 8-5-3(b)(6).

326 IAC 8-4-3 (Petroleum sources: petroleum liquid storage facilities)

The rule 326 IAC 8-4-3 does not apply to the extractor waste tank, because the capacity of the storage tank is less than 39,000 gallons.

326 IAC 8-6 (Organic Solvent Emission Limitation)

None of the sources have potential emissions of 100 tons per year. Therefore, this equipment is not subject to 326 IAC 8-6 (Organic Solvent Emission Limitation) rule.

326 IAC 2-1-3.4 (New Source Toxics Control Rule)

The effective date of this rule is July 27, 1997. Only the process tanks C12TK12, and C13TK29; the filters C13FLT1, and C13FLT2; the centrifuge hoppers C13H1, C13H2, and C13H3; the basket centrifuges, C12CENT3A, and C12CENT3B; will be constructed after July 27, 1997, the applicability date of this rule. The new equipment covered by this permit does not constitute a collection of all the equipment necessary for the production of an intermediate or final product; thus, this is not construction of a new process or production unit. Therefore the rule 326 IAC 2-1-3.4 does not apply to the new equipment.

Existing Equipment

All existing facilities are permitted facilities for synthesized pharmaceutical processes. They are integrated into one permit for simplicity in tracking in the emissions.

Air Toxic Emissions

Indiana presently requests applicants to provide information on emissions of the 187 hazardous air pollutants set out in the Clean Air Act Amendments of 1990. These pollutants are either carcinogenic or otherwise considered toxic and are commonly used by industries. They are listed as air toxics on the Office of Air Management (OAM) Construction Permit Application Form Y.

(a) The new equipment will emit levels of air toxics greater than those that constitute major source applicability according to Section 112 of the Clean Air Act. The concentrations of these air toxics were modeled and found to be (in worst case possible) as follows:

Substance	Modeled Concentration (μg/m^3)	% of OSHA PEL
Acetonitrile	21.7	0.03
Hydrochloric acid	0.22	0.003
Methanol	3.4	0.001
Methylene chloride	116.4	0.007
Toluene	24.2	0.003

The concentrations of these air toxics were compared to the Permissible Exposure Limits (PEL) developed by the Occupational Safety and Health Administration (OSHA).

Conclusion

The construction of these replacement tanks will be subject to the conditions of the attached proposed **Construction Permit No. CP-165-9135, Plt ID No. 165-00009.**

APPENDIX A

Emissions Calculations

Introduction

Eli Lilly and Company (Lilly) is a research- based corporation which develops, manufactures, and markets human medicines and animal health products. The human medicines and animal health products are manufactured at Lilly's Clinton Laboratories.

The purpose of this application is to obtain the permit necessary for the construction and modification of synthesized pharmaceutical manufacturing facilities that will be used to resume production of three intermediate compounds of the antibiotic Cefaclor. Cefaclor has been manufactured at Clinton since 1980. In 1993, three intermediate steps in the Cefaclor production process were outsourced to companies in Europe. The three process steps are called Process E, Process L, and Process I. Lilly now plans to resume production of the three intermediates at Clinton in September 1998.

The project to resume production of the three intermediates involves more than 80 different pieces of production, solvent recovery, and solvent storage equipment. Almost all of the equipment is existing equipment that has been operating under IDEM issued construction or operating permits. A large percentage of the equipment will be running the same process it ran in 1993. Most of the equipment used to produce the three intermediate steps in 1993 is still in place. Some equipment, however, will be replaced due to maintenance reasons. Other equipment is being replaced to improve the process operation. Because of the equipment limitations (bottlenecks), the capacity of the process equipment will be only 40% of the capacity the production equipment had in 1993.

This application does not cover all 80^+ pieces of equipment associated with resuming production of the three intermediate compounds. Instead, the application covers only installation of 10 pieces of new equipment and 35 pieces of existing equipment that were not permitted for VOC service.

In order to simplify the determination of the emissions from the existing equipment, the new permit will replace all old permits applicable to the existing equipment as if they are all new equipment. The new permit will supersede the old permits covering this equipment. In this permit, the determination of the emissions will be based only on the future potential emissions from the existing equipment.

It is important to note that some of the existing equipment is currently in use on other processes. Lilly intends to continue to use this equipment for existing and the Cefaclor processes. It will be campaigned between the production of compounds currently made at Clinton and the three intermediate compounds to make Cefaclor. Lilly has opted to determine the potential emissions from this campaigned equipment by including the emissions from all processes to be produced in that equipment set. It means that emissions originating from the existing processes will be included in this permit.

Process Description:

This permit involves the construction and modification of the synthesized pharmaceutical manufacturing facilities involved in the production of three separate intermediates in the Cefaclor production process. The process intermediates include Process E, Process L, and Process I. The processes are produced in buildings C-2, C-12, C-13, and C-13A. The solvent recovery and storage is conducted in buildings C-63, C-64, and C-82.

Antibiotic Intermediate E: Process Description

The antibiotic Intermediate E process is a batch process which takes an antibiotic intermediate. The process utilizes tanks of various sizes. The tanks are used as charge tanks, reactors, crystallizers, and holding/feed tanks. The process also utilizes basket centrifuges and pressure filters for liquid/solid separations.

A solvent is charged to vessel 1 along with one of the reactants. The temperature of the vessel 1 is brought to boiling and a portion of the solvent is boiled off and sent to solvent recovery for reclamation. Vessel 1 is cooled to appropriate temperature range and the antibiotic intermediate and another reactant is added. Once again the contents of vessel 1 are brought to boiling and a portion of the solvent boiled off for a sufficient amount of time to allow the reaction to occur. The solvent removed is again condensed and sent to solvent recovery for reclamation.

After completion of the reaction, the contents of vessel 1 are cooled, transferred through a filter to vessel 2. Two other reactants are then added to the contents of vessel 2 from vessel 3 while controlling the temperature, and the reaction is allowed to go to completion. Once the reaction is complete, the agitation on vessel 2 is stopped and the solids are allowed to settle out from the solvent mixture. Most of the solvent is decanted off of the solids and, after pH is adjusted, is sent to solvent recovery for reclamation.

A third solvent is added to the solids remaining in vessel 2 and agitation is resumed. The agitation continues for the time required for the reaction to go to completion. After completion of reaction, the contents of vessel 2 are transferred to vessel 4. A specified amount of water is charged into vessel 4 and the temperature adjusted to the desired range.

The contents of vessel 4 are centrifuged on two basket centrifuges operating in parallel. The separated liquid is sent to solvent recovery for reclamation and reuse. The filtered and washed solids, which is the desired antibiotic intermediate, is collected in appropriate containers and stored for future use.

Antibiotic Intermediate L: Process Description.

The Antibiotic intermediate L process is a semi-continuous process which takes an antibiotic intermediate and through chemical transformation, converts it into another antibiotic intermediate. The process utilizes tanks of various sizes. The tanks are utilized as charge tanks, reactors, crystallizers, and holding/feed tanks. The process also utilizes a rotary vacuum filter for liquid/solid separations and two fluid bed dryers for removal of residual solvents to the required final specification.

A specified amount of solvent, water, and antibiotic intermediate is added to vessel 1 to form a slurry. The contents of vessel 1 are cooled to the required temperature range and transferred to vessel 2. This process is repeated numerous times over the course of a production run to maintain the volume in vessel 2 within the desired range.

A specified amount of the same solvent as used above is charged into vessel 3 and vessel 4; and the contents cooled to the required temperature range. The contents of vessel 2 and other reactants are added at a predetermined ratio to vessel 3 and then to vessel 4 for start-up of the continuous process. The continuous operation is conducted by setting and maintaining the specified flow rate to each vessel, and vessel 4 is sent to the rotary vacuum filter.

Thus, the desired antibiotic intermediate solid is continuously being separated from the solvent via the rotary vacuum filter. The separated solvent is transferred to the solvent recovery area where it is reclaimed for use. The separated antibiotic intermediate is dried in either of two fluid bed dryers. The dried antibiotic intermediate is then packaged in the appropriate container for future use.

This continuous operation is maintained for several days at which time the system is emptied by stopping the charging and transferring of vessel 1 into vessel 2 and forward processing the remaining material in the vessels through the system.

Antibiotic Intermediate I: Process Description

The Antibiotic Intermediate I process is a batch process which takes an antibiotic intermediate and through chemical transformations converts it into another antibiotic intermediate. The process utilizes tanks of varying sizes. The tanks are utilized as charge tanks, reactors, crystallizers, and holding/feed tanks. The process also utilizes basket centrifuges for liquid/solid separations and a rotary vacuum dryer for final removal of residual solvents to the required specification.

Initially, reactants A and B are drawn into their respective charge tanks and the temperatures are adjusted accordingly. As the contents of the charge tanks are being brought to their desired temperature range, a specified amount of solvent and reactant C are charged into a separate, agitated vessel (vessel 1) and cooled to the required temperature. When the temperature of the solvent and reactant C reach the required temperature, the other reactants are added in a sequential manner while the temperature is carefully controlled.

Into vessel 2 a specified quantity of a different solvent is added and cooled to the appropriate temperature. After vessel 2 reaches the desired temperature range, the intermediate antibiotic is added to vessel 1. After a sufficient reaction time, the entire contents of vessel 1 is transferred into vessel 2, and the final reactant is added to vessel 2 to complete the desired reaction. After the reaction is complete and the temperature adjusted to the desired range, the solids are separated from the liquid via two centrifuges operated in parallel fashion. The separated liquid is transferred to the solvent recovery area for reclamation for reuse and the solids are slurried in a solvent-water mixture and transferred to vessel 3. In vessel 3, the pH of the slurry is adjusted to the desired range and the resulting slurry is again centrifuged to separate the liquid from the solids. The separated liquid is once again sent to the solvent recovery area for reclamation for reuse. The separated solids are dried in a vacuum dryer. This final dried solid is the desired antibiotic intermediate.

Solvent Recovery and Storage: Process Description

The waste solvents are pumped to solvent recovery from the appropriate building and stored in waste storage tanks. Once a pre-determined amount of waste is accumulated, the desired solvent is recovered from the waste by utilizing a series of liquid-liquid extraction columns, evaporators, and distillation columns. The recovered stream from these processes is sent back to a series of storage tanks to be re-used by the building which originally created the waste. The waste streams created by the recoveries are sent to holding tanks in the Environmental Control Area to be incinerated.

When a process building reaches a solvent addition step in one of their processes, they will have solvent recovery pump recovered solvent to their building. New solvent storage tanks are kept for each solvent. The new solvent is fed into the process to account for solvent losses and to maintain a constant desired solvent inventory.

Emission Controls

All of the production and solvent recovery equipment will vent to the plant's existing Regenerative Thermal Oxidizers (RTOs). The solvent storage operations are controlled by vent condensers. Potential fugitive emissions have been minimized by the use of leakless technology. In addition, fugitive emissions will be further reduced by the use of Lilly's Leak Detection And Repair (LDAR) program.

Emissions Estimates

Process emissions were calculated using the Lilly's Program for Air Emission Calculation and Management (PACMAN). This program utilizes the 1978 Control Technique Guidelines (CTG) for the pharmaceutical industry. The solvent storage emissions were calculated using Lilly's Excel program for the storage tanks. This program is based on AP42 equations.

Equipment and Emissions Summary

		Potential Uncontrolled Emissions			Rule 8-3-5 Applicability		Allowable Emissions		Proposed cont. efficiency (%)	PTE (with proposed limits)	
		lbs/day	tons/yr		Rule applies?	Applicable provisions	tons/yr			(tons/yr)	
Process	Equipment	VOCs	VOCs	HAPs			VOCs	HAPs		VOCs	HAPs
Process L	C2TK2	1.6	0.3	0.0	No		0.3	0.0	93.1	0.0	0.0
	C2TK24	2.2	0.4	0.0	No		0.4	0.0	93.1	0.0	0.0
	C2TK23	441.6	80.6	0.0	No		80.6	0.0	93.1	5.6	0.0
	C2TK22	1.1	0.2	0.0	No		0.2	0.0	93.1	0.0	0.0
	C2RVF4	7.1	1.3	0.0	No		1.3	0.0	93.1	0.1	0.0
	C2FBD5	811.5	148	0.0	No		148	0.0	93.1	10.2	0.0
	C2FBD6	811.5	148	0.0	No		148	0.0	93.1	10.2	0.0
	C2TK23A	0.0	0.0	0.0	No		0.0	0.0	93.1	0.0	0.0
	C2TBFS01	0.0	0.0	0.0	No		0.0	0.0	93.1	0.0	0.0
	Subtotal 0.0		379	0.0			379	0.0		26.1	

Process I	C13FLT1	0.0	0.0	2.4	No		0.0	2.4	93.1	0.0	0.0
	C13FLT2	1.1	0.2	0.2	No		0.2	0.2	93.1	0.0	0.2
	C13TK29	0.0	0.0	1.8	No		0.0	1.8	93.1	0.0	0.1
	C13H1	0.0	0.0	0.0	No		0.0	0.0	93.1	0.0	0.0
	C13H2	0.0	0.0	0.0	No		0.0	0.0	93.1	0.0	0.0
	C13H3	0.0	0.0	0.0	No		0.0	0.0	93.1	0.0	0.0
	Subtotal 0.3		0.2	4.4			0.2	4.4		0.0	
Process E	C12TK12	65.2	11.9	11.9	Yes	(b)(1), (b)(5)	11.9	11.9	93.1	0.8	0.8
	C12RF1 75	2.7	0.5	0.5	No		0.5	0.5	93.1	0.0	0.0
	C12RF1 76	5.5	1.0	1.0	No		1.0	1.0	93.1	0.1	0.1
	C12TK01	0.5	0.1	0.0	No		0.1	0.0	93.1	0.0	0.0
	C12TK25	7.1	1.3	1.3	No		1.3	1.3	93.1	0.1	0.1
	C12TK26	23	4.2	4.1	No		4.2	4.1	93.1	0.3	0.3
	C12TK27	11.5	2.1	1.8	No		2.1	1.8	93.1	0.1	0.1
	C12TK28	2.7	0.5	0.4	No		0.5	0.4	93.1	0.0	0.0
	C12TK20	1.1	0.2	0.2	No		0.2	0.2	93.1	0.0	0.0
	C12TK34	1.6	0.3	0.3	No		0.3	0.3	93.1	0.0	0.0
	C12TK36	1.6	0.3	0.2	No		0.3	0.2	93.1	0.0	0.0
	C12TK37	0.0	0.0	0.0	No		0.0	0.0	93.1	0.0	0.0
	C12TK38	2.2	0.4	0.4	No		0.4	0.4	93.1	0.0	0.0
	C12CEN T3A	6.0	1.1	0.9	No		1.1	0.9	93.1	0.1	0.1
	C12CEN T3B	0.0	1.1	0.9	No		1.1	0.9	93.1	0.1	0.1

	C12TK34 B	6.0	0.0	0.0	No		0.0	0.0	93.1	0.0	0.0
	C12TK34 C	0.0	0.0	0.0	No		0.0	0.0	93.1	0.0	0.0
	C12TK34 8A	0.0	0.0	0.0	No		0.0	0.0	93.1	0.0	0.0
	C12TK17 C	0.0	0.0	0.0	No		0.0	0.0	93.1	0.0	0.0
1.6	Subtotal		25.0	23.9			25.0	23.9		1.6	
Solvent Recovery	C63TK20	0.5	0.1	8.0	No		0.1	8.0	93.1	0.0	0.6
0.6	Subtotal		0.1	8.0			0.1	8.0		0.0	
Solvent Storage	C64BTK 163	0.5	0.1	4.5	No		0.1	4.5	99.5	0.0	0.0
	C64BTK 165	0.5	0.1	4.5	No		0.1	4.5	99.5	0.0	0.0
	C64BTK 167	0.0	0.0	5.1	No		0.0	5.1		0.0	5.1
	C64BTK 169	0.0	0.0	5.1	No		0.0	5.1		0.0	5.1
	C64ETK 158	5.5	1.0	0.8	No		1.0	0.8	49.4	0.5	0.4
	C64ETK 160	5.5	1.0	0.8	No		1.0	0.8	49.4	0.5	0.4
	C64ETK 162	19.7	3.6	3.6	Yes	None	3.6	3.6	86.6	0.5	0.5
	C64ETK 164	6.6	1.2	1.2	No		1.2	1.2	56.9	0.5	0.5
	C64ETK 174	11.5	2.1	0.0	No		2.1	0.0	54.4	1.0	0.0
	C64FTK 203	0.5	0.1	0.1	No		0.1	0.1	93.3	0.0	0.0

Subtotal	9.2	25.7	9.2	25.7	3.0	12.0
Point source total	414.0	62.0	414.0	62.0	30.7	14.5
Fugitives	36.3	38.6	36.3	38.6	8.1	9.2
Grand total	450.0	101.0	450.0	101.0	38.8	23.7

Potential uncontrolled VOC and HAP point source emissions were based on the emissions from the equipment operating at its maximum capacity for 8760 hours per year, before control. Potential uncontrolled VOC and HAP fugitive emissions were calculated using SOCMI emission factors.

Potential Emissions (Potential Uncontrolled Emissions)

	VOC (ton/yr)	HAPs (ton/yr)	PM/PM10 (ton/yr)
Point	414	62.0	< 0.1
Fugitive	36.3	38.6	0.0
Total	450	101	< 0.1

PACMAN PROGRAM THEORY AND SAMPLE CALCULATION INERT SWEEP FOR IDEAL SYSTEMS

PROGRAM BACKGROUND AND ASSUMPTIONS

The PACMAN Program for an inert sweep step calculates the vent stream of a vessel being purged with an inert gas. This program models the emission from a vessel containing a vapor phase and a totally miscible liquid phase. (For an empty vessel or for a vessel containing residual liquid, see “PACMAN Theory- Empty Vessel Sweep for Ideal Systems”.) The vessel system can contain volatile, non-volatile and inert components. Volatile components appear in both the liquid and vapor phases. Non-volatile components appear only in the liquid phase, and inert components appear only in the vapor phase.

The program calculates the composition of the vapor stream leaving the vessel while maintaining vapor/liquid equilibrium. Multiple consecutive vent condensers can be used in the vapor line (see “PACMAN Program Theory - Vent Condenser(s)”.). A final control device, such as Regenerative Thermal Oxidizer (RTO), can also be used in the vapor line (see “PACMAN Program Theory - Final Control Device.”).

1. This program assumes that the liquid is totally miscible, that is, there is only one liquid phase. Solids in solution are included in this phase; however, solids in suspension must not be included in the program since they do not effect the vapor pressure of the system.

2. The model assumes the vessel contains perfectly mixed, ideal liquid and vapor phases that are continuously in phase equilibrium.

3. It is assumed during the sweep step that the vapor-liquid equilibrium is maintained. Therefore, the composition in the vapor space is constant during the sweep step.

4. The vapor leaving the vessel is assumed to have the same composition as the vapor in the vessels vapor space.

5. The program calculations assume that the temperature and pressure in the vessel system are uniform and do not change over time.

6. It is also assumed that the amount of liquid being vaporized in the vessel is small when compared to the total liquid volume, therefore the liquid composition and the volume of the vapor space can be assumed to be constant.

A material balance check can be completed, if desired, to prevent the quantity of an exiting vapor component from exceeding the initial liquid amount in the vessel, which may happen in situations with a long sweep time. If the exiting vapor quantity exceeds the initial liquid amount, the initial liquid amount is substituted in the emission output.

PROGRAM STRUCTURE

The input information necessary to run the program is:

Molecular Weight of the inert sweep gas (LB/LB-mole)	*28.01*
Inert Sweep Rate (CFM @ 60°F, 1 ATM)	10
The inert sweep step time (minutes)	*30*
Temperature in vessel (°C, °F, °K)	21°C
Pressure in vessel (mmHg, in H_2O, PSIA, PSIG, kPa)	*760 mmHg*
Composition of the liquid phase (LB, Kg, Liters)	*See below*
Density (LB/ft^3) and Molecular Weight (LB/LB-mole) of components	See below
Antoine coefficients for the volatile liquid components (a, b, c)	*See below*
Activity coefficient of the volatile	1 for all components
Inert saturation factor (≤1)	*1 for all components*

	Composition	Density (LB/ft^3)	Molecular Weight (LB/LB-mole)	Antoine coefficients a	b	c
Acetone	3300 LB	49.44	58.08	16.82	2993	-35.63
Acetonitrile	3300 LB	49.05	41.05	16.16	2962	-44.24
Other	200 LB	50.0	200			

The density, molecular weight and Antoine coefficients for the volatile, non-volatile and inert components are automatically accessed from a component data base.

The program calculations are broken down into four steps:

Step 1 - The input data is converted and the liquid and vapor compositions in the vessel are determined.

Step 2 -The mass of inert vapors being swept from the vessel is calculated.

Step 3 -The mass of volatile components leaving the vessel is calculated.

Step 4 -Optional: A material balance check between the calculated emission vapor quantity and initial liquid quantity in the vessel is performed and the smaller number is displayed in the emission output.

PROGRAM THEORY AND CALCULATIONS

This section will explain the theory and calculation methods for each step in the inert sweep program. A summary of the nomenclature used is located at the beginning of the Theory section.

For most calculations, three sets of equations are shown:

1. The first equation is written using generally accepted engineering nomenclature.
2. The second equation is written using PACMAN nomenclature, and is presented in BOLD Geneva font.
3. Following every PACMAN equation, as described in number two above, there are sample calculations which appear in italics.

Step 1

Unit Conversions

It is necessary to convert the units of some of the input data. PACMAN automatically converts all temperature into degrees Kelvin, all pressure to mmHg and all compositions into pounds.

Temperature: input either °C, °F or °K

$$T\ (^\circ K) = t\ (^\circ C) + 273.15 \qquad (1.1)$$

$$T\ (^\circ K) = (t\ (^\circ F) - 32)\ 5/9 + 273.15 \qquad (1.2)$$

Pressure: input either mmHg, in H_2O, PSIA, PSIG or kPa

$$P(mmHg) = P(in\ H_2O) * 1.868\ (mmHg/in\ H_2O) \qquad (1.3)$$

$$P(mmHg) = P(PSIA) * 51.718\ (mmHg/PSIA) \qquad (1.4)$$

$$P(mmHg) = (\ P(PSIG) + 14.7) * 51.718\ (mmHg/PSIA) \qquad (1.5)$$

$$P(mmHg) = P(kPa) * 7.4983\ (mmHg/kPa) \qquad (1.6)$$

Mass of components (M_i) in vessel (liquid phase): input either LB, Kg, or liters

M_i (LB) = M_i (Kg) * 2.2046 (LB/Kg) (1.7)

M_i (LB) = V_{Li} (l) * ρ_i (LB/ft^3) / 28.31685 l/ft^3 (1.8)

Mole Fraction Calculation

Moles (L_i) of components in vessel (liquid phase):

L_i (LB-Mole) = M_i (LB) / MW_i (LB/LB-Mole) (1.11)

Nexisting<vo> = Me<vo> / mw<vo> (1.11.1)

Nexisting<ACE> = 3300 LB / 58.08 LB/LB-Mole
= 56.812 LB-Mole

Nexisting<ACN> = 3300 LB / 41.05 LB/LB-Mole
= 80.39 LB-Mole

Nexisting<Other> = 200 LB / 200 LB/LB-Mole
= 1.00 LB-Mole

Total moles (L_{total}) in vessel (liquid phase):

L_{total} (LB-Mole) = Σ L_i (1.12)

Ltotal = SUM(Nexisting<vo>) (1.12.1)

Ltotal = SUM(56.82 LB-Mole + 80.39 LB-Mole + 1.00 LB-Mole)
= 138.21 LB-Mole

Mole fractions (x_i) of components in vessel (liquid phase):

x_i = L_i (LB-Mole) / L_{total} (LB-Mole) (1.13)

X<vo> = (Nexisting<vo>) / Ltotal (1.13.1)

X<ACE> = (56.82 LB-Mole) / 138.21 LB-Mole
= 0.411

X<ACN> = (80.39 LB-Mole) / 138.21 LB-Mole
= 0.582

X<Other>= (1 LB-Mole) / 138.21 LB-Mole
= 0.0072

Vapor Pressure Calculations

Vapor pressure, p_i°, of each volatile component can be calculated using the Antoine equation. The Antoine equation has the general form:

$$\ln (p_i^\circ(\text{mmHg})) = [\, a - (b/(T(^\circ K) + c))\,] \qquad (1.14)$$

The program calculates the vapor pressure of each volatile component using the Antoine equation in the form:

$$p_i^\circ\ (\text{mmHg}) = \exp [\, a - (b/(T(^\circ K) + c))\,] \qquad (1.15)$$

Pvapor,1<vm> = exp (a<vm> - (b<vm> / (Tsystem + c<vm>))) (1.15.1)

T(°K) = T(°C)+273.15
= 21 °C+273.15
= 294.15 °K

Pvapor,1<ACE> = exp (16.82 - (2993 / (294.15 °K + (-35.63))))
= exp (5.243)
= 189.154 mmHg

Pvapor,1<ACN> = exp (16.16 - (2962 / (294.15 °K + (-44.24))))
= exp (4.3077)
= 74.27 mmHg

Equilibrium Concentrations

For a system of ideal liquids and vapors at a given temperature, Raoult's Law gives a relationship to calculate the relative vapor and liquid equilibrium mole fractions.

Raoult's Law states that the partial pressure of a component, $_i$Pcan be calculated by multiplying the components vapor pressure, p_i°, by the liquid mole fraction, x_i, which is equal to the total pressure, P_{total}, multiplied by the vapor mole fraction, y_i, or:

$$P_i = p_i^\circ\_ * x_i = P_{total} * y_i \qquad (1.16)$$

PACMAN also includes individual Activity Coefficients for each volatile component, and an Inert Saturation Factor that is applied to the partial pressure calculation. These values are pre-set to 1 and can be changed if information is available.

Ppartial,1<v> = Pvapor,1<v> * X<v> * ac<v> * Inert Saturation Factor (1.16.1)

*Ppartial,1<ACE>=189.15 mmHg * 0.411 * 1 * 1*
= 77.76 mmHg

*Ppartial,1<ACN>=74.27 mmHg * 0.581658062 * 1 * 1*
= 43.20 mmHg

The vapor mole fraction, y_i, can then be determined for each component:

$y_i = p_i^{\circ} * x_i / P_{total}$ (1.17)

The total partial pressure for the system is the sum of the partial pressures for all volatile components:

Ppartial, sum = SUM (Ppartial, 1<v>) + SUM (Ppartial, 1<m>) (1.17.1)

Ppartial, sum = SUM (77.76 mmHg +43.20 mmHg)
= 120.96 mmHg

The partial pressure of the inert makes up the balance of the total system pressure, and therefore can be determined as follows:

$P_{total} = \{ \text{sum of } P_i \} + P_{inert}$ (1.18)

or, $P_{inert} = P_{total} - \{ \text{sum of } P_i \}$ (1.19)

Pinert,1 = Psystem - Ppartial, sum (1.19.1)

Pinert,1= 760 mmHg - 120.96 mmHg
= 639.04 mmHg

Step 2.

In Step 2 the mass of inert vapors being swept from the vessel is calculated.

It is assumed during the sweep step that vapor-liquid equilibrium in the vessel is maintained. Therefore the composition in the vapor space of the vessel is constant during the sweep step. To maintain this constant vapor composition, the mass of inert vapor entering the vessel must be equal to the mass of inert vapor leaving the vessel.

$m_{inert}(\text{entering}) = m_{inert}(\text{leaving})$ (2.22)

The inert volumetric rate, v_{inert}, entering the vessel is supplied as input data to the program, and the molecular weight, MW_{inert}, is accessed from the data base. The mass rate of inert vapor entering the vessel is calculated from these two variables.

The volume and mass of a vapor can be related by the Ideal Gas law. For an ideal, single component, closed system:

$P*V_{vs} = (M/MW)*R*T$ (2.23)

or for an ideal, single component, open system:

$P*v = (m/MW)*R*T$ (2.24)

which can be arranged to yield:

$m = P*v*MW/(R*T)$ (2.25)

This equation is used to calculate the mass rate, m_{inert}, of inert vapor entering (and leaving) the vessel. The program assumes the following conditions of the inert vapor stream:

T = 60°F (520°R)
P = 1 ATM (14.7 psia)

yielding a final equation:

$$m_{inert}\,(\mathrm{LB/Hr}) = \frac{\underline{v(\mathrm{CFM})*(60\mathrm{min/Hr})*\mathrm{MW}*14.72\mathrm{psia}}}{R*(520°\mathrm{R})} \qquad (2.26)$$

where the gas constant, R = 10.73(ft^3)(psia)/(lb-mole)(°R)

Msweeprate<i> = v * 60 * 14.7 * mw<i> / (10.73 * 520) (2.26.1)

*Msweeprate<Inert> = 10 ft^3/min * 60 min/hr * 14.7psia *28.01 LB/LB-mole /*
*(10.73ft^{3}psia/LB-mole ^{o}R * 520 ^{o}R)*
= 44.28 LB/hr

To calculate the overall mass of inerts, M_{inert}, leaving the vessel the mass rate is multiplied by the inert sweep step time:

$$M_{inert}\,(\mathrm{LB}) = m_{inert}\,(\mathrm{LB/Hr}) * \tau\,(\mathrm{min})/\,60\,(\mathrm{min/Hr}) \qquad (2.27)$$

Msweep<i> = Msweeprate<i> * Sweeptime / 60 (2.27.1)

*Msweep<Inert> = 44.28 LB/hr *30 min / 60 min/hr*

= 22.14 LB

And, finally the total moles of inert, N_{inert}, leaving the vessel is calculated using the molecular weight of the inert:

$$N_{inert}\,(\mathrm{LB - moles}) = M_{inert}\,(\mathrm{LB}) / MW_{inert} \qquad (2.28)$$

Nsweep<i> = Msweep<i> / mw<i> (2.28.1)

Nsweep<Inert> = 22.14 LB / 28.01 LB/LB-mole
= 0.7904 LB-mole

Step 3.

In Step 3, the mass of volatile components leaving is calculated.

It is assumed that the vapor leaving the vessel has the same composition of the vapor in the vessel's vapor space. This composition is assumed to remain constant during the sweep step and is equal to the composition calculated in Step 1.

As volatile compounds leave the vessel in the vapor phase, liquid volatile compounds are vaporized, thus maintaining equilibrium in the vapor space of the vessel.

The number of moles of volatile components leaving the vessel is related to the number of moles of inerts leaving the system and the partial pressures of the volatile and inert components. For ideal gases, Dalton's Law can be applied. For an ideal closed system:

$$P_i * V_{vs} = N_i * R * T \qquad (2.11)$$

And for an ideal open system:

$$P_i * v = n_i * R * T \qquad (3.1)$$

Where v, R, and T are assumed constant for the inert sweep step. Therefore, the ratio of moles of inert to volatile compounds can be calculated as:

$$P_i / P_{inert} = n_i / n_{inert} \qquad (3.2)$$

which can be arranged to yield:

$$n_i = n_{inert} * (P_i / P_{inert}) \qquad (3.3)$$

Since the total moles of inert, N_{inert}, leaving the vessel during the sweep operation has been determined in Step 2, the total moles of each volatile component, N_i, is calculated:

$$N_i = N_{inert} * (P_i / P_{inert}) \qquad (3.4)$$

Nsweep<v> = Nsweep<i> * Ppartial,1<v> / Pinert,1 (3.4.1)

*Nsweep<ACE> = 0.7904 LB-mole * 77.76 mmHg / 639.04 mmHg*
= 0.0962 LB-mole

*Nsweep<ACN> = 0.7904 LB-mole * 43.20 mmHg / 639.034 mmHg*
= 0.0534 LB-mole

To calculate the overall mass, M_i, of each volatile leaving the vessel, the total moles of each volatile is multiplied by its molecular weight:

$$M_i = N_i * MW_i \qquad (3.5)$$

Msweep<v> = Nsweep<v> * mw<v> (3.5.1)

*Msweep<ACE> = 0.0962 LB-mole * 58.08 LB / LB-mole*
= 5.59 LB

*Msweep<ACN> = 0.05343 LB-mole * 41.05 LB / LB-mole*
= 2.19 LB

Step 4 - Optional

If the mass balance option has been chosen by the user, a comparison of the calculated vapor mass exiting the vessel is made against the initial liquid mass in the vessel. The calculated exiting amount is determined by steps 1 through 3.

If the calculated exiting vapor amount is greater than the vessel's initial liquid amount, the initial liquid amount is displayed in the output for the quantity per step.

The rate is determined by dividing the reported output value by the step time, giving the rate in pounds per hour:

$$m_i = M_i / \tau \text{ (min)} * \text{(60 min/ HR)} \qquad (3.6)$$

PACMAN PROGRAM THEORY AND SAMPLE CALCULATION
EMPTY VESSEL SWEEP FOR IDEAL SYSTEMS

PROGRAM BACKGROUND AND ASSUMPTIONS

The PACMAN Program for an empty vessel sweep step uses the EPA's fractional dilution method to calculate the vent stream of an empty vessel (or vessel containing residual liquid) being purged with an inert gas. This program models the emission from a vessel containing a vapor phase, and which previously contained a totally miscible liquid phase. The vessel system can contain volatile, non-volatile and inert components. Volatile components appear in both the liquid and vapor phases. Non-volatile components appear only in the liquid phase, and inert components appear only in the vapor phase.

The sweeping of an empty vessel follows the guidelines of an empirical equation developed by the EPA, which is based on fractional dilution of the vapor space. Initially, the vapor concentration is the equilibrium concentration with the liquid which was previously in the vessel (or residual liquid). The vapor concentration decreases with the number of volumes of purge gas used.

The recovery of the volatiles from the vessel's condensers will decrease as the concentration decreases with time. Toward the latter part of the sweep step, the condenser may not remove any volatiles if the exiting vapor/inert dew point is not reached. Therefore, condensers should not be included with the empty vessel sweep program.

A final control device, such as Regenerative Thermal Oxidizer (RTO), can be used in the vapor line (see "PACMAN Program Theory - Final Control Device.").

1. This program assumes that the residual liquid (or liquid previously in the vessel) is totally miscible, that is, there is only one liquid phase. Solids in solution are included in this phase; however, solids in suspension must not be included in the program since they do not effect the vapor pressure of the system.

2. The model assumes the vessel previously contained perfectly mixed, ideal liquid and vapor phases.

3. The program calculations assume that the temperature and pressure in the vessel system are uniform and do not change over time.

4. It is also assumed that the volume of the vapor space is constant.

5. It is assumed that the residual liquid in the vessel is insignificant and is used for equilibrium composition calculations only. The vessel is essentially "empty" of liquid.

A material balance check is not required for the empty vessel sweep since the fractional dilution equation will not allow more volatile to be emitted than is initially contained in the vessel's vapor space.

PROGRAM STRUCTURE

The input information necessary to run the program is:

Molecular Weight of the inert sweep gas (LB/LB-mole)	*28.01*
Total system volume (ft^3, L, gal)	*285* ft^3
Inert Sweep Rate (CFM @ 60°F, 1 ATM)	*10*
The inert sweep step time (minutes)	*30*
Temperature in vessel (°C, °F, °K)	*21 °C*
Pressure in vessel (mmHg, in H_2O, PSIA, PSIG, kPa)	*760 mmHg*
Composition of the liquid phase (LB, Kg, Liters)	*See below*
Density (LB/ft^3) and Molecular Weight (LB/LB-mole) of components	*See below*
Antoine coefficients for the volatile liquid components (a, b, c)	*See below*
Activity coefficient of the volatile	*1 for all components*
Inert saturation factor (≤1)	*1 for all components*

	Composition	*Density (LB/ft^3)*	*Molecular Weight (LB/LB-mole)*	*Antoine coefficients a*	*b*	*c*
Acetone	*3300 LB*	*49.44*	*58.08*	*16.82*	*2993*	*-35.63*
Acetonitrile	*3300 LB*	*49.05*	*41.05*	*16.16*	*2962*	*-44.24*
Other	*200 LB*	*50.0*	*200*			

The density, molecular weight and Antoine coefficients for the volatile, non-volatile and inert components are automatically accessed from a component data base.

The program calculations are broken down into three steps:

Step 1 -The input data is converted and the liquid and vapor compositions in the vessel are determined.

Step 2 -The mass of inert vapors being swept from the vessel is calculated.

Step 3 -The mass of volatile components leaving the vessel is calculated.

PROGRAM THEORY AND CALCULATIONS

This section will explain the theory and calculation methods for each step in the empty vessel sweep program. A summary of the nomenclature used is located at the beginning of the Theory section.

For most calculations, three sets of equations are shown:

1. The first equation is written using generally accepted engineering nomenclature.
2. The second equation is written using PACMAN nomenclature, and is presented in BOLD Geneva font.
3. Following every PACMAN equation, as described in number two above, there are sample calculations which appear in italics.

Step 1

Unit Conversions

It is necessary to convert the units of some of the input data. PACMAN automatically converts all temperature into degrees Kelvin, all pressure to mmHg, all compositions into pounds and total system volume into cubic feet.

Temperature: input either °C, °F or °K

$$T\ (^\circ K) = t\ (^\circ C) + 273.15 \qquad (1.1)$$

$$T\ (^\circ K) = (t\ (^\circ F) - 32)\ 5/9 + 273.15 \qquad (1.2)$$

Pressure: input either mmHg, in H_2O, PSIA, PSIG or kPa

$$P(mmHg) = P(in\ H_2O) * 1.868\ (mmHg/in\ H_2O) \qquad (1.3)$$

$$P(mmHg) = P(PSIA) * 51.72\ (mmHg/PSIA) \qquad (1.4)$$

$$P(mmHg) = (\ P(PSIG) + 14.7) * 51.72\ (mmHg/PSIA) \qquad (1.5)$$

$$P(mmHg) = P(kPa) * 7.498\ (mmHg/kPa) \qquad (1.6)$$

Mass of components (M_i) in vessel (liquid phase): input either LB, Kg, or liters

$$M_i\ (LB) = M_i\ (Kg) * 2.205\ (LB/Kg) \qquad (1.7)$$

$$M_i\ (LB) = V_{Li}\ (l) * \rho_i\ (LB/ft^3) / 28.32\ l/ft^3 \qquad (1.8)$$

Total system volume (V_{system}): input either ft^3, L or gal

$$V_{system}\ (ft^3) = V_{system}\ (L) * 0.03532\ (ft^3/L) \qquad (1.9)$$

$$V_{system}\ (ft^3) = V_{system}\ (gal) * 0.13368\ (ft^3/gal) \qquad (1.10)$$

Mole Fraction Calculation

Moles (L_i) of components in vessel (liquid phase):

L_i (LB-Mole) = M_i (LB) / MW_i (LB/LB-Mole) (1.11)

Nexisting<vo> = Me<vo> / mw<vo> (1.11.1)

Nexisting<ACE> = 3300 LB / 58.08 LB/LB-Mole
= 56.82 LB-Mole

Nexisting<ACN> = 3300 LB / 41.05 LB/LB-Mole
= 80.39 LB-Mole

Nexisting<Other> = 200 LB / 200 LB/LB-Mole
= 1.00 LB-Mole

Total moles (L_{total}) in vessel (liquid phase):

L_{total} (LB-Mole) = $\Sigma\ L_i$ (1.12)

Ltotal = SUM(Nexisting<vo>) (1.12.1)

Ltotal = SUM(56.82 LB-Mole + 80.39 LB-Mole + 1.00 LB-Mole)
= 138.21 LB-Mole

Mole fractions (x_i) of components in vessel (liquid phase):

x_i = L_i (LB-Mole) / L_{total} (LB-Mole) (1.13)

X<vo> = (Nexisting<vo>) / Ltotal (1.13.1)

X<ACE> = (56.82 LB-Mole) / 138.21 LB-Mole
= 0.411

X<ACN> = (80.39 LB-Mole) / 138.21 LB-Mole
= 0.582

X<Other> = (1 LB-Mole) / 138.21 LB-Mole
= 0.00723

Vapor Pressure Calculations

Vapor pressure, p_i°, of each volatile component previously in the vessel can be calculated using the Antoine equation. The Antoine equation has the general form:

$$\ln (p_i^\circ(\text{mmHg})) = [\ a - (b/(T(^\circ K) + c))\ ] \quad (1.14)$$

The program calculates the vapor pressure of each volatile component using the Antoine equation in the form:

$$p_i^\circ\ (\text{mmHg}) = \exp [\ a - (b/(T(^\circ K) + c))\ ] \quad (1.15)$$

$$\textbf{Pvapor,1<vm> = exp (a<vm> - (b<vm> / (Tsystem + c<vm>)))} \qquad (1.15.1)$$

$$\begin{aligned} T(^\circ K) &= T(^\circ C)+273.15 \\ &= 21\,^\circ C+273.15 \\ &= 294.15\ ^\circ K \end{aligned}$$

$$\begin{aligned} Pvapor,1\text{<ACE>} &= exp\ (\ 16.82 - (\ 2993\ \ / (294.15\ ^\circ K + (-35.63)\ )\ )\ ) \\ &= exp\ (\ 5.243) \\ &= 189.15\ mmHg \end{aligned}$$

$$\begin{aligned} Pvapor,1\text{<ACN>} &= exp\ (\ 16.16 - (\ 2962\ \ / (294.15\ ^\circ K + (-44.24)\ )\ )\ ) \\ &= exp\ (\ 4.308\ ) \\ &= 74.27\ mmHg \end{aligned}$$

Equilibrium Concentrations

To determine the equilibrium conditions of the vapor space of an empty vessel, the program uses the composition of the liquid last in the vessel.

For a system of ideal liquids and vapors at a given temperature, Raoult's Law gives a relationship to calculate the relative vapor and liquid equilibrium mole fractions.

Raoult's Law states that the partial pressure of a component, ${}_iP$can be calculated by multiplying the components vapor pressure, p_i°, by the liquid mole fraction, x_i, which is equal to the total pressure, P_{total}, multiplied by the vapor mole fraction, y_i, or:

$$P_i = p_i^\circ\_ * x_i = P_{total} * y_i \qquad (1.16)$$

PACMAN also includes individual Activity Coefficients for each volatile component, and an Inert Saturation Factor that is applied to the partial pressure calculation. These values are pre-set to 1 and can be changed if information is available.

$$\textbf{Ppartial,1<v> = Pvapor,1<v> * X<v> * ac<v> * Inert Saturation Factor} (1.16.1)$$

$$\begin{aligned} Ppartial,1\text{<ACE>} \quad &= 189.15\ mmHg\ \ * 0.411 * 1\ \ * 1 \\ &= 77.76\ mmHg \end{aligned}$$

$$\begin{aligned} Ppartial,1\text{<ACN>} \quad &= 74.27\ mmHg\ \ * 0.582 * 1\ \ * 1 \\ &= 43.2\ mmHg \end{aligned}$$

The vapor mole fraction, y_i, can then be determined for each component:

$$y_i \quad = p_i^\circ * x_i / P_{total} \qquad (1.17)$$

The total partial pressure for the system is the sum of the partial pressures for all volatile components:

Ppartial, sum = SUM (Ppartial, 1<v>) + SUM (Ppartial, 1<m>) (1.17.1)

Ppartial, sum = SUM (77.76 mmHg +43.20 mmHg)
= 120.9 mmHg

Vapor Space

The vapor space for an empty vessel sweep is the total system volume, V_{system}, as specified in the user input area.

<u>Step 2.</u>

In Step 2 the mass of inert vapors being swept from the vessel is calculated.

The mass of inert vapor entering the vessel must be equal to the mass of inert vapor leaving the vessel.

$$m_{inert}\,(\text{entering}) = m_{inert}\,(\text{leaving}) \qquad (2.22)$$

The inert volumetric rate, v_{inert}, entering the vessel is supplied as input data to the program, and the molecular weight, MW_{inert}, is accessed from the data base. The mass rate of inert vapor entering the vessel is calculated from these two variables.

The volume and mass of a vapor can be related by the Ideal Gas law. For an ideal, single component, closed system:

$$P*V_{vs} = (M/MW)*R*T \qquad (2.23)$$

or for an ideal, single component, open system:

$$P*v = (m/MW)*R*T \qquad (2.24)$$

which can be arranged to yield:

$$m = P*v*MW/(R*T) \qquad (2.25)$$

This equation is used to calculate the mass rate, m_{inert}, of inert vapor entering (and leaving) the vessel. The program assumes the following conditions of the inert vapor stream:

T = 60°F (520°R)

P = 1 ATM (14.7 psia)

yielding a final equation:

$$m_{inert}\,(\text{LB/Hr}) = \frac{v(\text{CFM})*(60\text{min/Hr})*MW*14.72\text{psia}}{R*(520^\circ R)} \qquad (2.26)$$

where the gas constant, $R = 10.73(ft^3)(psia)/(lb\text{-}mole)(^\circ R)$

Msweeprate<i> = v * 60 * 14.7 * mw<i> / (10.73 * 520) (2.26.1)

*Msweeprate<Inert> = 10 ft^3/min * 60 min/hr * 14.7 psia *28.01 LB/LB-mole / (10.73 ft^3psia/LB-mole ^oR * 520 ^oR)*
= 44.28 LB/hr

To calculate the overall mass of inerts, M_{inert}, leaving the vessel the mass rate is multiplied by the inert sweep step time:

M_{inert} (LB) = m_{inert} (LB/Hr) * τ (min)/ 60 (min/Hr) (2.27)

Msweep<i> = Msweeprate<i> * Sweeptime / 60 (2.27.1)

*Msweep<Inert> = 44.27 LB/hr *30 min / 60 min/hr*
= 22.14 LB

Step 3.

In Step 3, the mass of volatile components leaving is calculated.

The initial concentration of volatiles in the vapor space is calculated using the ideal gas law and the partial pressures calculated previously in step 1:

$P_i = p_i^\circ\_ * x_i = P_{total} * y_i$ (1.16)

and the following equation:

C°_i (Lb/ft^3) = [P_i (mmHg) * MW_i (Lb/Lb-mole)] / [R(999 mmHg-ft^3/Lb-mole K) * T(K)] (3.7)

Cinitial<v> = Ppartial,1<v> * mw<v> / (999 * Tsystem) (3.7.1)

*Cinitial<ACE> = 77.762 mmHg * 58.08 LB/LB-mole / (999 mmHg-ft^3/LB-mole ^0K * 294.15 ^0K)*
= 0.0154 LB/ft^3

*Cinitial<ACN> = 43.20 mmHg * 41.05 LB/LB-mole / (999 mmHg-ft^3/LB-mole ^0K * 294.15 ^0K)*
= 0.006 LB/ft3

The partial pressure is based on the mole fraction of liquid which was in the vessel before it was emptied. The amount or composition in the vessel before being emptied is entered by the user in the input section.

The number of volume changes of inert gas for the vessel is:

Number of volume changes = v(ACFM) * τ(min) / V_{system} (ft^3) (3.8)

NVC = ACFM * Sweeptime / Vsystem (3.8.1)

*NVC = 10.77 ACFM * 30 min / 285 ft^3*

= 1.13

Where: ACFM = SCFM * T(K) /273.15 (3.9)

ACFM = v * Tsystem / 273.15 (3.9.1)

$ACFM = 10\ SCFM * 294.15\ {}^0K / 273.15\ {}^0K$
$= 10.769\ ACFM$

The final concentration of vapor exiting the vessel is calculated by the following EPA equation:

$C^f_i = C^\circ_i * (0.37)^{\text{(no. of volume changes)}}$ (3.10)

Cfinal<v> = Cinitial<v> * 0.37 ^ NVC (3.10.1)

*Cfinal<ACE> = 0.0153 LB/ft^3 *(0.37* ^ 1.13)
= 0.00498 LB/ft^3

*Cfinal<ACN> = 0.006 LB/ft^3 * (0.37* ^ 1.13)
= 0.0019 LB/ft^3

The volatiles exiting the vessel are then calculated by multiplying the difference between the initial and final concentration by the vessel volume:

M_i (Lb/Step) = $[V_{system}\ (ft^3)] * [C^\circ_i - C^f_i, (Lb/ft^3)]$ (3.11)

Memptyvesselsweep<v> = (Cinitial<v> - Cfinal<v>) * Vsystem (3.11.1)

*Memptyvesselsweep<ACE> = (0.0154 LB/ft^3 - 0.0049 LB/ft^3) * 285 ft^3*
= 2.96 LB

*Memptyvesselsweep<ACN> = (0.00603 LB/ft^3 - 0.00196 LB/ft^3) * 285 ft^3*
= 1.163 LB

The rate is determined by dividing the reported output value by the step time, giving the rate in pounds per hour:

$m_i = M_i / \tau\ (min) * (60\ min/\ HR)$ (3.6)

PACMAN PROGRAM THEORY AND SAMPLE CALCULATIONS
HEATING FOR IDEAL SYSTEMS

PROGRAM BACKGROUND AND ASSUMPTIONS

The PACMAN Program for a heating step calculates the vent stream of a vessel being heated at a constant pressure. This program models the emission from a vessel containing a vapor phase and a totally miscible liquid phase. The vessel system can contain volatile, non-volatile and inert components. Volatile components appear in both the liquid and vapor phases. Non-volatile components appear only in the liquid phase, and inert components appear only in the vapor phase.

The program calculates the composition of the vapor stream leaving the vessel while maintaining vapor/liquid equilibrium. Multiple consecutive vent condensers can be used (see “PACMAN Program Theory - Vent Condenser(s)”.). A final control device, such as Regenerative Thermal Oxidizer (RTO), can also be used in the vapor line (see “PACMAN Program Theory - Final Control Device.”).

1. This program assumes that the liquid is totally miscible, that is, there is only one liquid phase. Solids in solution are included in this phase; however, solids in suspension must not be included in the program since they do not effect the vapor pressure of the system.
2. The model assumes the vessel contains perfectly mixed, ideal liquid and vapor phases that are continuously in phase equilibrium.
3. The program calculations assume that the pressure in the vessel system is uniform and does not change over time.
4. It is also assumed that the amount of liquid being vaporized in the vessel is small when compared to the total liquid volume, therefore the liquid composition and the volume of the vapor space can be assumed to be constant.

The computation of the volatile components exiting the vessel is based on the log mean pressure differential (LMPD) method. This assumes a constant value for the ratio of the component's molar quantity to LMPD.

A mass balance check is not required for the heating step calculation since the vessel contents will remain in the liquid phase throughout the heating step (see assumption number 4 above). The program will not allow the vessel to be heated above the boiling point of any volatile component.

PROGRAM STRUCTURE

The input information necessary to run the program is:

Molecular Weight of the inert vapors (LB/LB-mole)	*28.01*
Total System volume (Cu ft, L, gal)	*285 ft^3*
The heating step time (minutes)	45
Initial temperature in vessel (°C, °F, °K)	10 °C
Final temperature in vessel (°C, °F, °K)	*50 °C*
Pressure in vessel (mmHg, in H_2O, PSIA, PSIG, kPa)	*760 mmHg*
Composition of the liquid phase (LB, Kg, Liters)	*See below*
Density (LB/ft^3) and Molecular Weight (LB/LB-mole) of components	See below
Antoine coefficients for the volatile liquid components (a, b, c)	*See below*
Activity coefficient of the volatile	*1 for all components*
Inert Saturation factor ($\leq$1)	*1 for all components*

	Composition	*Density*	*Molecular Weight*	*Antoine coefficients*		
	(LB)	*(LB/ft^3)*	*(LB/LB-mole)*	*a*	*b*	*c*
Acetone	*3300*	*49.45*	*58.08*	*16.82*	*2993*	*-35.63*

Acetonitrile	*3300 LB*	*49.05*	*41.05*	*16.16*	*2962*	*-44.24*
Other	*200 LB*	*50.00*	*200*			

The density, molecular weight and Antoine coefficients for the volatile, non-volatile and inert components are automatically accessed from a component data base.

The program calculations are broken down into three steps:

Step 1 - The input data is converted and the initial and final vapor compositions in the vessel are determined.

Step 2 - The mass of inert vapors being displaced from the vessel is calculated.

Step 3 - The mass of volatile components leaving the vessel are calculated.

PROGRAM THEORY AND CALCULATIONS

This section will explain the theory and calculation methods for each step in the heating program. A summary of the nomenclature used is located at the beginning of the Theory section.

For most calculations, three sets of equations are shown:

1. The first equation is written using generally accepted engineering nomenclature.
2. The second equation is written using PACMAN nomenclature, and is presented in BOLD Geneva font.
3. Following every PACMAN equation, as described in number two above, there are sample calculations which appear in italics.

Step 1

Unit Conversions

It is necessary to convert the units of some of the input data. PACMAN automatically converts all temperature into degrees Kelvin, all pressure to mmHg, all compositions into pounds and total system volume into cubic feet.

Temperature: input either °C, °F or °K

$$T\ (^\circ K) = t\ (^\circ C) + 273.15 \qquad (1.1)$$

$$T\ (^\circ K) = (t\ (^\circ F) - 32)\ 5/9 + 273.15 \qquad (1.2)$$

Pressure: input either mmHg, in H_2O, PSIA, PSIG or kPa

$$P(mmHg) = P(in\ H_2O) * 1.868\ (mmHg/in\ H_2O) \qquad (1.3)$$

$$P(mmHg) = P(PSIA) * 51.718\ (mmHg/PSIA) \qquad (1.4)$$

P(mmHg) = (P(PSIG) + 14.7) * 51.718 (mmHg/PSIA) (1.5)

P(mmHg) = P(kPa) * 7.4983 (mmHg/kPa) (1.6)

Mass of components (M_i) in vessel (liquid phase): input either LB, Kg, or liters

M_i (LB) = M_i (Kg) * 2.2046 (LB/Kg) (1.7)

M_i (LB) = V_{Li} (l) * ρ_i (LB/ft^3) / 28.32 l/ft^3 (1.8)

Total system volume (V_{system}): input either ft^3, L or gal

V_{system} (ft^3) = V_{system} (L) * 0.03532 (ft^3/L) (1.9)

V_{system} (ft^3) = V_{system} (gal) * 0.13368 (ft^3/gal) (1.10)

Mole Fraction Calculation

Moles (L_i) of components in vessel (liquid phase):

L_i (LB-Mole) = M_i (LB) / MW_i (LB/LB-Mole) (1.11)

Nexisting<vo> = Me<vo> / mw<vo> (1.11.1)

Nexisting<ACE> = 3300 LB / 58.08 LB/LB-Mole
= 56.82 LB-Mole

Nexisting<ACN> = 3300 LB / 41.05 LB/LB-Mole
= 80.39 LB-Mole

Nexisting<Other> = 200 LB / 200 LB/LB-Mole
= 1.00 LB-Mole

Total moles (L_{total}) in vessel (liquid phase):

L_{total} (LB-Mole) = Σ L_i (1.12)

Ltotal = SUM(Nexisting<vo>) (1.12.1)

Ltotal = SUM(56.82 LB-Mole + 80.39 LB-Mole + 1.00 LB-Mole)
= 138.21 LB-Mole

Mole fractions (x_i) of components in vessel (liquid phase):

x_i = L_i (LB-Mole) / L_{total} (LB-Mole) (1.13)

X<vo> = (Nexisting<vo>) / Ltotal (1.13.1)

X<ACE> = (56.82 LB-Mole) / 138.21 LB-Mole
= 0.41

X<ACN> = (80.39 LB-Mole) / 138.21 LB-Mole
= 0.582

X<Other> = (1 LB-Mole) / 138.21 LB-Mole
= 0.0072

Vapor Pressure Calculations

Vapor pressure, p_i°, of each volatile component can be calculated using the Antoine equation. The Antoine equation has the general form:

$$\ln (p_i^\circ(\text{mmHg})) = [\, a - (b/(T(^\circ K) + c))\,] \qquad (1.14)$$

The program calculates the vapor pressure of each volatile component at the initial and final temperatures using the Antoine equation in the form:

$$p_i^\circ\ (\text{mmHg}) = \exp [\, a - (b/(T(^\circ K) + c))\,] \qquad (1.15)$$

Pvapor,1<vm> = exp (a<vm> - (b<vm> / (Tsystem + c<vm>))) (1.15.1)

T(°K) = T(°C)+273.15
= 10°C+273.15
= 283.15 °K

Pvapor,1<ACE> = exp (16.82 - (2993 / (283.15 °K + (-35.63)))) mmHg
= exp (4.72) mmHg
= 113.07 mmHg

Pvapor,1<ACN> = exp (16.16 - (2962 / (283.15 °K + (-44.24)))) mmHg
= exp (3.76) mmHg
= 43.04 mmHg

and: **Pvapor,2<vm> = exp (a<vm> - (b<vm> / (Tfinal + c<vm>)))** (1.15.2)

T(°K) = T(°C)+273.15
= 50°C+273.15
= 323.15 °K

Pvapor,2<ACE>= exp (16.82 - (2993 / (323.15 °K + (-35.63)))) mmHg
= exp (6.41) mmHg
= 608.07 mmHg

Pvapor,2<ACN>= exp (16.16 - (2962 / (323.15 °K + (-44.24))))mmHg
= exp (5.54) mmHg
= 254.70 mmHg

Equilibrium Concentrations

For a system of ideal liquids and vapors at a given temperature, Raoult's Law gives a relationship to calculate the relative vapor and liquid equilibrium mole fractions.

Raoult's Law states that the partial pressure of a component, $_i$Pcan be calculated by multiplying the components vapor pressure, p_i°, by the liquid mole fraction, x_i, which is equal to the total pressure, P_{total}, multiplied by the vapor mole fraction, y_i, or:

$P_i = p_i^{\circ}\_ * x_i = P_{total} * y_i$ (1.16)

PACMAN also includes individual Activity Coefficients for each volatile component, and an Inert Saturation Factor that is applied to the partial pressure calculation. These values are pre-set to 1 and can be changed if information is available.

Ppartial,1<v> = Pvapor,1<v> * X<v> * ac<v> * Inert Saturation Factor (1.16.1)

*Ppartial,1<ACE>= 113.07 mmHg * 0.41 * 1 * 1*
= 46.49 mmHg

*Ppartial,1<ACN>= 43.04 mmHg * 0.58 * 1 * 1*
= 25.03 mmHg

and: **Ppartial,2<v> = Pvapor,2<v> * X<v> * ac<v> * Inert Saturation Factor** (1.16.4)

*Ppartial,2<ACE>= 608.07 mmHg * 0.41 * 1 * 1*
= 249.98 mmHg

*Ppartial,2<ACN>= 254.70 mmHg * 0.58 * 1 * 1*
= 148.15 mmHg

The vapor mole fraction, y_i, can then be determined for each component:
$y_i = p_i^{\circ} * x_i / P_{total}$ (1.17)

The total partial pressure at initial and final temperatures is the sum of the partial pressures for all volatile components:

Ppartial, sum = SUM (Ppartial, 1<v>) + SUM (Ppartial, 1<m>) (1.17.1)

Ppartial, sum= (Ppartial,1<ACE> + Ppartial,1<ACN>) + SUM (Ppartial, 1<m>)
= (46.48 mmHg + 25.03 mmHg) + 0.0 mmHg
= 71.5 mmHg

and: **Ppartial, 2, sum = SUM (Ppartial, 2<v>) + SUM (Ppartial, 2<m>)** (1.17.2)

Ppartial,2, sum = (Ppartial,2<ACE> + Ppartial,2<ACN>) + SUM (Ppartial, 2<m>)

= (249.98 mmHg + 148.14 mmHg) + 0.0 mmHg
= 398.13 mmHg

The partial pressure of the inerts is calculated from the total pressure and the partial pressure of the volatile components.

P_{total} = { sum of P_i } + P_{inert} (1.18)

The partial pressure of the inert vapor is the difference between the total pressure and the sum of the partial pressures of the volatile components at the initial and final temperatures.

P_{inert} = P_{total} - {Sum of P_i's} (1.19)

and: **Pinert,1 = Psystem - Ppartial,sum** (1.19.1)

Pinert,1 = 760 mmHg - 71.52 mmHg
= 688.48 mmHg

Pinert,2 = Psystem - Ppartial,2,sum (1.19.3)

Pinert,2 = 760 mmHg - 398.13 mmHg
= 361.87 mmHg

Vapor Space

The vapor space for the system being heated is calculated by subtracting the volume of the liquid/solid in the vessel from the total system volume. The volume existing in the vessel is:

$V_{Li} = M_i / \rho_i$ (1.20)

Volume,existing<vom> = (Me<vom> / density<vom>) (1.20.1)

Volume,existing<ACE> = 3300 LB /49.44456 LB/ft^3
= 66.74 ft^3

Volume,existing<ACN> = 3300 LB /49.051LB/ft^3
= 67.286 ft^3

Volume,existing<Other> = 200 LB /50.0 LB/ft^3
= 4.0 ft^3

The vapor space is:

$V_{VS} = V_{system} - \Sigma V_{Li}$ (1.21)

Vapor = Vsystem - SUM(Volume,existing<vom>) (1.21.1)

Vapor =285 ft^3 *- (66.74 ft*^{3} *+ 67.286 ft*^{3} *+ 4.0 ft*^{3} *)*

$= 146.98\ ft^3$

Step 2.

In Step 2 the mass of inert vapors being displaced from the vessel is calculated.

The moles of inerts in the vessel at the initial and final conditions are calculated using Dalton's Law:

$$P_{inert} * V_{VS} = N_{inert} * R * T \qquad (2.7)$$

or

$$N_{inert} = P_{inert} * V_{VS} \ / (R * T) \qquad (2.8)$$

Since V_{VS} and R are constant, the change in moles of inerts between the initial and final conditions can be calculated as:

$$N_{inert}^{initial} - N_{inert}^{final} = [(P_{inert}^{initial} / T^{final}) - (P_{inert}^{final} / T^{initial})] * (V_{VS} / R) \qquad (2.9)$$

Ninert,heat = ((Pinert,1 / Tsystem) - (Pinert,2 / Tfinal)) * (Vapor / 999) (2.9.1)

Ninert,heat = ((688.48 mmHg / 283.15 °K) - (361.87 mmHg / 323.15 °K))
** (146.98 ft³ / 999 mmHg ft³ / LB-Mole °K)*
= 0.193 LB-Mole

The mass of inert, M_{inert}, displaced during the heating step is:

$$M_{inert} = \Delta N_{inert} * MW_{inert} \qquad (2.33)$$

Mheat<i> = Ninert,heat * mw<i> (2.33.1)

*Mheat<Inert> = 0.193 LB-Mole * 28.01LB/LB-Mole*
= 5.41 LB

To calculate the mass rate of inert moles displaced, m_{inert}, the program averages the amount of inerts displaced over the heating time:

$$m_{inert}\ (LB/HR) = N_{inert}\ (LB\text{-}Moles) * MW_{inert}\ (LB/LB\text{-}Mole) * \frac{60\ (min/Hr)}{\tau\ (min)} \qquad (2.34)$$

The mass rates calculated by the program therefore are <u>average</u> rates over an entire heating step.

Step 3.

In Step 3, the mass of volatile components being displaced from the vessel are calculated.

The total number of moles in the vapor space and the vapor phase composition are both functions of temperature. Since the molar rate at which vapors leave the vessel is greatly influenced by the components partial pressure, the program assumes that for any component:

N_i / $(LMPD)_i$ = Constant (3.12)

Where N_i is the number of moles of component i having left the vessel and the log mean pressure difference of i, $(LMPD)_i$, is calculated:

$(LMPD)_i = (P^{initial} - P^{final})_i / \ln(P^{initial} / P^{final})_i$ (3.13)

LMPDheat<v> = (Ppartial,1<v> - Ppartial,2<v>) / ln ((Ppartial,1<v>) / (Ppartial,2<v>)) (3.13.1)

LMPDheat<ACE> = (46.48 mmHg - 249.98 mmHg) / ln ((46.48 mmHg / 249.98 mmHg)
= 120.97 mmHg

LMPDheat<ACN> = (25.032 mmHg - 148.15 mmHg) / ln ((25.03 mmHg / 148.15 mmHg)
= 69.24 mmHg

Therefore, knowing the number of moles of inerts leaving the vessel and the LMPD of the inert and volatile components, the number of moles of a volatile component, i, being displaced from the vessel can be estimated by:

$N_i = N_{inert} * (LMPD)_i / (LMPD)_{inert}$ (3.14)

Nheat<v> = Ninert,heat * LMPDheat<v> / LMPDinert,heat (3.14.1)

*Nheat<ACE> = 0.193 LB-Mole * 120.97 mmHg / 507.79 mmHg*
= 0.0459 LB-Mole

*Nheat<ACN> = 0.193 LB-Mole * 69.24 mmHg / 507.79 mmHg*
= 0.0263 LB-Mole

where, $LMPD_{inert} = (P^{initial} - P^{final})_{inert} / \ln (P^{initial}/P^{final})_{inert}$ (3.15)

LMPDinert,heat = (Ppartial,2,sum - Ppartial,sum) / ln ((Psystem - **Ppartial,sum) / (Psystem - Ppartial,2,sum))** (3.15.1)

LMPDinert,heat = (398.13 mmHg - 71.52 mmHg) / ln ((760 mmHg - 71.52 mmHg) / (760 mmHg - 398.13 mmHg))
= 507.79 mmHg

The mass of the volatile components, M_i, are related to the moles by:

$M_i = N_i * MW_i$ (3.5)

Mheat<v> = Nheat<v> * mw<v> (3.5.5)

*Mheat<ACE> = 0.0459 LB-Mole * 58.08 LB/ LB-Mole*
= 2.67 LB

*Mheat<ACN> = 0.0263 LB-Mole * 41.05 LB/ LB-Mole*

= 1.08 LB

The rate is determined by dividing the reported output value by the step time, giving the rate in pounds per hour:

$$m_i = M_i / \tau \text{ (min)} * \text{(60 min/ HR)} \qquad (3.6)$$

PACMAN PROGRAM THEORY AND SAMPLE CALCULATIONS
EVACUATION FOR IDEAL SYSTEMS

PROGRAM BACKGROUND AND ASSUMPTIONS

The PACMAN Program for an evacuation step calculates the vent stream of a vessel undergoing a change from a higher to a lower pressure. This program models the emission from a vessel containing a vapor phase and a totally miscible liquid phase. The vessel system can contain volatile, non-volatile and inert components. Volatile components appear in both the liquid and vapor phases. Non-volatile components appear only in the liquid phase, and inert components appear only in the vapor phase.

The program calculates the composition of the vapor stream leaving the vessel while maintaining vapor/liquid equilibrium. Multiple consecutive vent condensers can be used (see “PACMAN Program Theory - Vent Condenser(s)”.). A final control device, such as Regenerative Thermal Oxidizer (RTO), can be used in the vapor line (see “PACMAN Program Theory - Final Control Device.”).

1. This program assumes that the liquid is totally miscible, that is, there is only one liquid phase. Solids in solution are included in this phase; however, solids in suspension must not be included in the program since they do not effect the vapor pressure of the system.

2. The model assumes the vessel contains perfectly mixed, ideal liquid and vapor phases that are continuously in phase equilibrium.

3. The program calculations assume that the temperature in the vessel system is uniform and does not change over time.

4. It is also assumed that the amount of liquid being vaporized in the vessel is small when compared to the total liquid volume, therefore the liquid composition and the volume of the vapor space can be assumed to be constant.

A material balance check can be completed, if desired, to prevent the quantity of an exiting vapor component from exceeding the initial liquid amount in the vessel, which may happen in situations with a large vapor space and large pressure changes. If the exiting vapor quantity exceeds the initial liquid amount, the initial liquid amount is substituted in the emission output.

PROGRAM STRUCTURE

The input information necessary to run the program is:

Molecular Weight of the inert vapors (LB/LB-mole)	*28.01*

Total system volume (Cu ft, L, gal)	*285* ft^3
The evacuation step time (minutes)	*45*
Temperature in vessel in degrees (°C, °F, °K)	*21 °C*
Initial pressure in vessel (mmHg, in H_2O, PSIA, PSIG, kPa)	*760 mmHg*
Final pressure in vessel (mmHg, in H_2O, PSIA, PSIG, kPa)	*150 mmHg*
Composition of the liquid phase (LB, Kg, Liters)	*See below*
Density (LB/ft^3) and Molecular Weight (LB/LB-mole) of components	*See below*
Antoine coefficients for the volatile liquid components (a, b, c)	*See below*
Activity coefficient of the volatile	1 for all components
Inert saturation factor (≤1)	*1 for all components*

	Composition	*Density (LB/ft^3)*	*Molecular Weight (LB/LB-mole)*	*Antoine coefficients*		
				a	*b*	*c*
Acetone	*3300 LB*	*49.44*	*58.08*	*16.82*	*2993*	*-35.63*
Acetonitrile	*3300 LB*	*49.05*	*41.05*	*16.16*	*2962*	*-44.24*
Other	*200 LB*	*50.00*	*200*			

The density, molecular weight and Antoine coefficients for the volatile, non-volatile and inert components are automatically accessed from a component data base.

The program calculations are broken down into four steps:

Step 1 -The input data is converted and the initial and final vapor compositions in the vessel are determined.

Step 2 -The mass of inert vapors being evacuated from the vessel is calculated.

Step 3 -The mass of volatile components leaving the vessel are calculated.

Step 4 -Optional: A material balance check between the calculated emission vapor quantity and initial liquid quantity in the vessel is performed and the smaller number is displayed in the emission output.

PROGRAM THEORY AND CALCULATIONS

This section will explain the theory and calculation methods for each step in the evacuation program. A summary of the nomenclature used is located at the beginning of the Theory section.

For most calculations, three sets of equations are shown:

1. The first equation is written using generally accepted engineering nomenclature.

2. The second equation is written using PACMAN nomenclature, and is presented in BOLD Geneva font.

3. Following every PACMAN equation, as described in number two above, there are sample calculations which appear in italics.

Step 1

Unit Conversions

It is necessary to convert the units of some of the input data. PACMAN automatically converts all temperature into degrees Kelvin, all pressure to mmHg, all compositions into pounds and total system volume into cubic feet.

Temperature: input either °C, °F or °K

$T\ (^\circ K) = t\ (^\circ C) + 273.15$ (1.1)

$T\ (^\circ K) = (t\ (^\circ F) - 32)\ 5/9 + 273.15$ (1.2)

Pressure: input either mmHg, in H_2O, PSIA, PSIG or kPa

$P(mmHg) = P(in\ H_2O) * 1.868\ (mmHg/in\ H_2O)$ (1.3)

$P(mmHg) = P(PSIA) * 51.718\ (mmHg/PSIA)$ (1.4)

$P(mmHg) = (\ P(PSIG) + 14.7) * 51.718\ (mmHg/PSIA)$ (1.5)

$P(mmHg) = P(kPa) * 7.4983\ (mmHg/kPa)$ (1.6)

Mass of components (M_i) in vessel (liquid phase): input either LB, Kg, or liters

$M_i\ (LB) = M_i\ (Kg) * 2.2046\ (LB/Kg)$ (1.7)

$M_i\ (LB) = V_{Li}\ (l) * \rho_i\ (LB/ft^3) / 28.31685\ l/ft^3$ (1.8)

Total system volume (V_{system}): input either ft^3, L or gal

$V_{system}\ (ft^3) = V_{system}\ (L) * 0.03532\ (ft^3/L)$ (1.9)

$V_{system}\ (ft^3) = V_{system}\ (gal) * 0.13368\ (ft^3/gal)$ (1.10)

Mole Fraction Calculation

Moles (L_i) of components in vessel (liquid phase):

$L_i\ (LB\text{-}Mole) = M_i\ (LB) / MW_i\ (LB/LB\text{-}Mole)$ (1.11)

Nexisting<vo> = Me<vo> / mw<vo> (1.11.1)

Nexisting<ACE> = 3300 LB / 58.08 LB/LB-Mole
= 56.82 LB-Mole

Nexisting<ACN> = 3300 LB / 41.05 LB/LB-Mole
= 80.39 LB-Mole

Nexisting<Other> = 200 LB / 200 LB/LB-Mole

= 1.00 LB-Mole

Total moles (L_{total}) in vessel (liquid phase):

L_{total} (LB-Mole) = Σ L_i (1.12)

Ltotal = SUM (Nexisting<vo>) (1.12.1)

Ltotal = SUM(56.82 LB-Mole + 80.39 LB-Mole + 1.00 LB-Mole)
= 138.21 LB-Mole

Mole fractions (x_i) of components in vessel (liquid phase):

x_i = L_i (LB-Mole) / L_{total} (LB-Mole) (1.13)

X<vo> = (Nexisting<vo>) / Ltotal (1.13.1)

X<ACE> = (56.82 LB-Mole) / 138.21 LB-Mole
= 0.411

X<ACN> = (80.39 LB-Mole) / 138.21 LB-Mole
= 0.582

X<Other> = (1 LB-Mole) / 138.21 LB-Mole
= 0.0072

Vapor Pressure Calculations

Vapor pressure, p_i°, of each volatile component can be calculated using the Antoine equation. The Antoine equation has the general form:

$$\ln (p_i^\circ(\text{mmHg})) = [\, a - (b/(T(^\circ K) + c))\,] \quad (1.14)$$

The program calculates the vapor pressure of each volatile component using the Antoine equation in the form:

$$p_i^\circ\ (\text{mmHg}) = \exp [\, a - (b/(T(^\circ K) + c))\,] \quad (1.15)$$

Pvapor,1<vm> = exp (a<vm> - (b<vm> / (Tsystem + c<vm>))) (1.15.1)

T(°K)= T(°C)+273.15
= 21 °C+273.15
= 294.15 °K

Pvapor,1<ACE>= exp (16.82 - (2993 / (294.15 °K + (-35.63))))
= exp (5.24)
= 189.15 mmHg

Pvapor,1<ACN>= exp (16.16 - (2962 / (294.15 °K + (-44.24))))

= exp (4.31)
= 74.27 mmHg

Equilibrium Concentrations

For a system of ideal liquids and vapors at a given temperature, Raoult's Law gives a relationship to calculate the relative vapor and liquid equilibrium mole fractions.

Raoult's Law states that the partial pressure of a component, $_i$Pcan be calculated by multiplying the components vapor pressure, p_i°, by the liquid mole fraction, x_i, which is equal to the total pressure, P_{total}, multiplied by the vapor mole fraction, y_i, or:

$$P_i = p_i^{\circ}\_ * x_i = P_{total} * y_i \qquad (1.16)$$

PACMAN also includes individual Activity Coefficients for each volatile component, and an Inert Saturation Factor that is applied to the partial pressure calculation. These values are pre-set to 1 and can be changed if information is available.

Ppartial,1<v> = Pvapor,1<v> * X<v> * ac<v> * Inert Saturation Factor (1.16.1)

*Ppartial,1<ACE> = 189.15 mmHg * 0.414 * 1 * 1*
= 77.76 mmHg

*Ppartial,1<ACN> =74.27 mmHg * 0.582 * 1 * 1*
= 43.2 mmHg

The vapor mole fraction, $_{yi}$, can then be determined for each component:

$$_{yi} = p^{i\circ} * x^{i} / P^{total} \qquad (1.17)$$

The total partial pressure for the system is the sum of the partial pressures for all volatile components:

Ppartial, sum = SUM (Ppartial, 1<v>) + SUM(Ppartial, 1<m>) (1.17.1)

Ppartial, sum = SUM (77.76 mmHg +43.2 mmHg)
= 120.96 mmHg

Vapor Space

The vapor space for the system being evacuated is calculated by subtracting the volume of the liquid/solid in the vessel from the total system volume. The volume existing in the vessel is:

$$V_{Li} = M_i / \rho_i \qquad (1.20)$$

Volume,existing<vom> = (Me<vom> / density<vom>) (1.20.1)

Volume,existing<ACE> = 3300 LB / 49.44 LB/ft^3

= 66.74 ft^3

Volume,existing<ACN> = 3300 LB / 49.05LB/ft^3
= 67.28 ft^3

Volume,existing<Other> = 200 LB / 50.0 LB/ft^3
= 4.0 ft^3

The vapor space is:

$$V_{VS} = V_{system} - \Sigma V_{Li} \quad (1.21)$$

Vapor = Vsystem - SUM(Volume,existing<vom>) (1.21.1)

Vapor = 285 ft^3 *- (66.74 ft*^{3} *+ 67.27 ft*^{3} *+ 4.0 ft*^{3} *)*
= 146.98 ft^3

Step 2.

In Step 2 the mass of inert vapors being evacuated from the vessel is calculated.

The amount of evacuated inert gases is easily calculated because the number of moles of the volatile components in the vapor phase of the vessel is constant under ideal conditions throughout.

This can be explained by examining Raoult's Law and the Dalton's Law for ideal gases. By Raoult's Law:

$$x_i * p_i^\circ = P_i \quad (2.10)$$

The program model assumes that the liquid mole fraction, x_i, and the temperature are constant throughout the evacuation. Since the vapor pressure, p_i°, is only a function of temperature it is also constant. Since x_i and p_i° are constant, the partial pressure of the volatile component, P_i, is also constant.

Now, applying Dalton's Law to each volatile component yields:

$$P_i * V_{VS} = N_i * R * T \quad (2.11)$$

or $$N_i = P_i * V_{VS} / (R * T) \quad (2.12)$$

Since P_i, V_{vs}, R and T are constant, N_i, the moles of volatile component in the vapor phase, must also be a constant.

The preceding arguments show that the vapor space in the vessel always contains a constant number of moles of volatile components. Any volatile component that leaves the vessel is replaced by an equal amount from the liquid phase. This amount of evaporation is typically small when compared to the total liquid volume, therefore having little effect on the composition of the liquid (x_i's) or the volume of the vapor space (V_{VS}).

Since the vapor space always contains the same moles of volatiles, the decrease in pressure is due solely to the evacuation of inert gases.

By applying Dalton's Law to the inert component of the vapor phase:

$$P_{inert} = N_{inert} * R * T / V_{VS} \qquad (2.13)$$

The change in pressure is directly related to a change in the number of moles of inert:

$$(P_{inert}^{initial} - P_{inert}^{final}) = (N_{inert}^{initial} - N_{inert}^{final}) * (R * T/V_{VS}) \qquad (2.14)$$

Since there is no change in the partial pressure of the volatile components:

$$P_{inert}^{initial} - P_{inert}^{final} = P^{initial} - P^{final} \qquad (2.15)^{)}$$

substituting:

$$P^{initial} - P^{final} = (N_{inert}^{initial} - N_{inert}^{final}) * (R * T/V_{VS}) \qquad (2.16)$$

The number of moles inert, N_{inert}, displaced in the vessel during an evacuation step is calculated by:

$$(N_{inert}^{initial} - N_{inert}^{final}) = (P^{initial} - P^{final}) * V_{VS} / R * T) \qquad (2.17)$$

Ninert,evac = (Psystem - Pfinal) * (Vapor / (Tsystem * 999)) (2.17.1)

*Ninert,evac = (760 mmHg - 150 mmHg) * (146.98 ft^3 / (294.15 °K * 999 mmHg ft^3 /LB- Mole °K)*
= 0.305 LB-Mole

The mass of inert, M_{inert}, is calculated by multiplying the number of moles inert by its molecular weight:

$$M_{inert} = N_{inert} * MW_{inert} \qquad (2.29)$$

Mevac<i> = Ninert,evac * mw<i> (2.29.2)

*Mevac<Inert> = 0.305 LB-Mole * 28.01 LB/LB-Mole*
= 8.55 LB

To calculate the mass rate of moles evacuated, the program averages the amount of inerts evacuated over an evacuation step time:

$$m_{inert}\text{ (LB/HR)} = N_{inert}\text{ (LB-Moles)} * MW_{inert}\text{ (LB/LB-Mole)} * \frac{60\text{ (min/Hr)}}{\tau\text{ (min)}} \qquad (2.34)$$

The mass rates calculated by the program therefore are <u>average</u> rates over an entire evacuation step.

Step 3.

In Step 3, the mass of volatile components leaving are calculated.

The number of moles of volatile components leaving the vessel is related to the number of moles of inerts leaving the system, the partial pressure of the volatile component and the change in inert's partial pressure. The number of moles of a volatile component, i, leaving the system during an evacuation can calculated by the equation:

$N_i = N_{inert} * P_i / LMPD_{inert}$ (3.16)

Nevac<v> = Ninert,evac * (Ppartial,1<v> / LMPDinert,evac) (3.16.1)

*Nevac<ACE> = 0.305 LB-Mole * (77.76 mmHg / 197.32 mmHg)*
= 0.120 LB-Mole

*Nevac<ACN> = 0.305 LB-Mole * (43.2 mmHg / 197.32 mmHg)*
= 0.0668 LB-Mole

Where the log mean pressure difference of the inert components $(LMPD)_{inert}$ is calculated:

LMPDinert $= (P^{initial} - P^{final})/\ln(P^{initial} / P^{final})$inert (3.17)

LMPDinert,evac = (Psystem - Pfinal) / ln ((Psystem - Ppartial,sum) / (Pfinal - Ppartial,sum)) (3.17.1)

LMPDinert,evac = (760 mmHg - 150 mmHg) / ln ((760 mmHg - 120.96 mmHg) / (150 mmHg - 120.96 mmHg))
= (610 mmHg) / ln (639.04 / 29.04)
= 610 mmHg / (3.09 mmHg)
= 197.32 mmHg

The mass of the volatile components are related to the moles by:

$M_i = N_i * MW_i$ (3.5)

Mevac<v> = Nevac<v> * mw<v> (3.5.7)

*Mevac<ACE> = 0.12 LB-Mole * 58.08 LB / LB-Mole*
= 6.98 LB

*Mevac<ACN> = 0.0668 LB-Mole * 41.05 LB / LB-Mole*
= 2.74 LB

Step 4 - Optional

If the mass balance option has been chosen by the user, a comparison of the calculated vapor mass exiting the vessel is made against the initial liquid mass in the vessel. The calculated exiting amount is determined by steps 1 through 3.

If the calculated exiting vapor amount is greater than the vessel's initial liquid amount, the initial liquid amount is displayed in the output for the quantity per step.

The rate is determined by dividing the reported output value by the step time, giving the rate in pounds per hour:

$m_i = M_i / \tau$ (min) * (60 min/ HR) (3.6)

PACMAN PROGRAM THEORY AND SAMPLE CALCULATIONS
EMPTY VESSEL EVACUATION FOR IDEAL SYSTEMS

PROGRAM BACKGROUND AND ASSUMPTIONS

The PACMAN Program for an empty vessel evacuation step calculates the vent stream of an empty vessel (or vessel containing residual liquid) undergoing a change from a higher to a lower pressure. This program models the emission from a vessel containing a vapor phase, and which previously contained a totally miscible liquid phase. The vessel system can contain volatile, non-volatile and inert components. Volatile components appear in both the liquid and vapor phases. Non-volatile components appear only in the liquid phase, and inert components appear only in the vapor phase.

The program calculates the composition of the vapor stream leaving the vessel while maintaining vapor/liquid equilibrium. Multiple consecutive vent condensers can be used (see “PACMAN Program Theory - Vent Condenser(s)”.). A final control device, such as Regenerative Thermal Oxidizer (RTO), can be used in the vapor line (see “PACMAN Program Theory - Final Control Device.”).

1. This program assumes that the liquid is totally miscible, that is, there is only one liquid phase. Solids in solution are included in this phase; however, solids in suspension must not be included in the program since they do not effect the vapor pressure of the system.

2. The model assumes the vessel previously contained perfectly mixed, ideal liquid and vapor phases that were continuously in phase equilibrium.

3. The program calculations assume that the temperature in the vessel system is uniform and does not change over time.

4. It is also assumed that the volume of the vapor space is constant.

5. It is assumed that the residual liquid in the vessel is insignificant and is used for equilibrium composition calculations only. The vessel is essentially “empty” of liquid.

A material balance check is always completed by the program internally to prevent the quantity of an exiting vapor component from exceeding the initial vapor amount in the vessel, which may happen in situations with a large vapor space and large pressure changes. If the exiting vapor quantity exceeds the initial vapor amount, the initial vapor amount is substituted in the emission output.

PROGRAM STRUCTURE

The input information necessary to run the program is:

Molecular Weight of the inert vapors (LB/LB-mole)	28.01
Total system volume (Cu Ft, L, gal)	*285* ft^3
The evacuation step time (minutes)	45
Temperature in vessel in degrees (°C, °F, °K)	*21 °C*
Initial pressure in vessel (mmHg, in H_2O, PSIA, PSIG, kPa)	760 mmHg
Final pressure in vessel (mmHg, in H_2O, PSIA, PSIG, kPa)	*150 mmHg*
Composition of the liquid phase (LB, Kg, Liters)	*See below*

Density (*LB/ft^3*) and Molecular Weight (LB/LB-mole) of components See below
Antoine coefficients for the volatile liquid components (a, b, c) *See below*
Activity coefficient of the volatile 1 for all components
Inert saturation factor ($\leq$1) *1 for all components*

	Composition	*Density (LB/ft^3)*	*Molecular Weight (LB/LB-mole)*	*Antoine coefficients a*	*b*	*c*
Acetone	*3300 LB*	*49.44*	*58.08*	*16.82*	*2993*	*-35.63*
Acetonitrile	*3300 LB*	*49.05*	*41.05*	*16.16*	*2962*	*-44.24*
Other	*200 LB*	*50.0*	*200*			

The density, molecular weight and Antoine coefficients for the volatile, non-volatile and inert components are automatically accessed from a component data base.

The program calculations are broken down into four steps:

Step 1 - The input data is converted and the initial and final vapor compositions in the vessel are determined.

Step 2 - The mass of inert vapors being evacuated from the vessel is calculated.

Step 3 - The mass of volatile components leaving the vessel are calculated.

Step 4 - A material balance check between the calculated vapor emission quantity and initial vapor quantity in the vessel is performed and the smaller number is displayed in the emission output.

PROGRAM THEORY AND CALCULATIONS

This section will explain the theory and calculation methods for each step in the empty vessel evacuation program. A summary of the nomenclature used is located at the beginning of the Theory section.

For most calculations, three sets of equations are shown:

1. The first equation is written using generally accepted engineering nomenclature.
2. The second equation is written using PACMAN nomenclature, and is presented in BOLD Geneva font.
3. Following every PACMAN equation, as described in number two above, there are sample calculations which appear in italics.

Step 1

Unit Conversions

It is necessary to convert the units of some of the input data. PACMAN automatically converts all temperature into degrees Kelvin, all pressure to mmHg, all compositions into pounds and total system volume into cubic feet.

Temperature: input either °C, °F or °K

$T\ (°K) = t\ (°C) + 273.15$ (1.1)

$T\ (°K) = (t\ (°F) - 32)\ 5/9 + 273.15$ (1.2)

Pressure: input either mmHg, in H_2O, PSIA, PSIG or kPa

$P(\text{mmHg}) = P(\text{in } H_2O) * 1.868\ (\text{mmHg/in } H_2O)$ (1.3)

$P(\text{mmHg}) = P(\text{PSIA}) * 51.718\ (\text{mmHg/PSIA})$ (1.4)

$P(\text{mmHg}) = (\ P(\text{PSIG}) + 14.7) * 51.718\ (\text{mmHg/PSIA})$ (1.5)

$P(\text{mmHg}) = P(\text{kPa}) * 7.4983\ (\text{mmHg/kPa})$ (1.6)

Mass of components (M_i) in vessel (liquid phase): input either LB, Kg, or liters

$M_i\ (\text{LB}) = M_i\ (\text{Kg}) * 2.2046\ (\text{LB/Kg})$ (1.7)

$M_i\ (\text{LB}) = V_{Li}\ (\text{l}) * \rho_i\ (\text{LB/ft}^3) / 28.32\ \text{l/ft}^3$ (1.8)

Total system volume (V_{system}): input either ft^3, L or gal

$V_{system}\ (\text{ft}^3) = V_{system}\ (\text{L}) * 0.03532\ (\text{ft}^3/\text{L})$ (1.9)

$V_{system}\ (\text{ft}^3) = V_{system}\ (\text{gal}) * 0.13368\ (\text{ft}^3/\text{gal})$ (1.10)

Mole Fraction Calculation

Moles (L_i) of components in vessel (liquid phase):

$L_i\ (\text{LB-Mole}) = M_i\ (\text{LB}) / MW_i\ (\text{LB/LB-Mole})$ (1.11)

Nexisting<vo> = Me<vo> / mw<vo> (1.11.1)

Nexisting<ACE> = 3300 LB / 58.08 LB/LB-Mole
= 56.82 LB-Mole

Nexisting<ACN> = 3300 LB / 41.05 LB/LB-Mole
= 80.39 LB-Mole

Nexisting<Other> = 200 LB / 200 LB/LB-Mole
= 1.00 LB-Mole

Total moles (L_{total}) in vessel (liquid phase):

$L_{total}\ (\text{LB-Mole}) = \Sigma\ Li$ (1.12)

$$L_{total} = \text{SUM(Nexisting<vo>)} \qquad (1.12.1)$$

$$L_{total} = \mathit{SUM(56.82\ LB\text{-}Mole + 80.39\ LB\text{-}Mole + 1.00\ LB\text{-}Mole)}$$
$$= \mathit{138.21\ LB\text{-}Mole}$$

Mole fractions (x_i) of components in vessel (liquid phase):

$$x_i = L_i\ \text{(LB-Mole)} / L_{total}\ \text{(LB-Mole)} \qquad (1.13)$$

$$\text{X<vo> = (Nexisting<vo>) / } L_{total} \qquad (1.13.1)$$

$$\mathit{X{<}ACE{>} = (56.82\ LB\text{-}Mole) / 138.2\ LB\text{-}Mole}$$
$$= \mathit{0.411}$$

$$\mathit{X{<}ACN{>} = (80.39\ LB\text{-}Mole) / 138.21\ LB\text{-}Mole}$$
$$= \mathit{0.582}$$

$$\mathit{X{<}Other{>} = (1\ LB\text{-}Mole) / 138.21\ LB\text{-}Mole}$$
$$= \mathit{0.0072}$$

Vapor Pressure Calculations

Vapor pressure, p_i°, of each volatile component previously in the vessel can be calculated using the Antoine equation. The Antoine equation has the general form:

$$\ln (p_i^\circ(\text{mmHg})) = [\ a - (b/(T(^\circ K) + c))\ ] \qquad (1.14)$$

The program calculates the vapor pressure of each volatile component using the Antoine equation in the form:

$$p_i^\circ\ (\text{mmHg}) = \exp [\ a - (b/(T(^\circ K) + c))\ ] \qquad (1.15)$$

$$\mathbf{Pvapor,1{<}vm{>} = exp\ (\ a{<}vm{>} - (\ b{<}vm{>} / (\ Tsystem + c{<}vm{>}\ )\ )\ )} \qquad (1.15.1)$$

$$T(^\circ K) = T(^\circ C)+273.15$$
$$= 21\,^\circ C+273.15$$
$$= 294.15\ ^\circ K$$

$$\mathit{Pvapor,1{<}ACE{>}} = \exp (\ 16.82 - (\ 2993\ / (294.15\ ^\circ K + (-35.63)\ )\ )\ )$$
$$= \exp (\ 5.242559183)$$
$$= 189.15\ \text{mmHg}$$

$$\mathit{Pvapor,1{<}ACN{>}} = \exp (\ 16.16 - (\ 2962\ / (294.15\ ^\circ K + (-44.24)\ )\ )\ )$$
$$= \exp (\ 4.31\ )$$
$$= 74.27\ \text{mmHg}$$

Equilibrium Concentrations

To determine the equilibrium conditions of the vapor space of an empty vessel, the program uses the composition of the liquid last in the vessel.

For a system of ideal liquids and vapors at a given temperature, Raoult's Law gives a relationship to calculate the relative vapor and liquid equilibrium mole fractions.

Raoult's Law states that the partial pressure of a component, $_i$Pcan be calculated by multiplying the components vapor pressure, p_i°, by the liquid mole fraction, x_i, which is equal to the total pressure, P_{total}, multiplied by the vapor mole fraction, y_i, or:

$$P_i = p_i^\circ\_ * x_i = P_{total} * y_i \qquad (1.16)$$

PACMAN also includes individual Activity Coefficients for each volatile component, and an Inert Saturation Factor that is applied to the partial pressure calculation. These values are pre-set to 1 and can be changed if information is available.

Ppartial,1<v> = Pvapor,1<v> * X<v> * ac<v> * Inert Saturation Factor (1.16.1)

*Ppartial,1<ACE> =189.15 mmHg * 0.411 * 1 * 1*
= 77.76 mmHg

*Ppartial,1<ACN> =74.27 mmHg * 0.581 * 1 * 1*
= 43.20 mmHg

The vapor mole fraction, y_i, can then be determined for each component:

$$y_i = p_i^\circ * x_i / P_{total} \qquad (1.17)$$

The total partial pressure for the system is the sum of the partial pressures for all volatile components:

Ppartial, sum = SUM (Ppartial, 1<v>) + SUM(Ppartial, 1<m>) (1.17.1)

Ppartial, sum = SUM (77.76 mmHg +43.2 mmHg)
= 120.96 mmHg

Vapor Space

The vapor space for an empty vessel evacuation is the total system volume, V_{system}, as specified in the user input area.

Step 2.

In Step 2 the mass of inert vapors being evacuated from the empty vessel is calculated.

Although the vessel is empty, the program assumes that there is residual liquid in the vessel to allow the same calculation procedure to be used as is used in the evacuation program (See "PACMAN Program Theory - Evacuation for Ideal Systems" for equation derivation). Therefore, the change in pressure is directly related to the change in number of moles inert:

The change in pressure is directly related to a change in the number of moles of inert:

$$(P_{inert}^{initial} - P_{inert}^{final}) = (N_{inert}^{initial} - N_{inert}^{final}) * (R * T/V_{VS}) \qquad (2.14)$$

Since there is no change in the partial pressure of the volatile components:

$$P_{inert}^{initial} - P_{inert}^{final} = P^{initial} - P^{final} \qquad (2.15)^{)}$$

substituting:

$$P^{initial} - P^{final} = (N_{inert}^{initial} - N_{inert}^{final}) * (R * T/V_{VS}) \qquad (2.16)$$

The number of moles inert, N_{inert}, displaced in the vessel during an evacuation step is calculated by:

$$(N_{inert}^{initial} - N_{inert}^{final}) = (P^{initial} - P^{final}) * V_{VS}/ R * T) \qquad (2.17)$$

Ninert,evac,ev = (Psystem - Pfinal) * (Vsystem / (Tsystem * 999)) (2.17.2)

*Ninert,evac, ev = (760 mmHg - 150 mmHg) * (285 ft^3 / (294.15 °K * 999 mmHg ft^3 / LB-Mole °K)*
= 0.592 LB-Mole

The mass of inert, M_{inert}, is calculated by multiplying the number of moles inert by its molecular weight:

$$M_{inert} = N_{inert} * MW_{inert} \qquad (2.29)$$

Mevac,ev<i> = Ninert,evac,ev * mw<i> (2.29.3)

*Mevac,ev<Inert> = 0.592 LB-Mole * 28.01 LB/LB-Mole*
= 16.57 LB

To calculate the mass rate of moles evacuated, the program averages the amount of inerts evacuated over an evacuation step time:

$$m_{inert}\,(LB/HR) = N_{inert}\,(LB\text{-}Moles) * MW_{inert}\,(LB/LB\text{-}Mole) * \frac{60\ (min/Hr)}{\tau\ (min)} \qquad (2.34)$$

The mass rates calculated by the program therefore are average rates over an entire evacuation step.

Step 3.

In Step 3, the mass of volatile components leaving are calculated.

The number of moles of volatile components leaving the vessel is related to the number of moles of inerts leaving the system, the partial pressure of the volatile component and the change in inert's partial pressure. The number of moles of a volatile component, i, leaving the system during an evacuation can calculated by the equation:

$N_i = N_{inert} * P_i / LMPD_{inert}$ (3.16)

Nevac,ev<v> = Ninert,evac,ev * (Ppartial,1<v> / LMPDinert,evac) (3.16.3)

*Nevac. ev<ACE> = 0.592 LB-Mole * (77.76 mmHg / 197.32 mmHg)*
= 0.233 LB-Mole

*Nevac, ev<ACN> = 0.592 LB-Mole * (43.2 mmHg / 197.32 mmHg)*
= 0.129 LB-Mole

Where the log mean pressure difference of the inert components $(LMPD)_{inert}$ is calculated:

$LMPD_{inert} = (P^{initial} - P^{final})_{inert} / \ln(P^{initial} / P^{final})_{inert}$ (3.17)

LMPDinert,evac = (Psystem - Pfinal) / ln ((Psystem - **Ppartial,sum) / (Pfinal - Ppartial,sum))** (3.17.1)

LMPDinert,evac = (760 mmHg - 150 mmHg) / ln ((760 mmHg - 120.96 mmHg) / (150 mmHg - 120.96 mmHg))
= (610 mmHg) / ln (639.03 / 29.03)
= 610 mmHg / (3.091 mmHg)
= 197.32 mmHg

The mass of the volatile components are related to the moles by:

$M_i = N_i * MW_i$ (3.5)

Mevac,ev<v> = Nevac,ev<v> * mw<v> (3.5.9)

*Mevac,ev<ACE> = 0.233 LB-Mole * 58.08 LB / LB-Mole*
= 13.54 LB

*Mevac,ev<ACN> = 0.1295 LB-Mole * 41.05 LB / LB-Mole*
= 5.317 LB

Step 4

In step 4, a comparison of the calculated vapor mass exiting the vessel is made against the initial vapor mass in the vessel. (The residual liquid mass is neglected.) The calculated exiting amount is determined by steps 1 through 3.

The concentration of volatiles initially in the vapor space is calculated using the ideal gas law and the partial pressures calculated previously in Step 1:

$P_i = p_i^{\circ}\_* x_i = P_{total} * y_i$ (1.16)

and the following equation:

C°_i (Lb/ft^3) = [P_i (mmHg) * MW_i (Lb/Lb-mole)] / [R(999 mmHg-ft^3/Lb-mole K) * T(K)] (3.7)

Cinitial<v> = Ppartial,1<v> * mw<v> / (999 * Tsystem) (3.7.1)

*Cinitial<ACE> = 77.76 mmHg * 58.08 LB/LB-Mole / (999 mmHg ft^3 / LB-Mole °K * 294.15 °K)*
= 0.0154 LB/ ft^3

*Cinitial<ACN> = 43.20 mmHg * 41.05 LB/LB-Mole / (999 mmHg ft^3 / LB-Mole °K * 294.15 °K)*
= 0.0060 LB/ ft^3

The partial pressure is based on the mole fraction of liquid which was in the vessel before it was emptied. The amount or composition in the vessel before being emptied is entered by the user in the input section.

The initial mass of volatiles in the vapor space is then calculated by multiplying the concentration by the vapor space volume.

M_i (LB/Step) = [V_{system} (ft^3)] * [C°_i (LB/ft^3)] (4.1)

Memptyvesselevac<v> = Cinitial<v> * Vsystem (4.1.1)

*Memptyvesselevac<ACE> = 0.0154 LB/ ft^3 * 285 ft^3*
= 4.38 LB

*Memptyvesselevac<ACN> = 0.0060 LB/ ft^3 * 285 ft^3*
= 1.72 LB

If the calculated exiting vapor amount from Step 3 is greater than the vessel's initial vapor amount as calculated above, the initial vapor amount is displayed in the output for the quantity per step. Otherwise, the amount calculated in Step 3 is displayed in the output.

Mevac,ev,min<v> = min(Mevac,ev<v>,Memptyvesselevac<v>) (4.2)

Mevac,ev,min<ACE> = 4.38 LB

Mevac,ev,min<ACN> = 1.72 LB

The rate is determined by dividing the reported output value by the step time, giving the rate in pounds per hour:

m_i = M_i / τ (min) * (60 min/ HR) (3.6)

PACMAN PROGRAM THEORY AND SAMPLE CALCULATIONS
GAS EVOLUTION FOR IDEAL SYSTEMS

PROGRAM BACKGROUND AND ASSUMPTIONS

The PACMAN Program for a gas evolution step calculates the vent stream from a vessel undergoing a gas evolution resulting from a liquid phase reaction (or from a vessel being sparged with a gas for reaction). This program models the emission from a vessel containing a vapor phase and a totally miscible liquid phase. The vessel system can contain volatile, non-volatile and inert components. Volatile components appear in both the liquid and vapor phases. Non-volatile components appear only in the liquid phase, and inert components appear only in the vapor phase.

The program calculates the composition of the vapor stream leaving the vessel assuming the initial vapor/liquid equilibrium remains constant throughout the evolution step. Multiple consecutive vent condensers can be used (see "PACMAN Program Theory - Vent Condenser(s)".). A final control device, such as Regenerative Thermal Oxidizer (RTO), can be used in the vapor line (see "PACMAN Program Theory - Final Control Device.").

1. This program assumes that the liquid is totally miscible, that is, there is only one liquid phase. Solids in solution are included in this phase; however, solids in suspension must <u>not</u> be included in the program since they do not effect the vapor pressure of the system.

2. The model assumes the vessel contains perfectly mixed, ideal liquid and vapor phases that are continuously in phase equilibrium.

3. The program calculations assume that the temperature and pressure in the vessel system is uniform and does not change over time.

4. It is also assumed that the amount of liquid being vaporized in the vessel is small when compared to the total liquid volume, therefore the liquid composition and the volume of the vapor space can be assumed to be constant.

5. The vapor being displaced from the vessel is assumed to have the same concentration as the original vapor space.

A material balance check can be completed, if desired, to prevent the quantity of an exiting vapor component from exceeding the initial liquid amount in the vessel. If the exiting vapor quantity exceeds the initial liquid amount, the initial vapor amount is substituted in the emission output.

PROGRAM STRUCTURE

The input information necessary to run the program is:

Molecular Weight of the inert vapors (LB/LB-mole)	*28.01*
Moles of vapor being evolved (LB-moles)	*1*
The reaction step time (minutes)	*30*
Total system volume (Cu ft, L, gal)	*285* ft^3
Temperature in vessel (°C, °F, °K)	*21 °C*
Pressure in vessel (mmHg, in H_2O, PSIA, PSIG, kPa)	*800 mmHg*
Composition of the liquid phase (LB, Kg, Liters)	*See below*
Density (LB/ ft^3) and Molecular Weight (LB/LB-mole) of components	*See below*
Antoine coefficients for the volatile liquid components (a, b, c)	*See below*
Activity coefficient of the volatile	1 for all components
Inert Saturation factor (≤ 1)	*1 for all components*

	Composition	*Density*	*Molecular Weight*	*Antoine coefficients*		
		(LB/ft^3)	*(LB/LB-mole)*	*a*	*b*	*c*
Acetone	*3300 LB*	*49.44*	*58.08*	*16.82*	*2993*	*-35.63*

Acetonitrile	*3300 LB*	*49.05*	*41.05*		*16.16*	*2962*	*-44.24*
Other	*200 LB*	*50.0*	*200*				

The density, molecular weight and Antoine coefficients for the volatile, non-volatile and inert components are automatically accessed from a component data base.

The program calculations are broken down into four steps:

Step 1 -The input data is converted and the initial and final vapor compositions in the vessel are determined.

Step 2 -The mass of inert vapors being displaced from the vessel is calculated.

Step 3 -The mass of volatile components leaving the vessel is calculated.

Step 4 -Optional: A material balance check between the calculated emission vapor quantity and initial liquid quantity in the vessel is performed and the smaller number is displayed in the emission output.

PROGRAM THEORY AND CALCULATIONS

This section will explain the theory and calculation methods for each step in the gas evolution program. A summary of the nomenclature used is located at the beginning of the Theory section.

For most calculations, three sets of equations are shown:

1. The first equation is written using generally accepted engineering nomenclature.
2. The second equation is written using PACMAN nomenclature, and is presented in BOLD Geneva font.
3. Following every PACMAN equation, as described in number two above, there are sample calculations which appear in italics.

Step 1

Unit Conversions

It is necessary to convert the units of some of the input data. PACMAN automatically converts all temperature into degrees Kelvin, all pressure to mmHg, all compositions into pounds and total system volume into cubic feet.

Temperature: input either °C, °F or °K

$$T\ (^\circ K) = t\ (^\circ C) + 273.15 \qquad (1.1)$$

$$T\ (^\circ K) = (t\ (^\circ F) - 32)\ 5/9 + 273.15 \qquad (1.2)$$

Pressure: input either mmHg, in H_2O, PSIA, PSIG or kPa

$P(\text{mmHg}) = P(\text{in } H_2O) * 1.868\ (\text{mmHg/in } H_2O)$ (1.3)

$P(\text{mmHg}) = P(\text{PSIA}) * 51.718\ (\text{mmHg/PSIA})$ (1.4)

$P(\text{mmHg}) = (P(\text{PSIG}) + 14.7) * 51.718\ (\text{mmHg/PSIA})$ (1.5)

$P(\text{mmHg}) = P(\text{kPa}) * 7.4983\ (\text{mmHg/kPa})$ (1.6)

Mass of components (M_i) in vessel (liquid phase): input either LB, Kg, or liters

$M_i\ (\text{LB}) = M_i\ (\text{Kg}) * 2.2046\ (\text{LB/Kg})$ (1.7)

$M_i\ (\text{LB}) = V_{Li}\ (\text{l}) * \rho_i\ (\text{LB/ft}^3) / 28.31685\ \text{l/ft}^3$ (1.8)

Total system volume (V_{system}): input either ft^3, L or gal

$V_{system}\ (\text{ft}^3) = V_{system}\ (\text{L}) * 0.03532\ (\text{ft}^3/\text{L})$ (1.9)

$V_{system}\ (\text{ft}^3) = V_{system}\ (\text{gal}) * 0.13368\ (\text{ft}^3/\text{gal})$ (1.10)

Mole Fraction Calculation

Moles (L_i) of components in vessel (liquid phase):

$L_i\ (\text{LB-Mole}) = M_i\ (\text{LB}) / MW_i\ (\text{LB/LB-Mole})$ (1.11)

Nexisting<vo> = Me<vo> / mw<vo> (1.11.1)

Nexisting<ACE> = 3300 LB / 58.08 LB/LB-Mole
= 56.82 LB-Mole

Nexisting<ACN> = 3300 LB / 41.05 LB/LB-Mole
= 80.39 LB-Mole

Nexisting<Other> = 200 LB / 200 LB/LB-Mole
= 1.00 LB-Mole

Total moles (L_{total}) in vessel (liquid phase):

$L_{total}\ (\text{LB-Mole}) = \Sigma\ Li$ (1.12)

Ltotal = SUM(Nexisting<vo>) (1.12.1)

Ltotal = SUM(56.82 LB-Mole + 80.39 LB-Mole + 1.00 LB-Mole)
= 138.21 LB-Mole

Mole fractions (x_i) of components in vessel (liquid phase):

$x_i = L_i$ (LB-Mole) / L_{total} (LB-Mole) (1.13)

X<vo> = (Nexisting<vo>) / Ltotal (1.13.1)

X<ACE> = (56.82 LB-Mole) / 138.21 LB-Mole
= 0.41

X<ACN> = (80.39 LB-Mole) / 138.21 LB-Mole
= 0.582

X<Other> = (1 LB-Mole) / 138.21 LB-Mole
= 0.00724

Vapor Pressure Calculations

Vapor pressure, p_i°, of each volatile component can be calculated using the Antoine equation. The Antoine equation has the general form:

$\ln (p_i^{\circ}(\text{mmHg})) = [\ a - (b/(T(^{\circ}K) + c))\ ]$ (1.14)

The program calculates the vapor pressure of each volatile component using the Antoine equation in the form:

$p_i^{\circ}\ (\text{mmHg}) = \exp\ [\ a - (b/(T(^{\circ}K) + c))\ ]$ (1.15)

Pvapor,1<vm> = exp (a<vm> - (b<vm> / (Tsystem + c<vm>))) (1.15.1)

T(°K)= T(°C)+273.15
= 21 °C+273.15
= 294.15 °K

Pvapor,1<ACE> = exp (16.82 - (2993 / (294.15 °K + (-35.63))))
= exp (5.24)
= 189.15 mmHg

Pvapor,1<ACN> = exp (16.16 - (2962 / (294.15 °K + (-44.24))))
= exp (4.31)
= 74.27 mmHg

Equilibrium Concentrations

For a system of ideal liquids and vapors at a given temperature, Raoult's Law gives a relationship to calculate the relative vapor and liquid equilibrium mole fractions.

Raoult’s Law states that the partial pressure of a component, $_i$Pcan be calculated by multiplying the components vapor pressure, p_i°, by the liquid mole fraction, x_i, which is equal to the total pressure, P_{total}, multiplied by the vapor mole fraction, y_i, or:

$P_i = p_i^{\circ}\_ * x_i = P_{total} * y_i$ (1.16)

PACMAN also includes individual Activity Coefficients for each volatile component, and an Inert Saturation Factor that is applied to the partial pressure calculation. These values are pre-set to 1 and can be changed if information is available.

Ppartial,1<v> = Pvapor,1<v> * X<v> * ac<v> * Inert Saturation Factor (1.16.1)

*Ppartial,1<ACE> =189.15 mmHg * 0.41 * 1 * 1*
= 77.76 mmHg

*Ppartial,1<ACN> =74.27 mmHg * 0.582 * 1 * 1*
= 43.2 mmHg

The vapor mole fraction, y_i, can then be determined for each component:

$y_i = p_i^\circ * x_i / P_{total}$ (1.17)

The total partial pressure for the system is the sum of the partial pressures for all volatile components:

Ppartial, sum = SUM (Ppartial, 1<v>) + SUM (Ppartial, 1<m>) (1.17.1)

Ppartial, sum = SUM (77.76 mmHg +43.2 mmHg)
= 120.96 mmHg

The volatile and inert vapor partial pressures are related by:

$P_{total} = \{\text{Sum of } P_i\} + P_{inert}$ (1.18)

The partial pressure of the inert component can be calculated by:

$P_{inert} = P_{total} - \{\text{Sum of } P_i\}$ (1.19)

Pinert,1 = Psystem - Ppartial,sum (1.19.1)

Pinert,1 = 800 mmHg - 120.96 mmHg
= 679.04 mmHg

Vapor Space

The vapor space for the system is calculated by subtracting the volume of the liquid/solid in the vessel from the total system volume. The volume existing in the vessel is:

$V_{Li} = M_i / \rho_i$ (1.20)

Volume,existing<vom> = (Me<vom> / density<vom>) (1.20.1)

Volume,existing<ACE> = 3300 LB / 49.44 LB/ft^3
= 66.74 ft^3

Volume,existing<ACN> $= 3300\ LB / 49.051 LB/ft^3$
$= 67.28\ ft^3$

Volume,existing<Other> $= 200\ LB / 50.0\ LB/ft^3$
$= 4.0\ ft^3$

The vapor space is:

$$V_{VS} = V_{system} - \Sigma V_{Li} \qquad (1.21)$$

Vapor = Vsystem - SUM(Volume,existing<vom>) (1.21.1)

Vapor $= 285\ ft^3 - (66.74\ ft^3 + 67.28\ ft^3 + 4.0\ ft^3)$
$= 146.98\ ft^3$

Step 2.

In Step 2 the mass of inert vapors being displaced from the vessel is calculated.

It is assumed that the gas evolved produces an increase in vapor volume, thus forcing vapor from the vessel. The vapor being displaced from the vessel is assumed to have the same concentration as the original vapor space, which is in equilibrium with the original liquid components of the vessel.

Applying Dalton's Law to the volatile and inert components, the moles of each component originally in the vapor space can be calculated:

$$P_i * V_{VS} = N_i * R * T \qquad (2.11)$$

or

$$N_i = P_i * V_{VS} / (R * T) \qquad (2.12)$$

Nge<v> = (Ppartial,1<v> * Vapor) / (999 * Tsystem) (2.12.1)

Nge<ACE> $= (77.76\ mmHg * 146.98\ ft^3) / (999\ mmHg\ ft^3 / LB\text{-}Mole\ °K * 294.15\ °K)$
$= 0.0389\ LB\text{-}Mole$

Nge<ACN> $= (43.20\ mmHg * 146.98\ ft^3) / (999\ mmHg\ ft^3 / LB\text{-}Mole\ °K * 294.15\ °K)$
$= 0.0216\ LB\text{-}Mole$

and: **Ninert,ge = (Pinert,1 * Vapor) / (999 * Tsystem)** (2.12.2)

Ninert,ge $= (679.036\ mmHg * 146.98\ ft^3) / (999\ mmHg\ ft^3 / LB\text{-}Mole\ °K * 294.15\ °K)$
$= 0.34\ LB\text{-}Mole$

Since the moles of gas evolved during the reaction is known, a theoretical total number of moles is calculated as:

$$N_{total} = N_{inert}^{initial} + \Sigma N_i^{initial} + N_{evolved} \qquad (2.18)$$

Ntotal = Ninert,ge + SUM(Nge<v>) + Nevolved (2.18.1)

Ntotal = 0.34 LB-Mole + (Nge<ACE> + Nge<ACN>) + 1.0 LB-Mole
= 0.34 LB-Mole + (0.0389 LB-Mole + 0.022 LB-Mole) + 1.0 LB- Mole
= 0.34 LB-Mole + 0.060 LB-Mole + 1.0 LB-Mole
= 1.40 LB-Mole

From this number of moles, a theoretical vapor volume is calculated at the temperature and pressure of the vessel contents.

$V_{total} = N_{total} * R * T / P$ (2.19)

Vtheoretical = Ntotal * 999 * Tsystem / Psystem (2.19.1)

Vtheoretical = 1.400 LB-Mole * 999 mmHg ft^3 / LB-Mole °K * 294.15 °K / 800 mmHg
= 514.30 ft^3

Since the vapor space in the vessel is assumed constant, the volume of the gas displaced from the vessel must be the difference between the theoretical total volume and the volume of the vessel vapor space.

$V_{displaced} = V_{total} - V_{VS}$ (2.20)

Vdisplaced = Vtheoretical - Vapor (2.20.1)

Vdisplaced = 514.30 ft^3 - 146.98 ft^3
= 367.32 ft^3

The program assumes that this volume of vapor displaced has the same composition as the original vapor in the vessel. Therefore, the moles of inert vapor displaced can be calculated using Dalton's Law:

$N_{inert\ displaced} = P_{inert} * V_{displaced} / (R*T)$ (2.21)

Ninert,ge,dis = Pinert,1 * Vdisplaced / (999 * Tsystem) (2.21.1)

*Ninert,ge,dis = 679.037 mmHg * 367.32 ft^3 / (999 mmHg ft^3 / LB-Mole °K * 294.15 °K)*
= 0.849 LB-Mole

The mass of the inert vapors can be calculated by:

$M_{inert\ displaced} = N_{inert\ displaced} * MWinert$ (2.35)

Mge<i> = Ninert,ge,dis * mw<i> (2.35.1)

Mge<Inert> = 0.849 LB-Mole * 28.01LB/LB-Mole
= 23.77 LB

The mass rate of the inert, m_{inert}, can be calculated from the molecular weight:

$$m_{inert} = N_{inert\,displaced}\ (\text{LB-mole}) * MW_{inert}\ (\text{LB/LB-mole}) * \frac{60\ (\text{min/HR})}{\tau\ (\text{min})} \qquad (2.48)$$

Step 3.

In Step 3, the mass of volatile components leaving are calculated.

The number of moles of volatile components leaving the vessel is calculated in an analogous way to the number of moles of inert vapor leaving the vessel. It is assumed that the vapor displaced has the same equilibrium composition of the original vapor space.

Therefore the moles of volatile compounds being displaced from the vessel is calculated using Dalton's Law:

$$N_{i\ displaced} = P_i * V_{displaced} / (R*T) \qquad (3.18)$$

Nge,dis<v> = Ppartial,1<v> * Vdisplaced / (999 * Tsystem) (3.18.1)

Nge,dis<ACE> = *77.76 mmHg * 367.32* ft^3 */ (999 mmHg* ft^3 */ LB-Mole °K * 294.15 °K)*
= 0.097 LB-Mole

Nge,dis<ACN> = 43.20 mmHg * 367.32 ft^3 / (999 mmHg ft^3 / LB-Mole °K * 294.15 °K)
= 0.054 LB-Mole

The mass of the volatile vapors can be calculated by:

$$M_i = N_i * MW_i \qquad (3.5)$$

Mge<v> = Nge,dis<v> * mw<v> (3.5.11)

*Mge<ACE> = 0.097 LB-Mole * 58.08 LB/LB-Mole*
= 5.646 LB

*Mge<ACN> = 0.054 LB-Mole * 41.05 LB/LB-Mole*
= 2.217 LB

Step 4 - Optional

If the mass balance option has been chosen by the user, a comparison of the calculated vapor mass exiting the vessel is made against the initial liquid mass in the vessel. The calculated exiting amount is determined by steps 1 through 3.

If the calculated exiting vapor amount is greater than the vessel's initial liquid amount, the initial liquid amount is displayed in the output for the quantity per step.

The rate is determined by dividing the reported output value by the step time, giving the rate in pounds per hour:

$$m_l = M_i / \tau \text{ (min)} * \text{(60 min/ HR)} \qquad (3.6)$$

Vent Condensers

The theory of vent condensers in PACMAN is addressed through these topics:

- Program background and assumptions
- Program structure
- Program theory and calculations
- Program equations

Program Background and Assumptions

The user can designate multiple consecutive vent condensers for each emission step calculation in the PACMAN program. The vent condenser calculation can only be used in conjunction with an emission step calculation and is not a stand-alone program.

The vent condenser calculation determines the vapor/liquid equilibrium composition leaving each vent condenser.

1. The streams leaving the condenser(s) are calculated assuming ideal liquid and vapors in equilibrium at a given temperature and pressure.

2. The inert vapors entering the condenser(s) are considered non-condensables.

Program Structure

The input information necessary to run the program is:

- Temperature of streams leaving the first condenser (8C, °F, °K)
- Pressure of streams leaving the first condenser (mmHg, in H2O, PSIA, PSIG, kPa)
- Temperature of streams leaving the second condenser (8C, °F, °K)
- Pressure of streams leaving the second condenser (mmHg, in H2O, PSIA, PSIG, kPa)
- Mass of each vapor component leaving vessel (LB)
- Molecular weight of each component (LB/LBmole)
- Antoine coefficients for each volatile component (a,b,c)
- Step time (minutes)

The molecular weights, Antoine coefficients and step time are the same as specified in the emission step input information. The mass of each component leaving the vessel (inert and volatile) is the result of the associated emission step calculation.

The program calculations are broken down into four steps:

Step 1 - The input temperature and pressure data is converted.

Step 2 - The vapor/liquid equilibrium is determined using an iterative procedure.

Step 3 - The vapor composition leaving the vent condenser is calculated.

Step 4 -

Optional: A material balance check between the calculated emission vapor quantity and initial liquid quantity in the vessel is performed and the smaller number is displayed in the emission output.

If multiple vent condensers are designated, the program repeats the calculation using the mass of each vapor component leaving the previous condenser. The inert mass entering and leaving each condenser is constant (non-condensable).

Program Theory and Calculations

This section will explain the theory and calculation methods for the vent condenser program. A summary of the nomenclature used is located at the beginning of the Theory section.

For most calculations, two sets of equations are shown:

1. The first equation is written using generally accepted engineering nomenclature.
2. The second equation is written using PACMAN nomenclature, and is presented in BOLD Geneva font.

Step 1

Unit Conversions

It is necessary to convert the units of some of the input data. PACMAN automatically converts all temperature into degrees Kelvin and all pressure into mmHg.

Temperature: input either °C, °F or °K

T (8K) = t (8C) + 273.15 (1.1)

T (°K) = (t (°F) - 32) 5/9 + 273.15 (1.2)

Pressure: input either mmHg, in H2O, PSIA, PSIG or kPa

P(mmHg) = P(in H2O) * 1.868 (mmHg/in H2O) (1.3)

P(mmHg) = P(PSIA) * 51.718 (mmHg/PSIA) (1.4)

P(mmHg) = (P(PSIG) + 14.7) * 51.718 (mmHg/PSIA) (1.5)

P(mmHg) = P(kPa) * 7.4983 (mmHg/kPa) (1.6)

Step 2.

Step 2 calculates the vapor and liquid equilibrium leaving the vent condensers at a given temperature and pressure.

First, the vapor pressures of the volatile components are calculated at the desired condensation temperature. The vapor pressures are calculated using the Antoine equation:

pi8 (mmHg) = exp [a - (b/(T(8K) + c))] (1.15)

Pvapor,1<vm> = exp (a<vm> - (b<vm> /
(Tsystem + c<vm>))) (1.15.1)

Kideal for each component is calculated:

Kideal = pi8 / P (2.37)

Kideal<vm> = Pvapor,1<vm> / Psystem (2.37.1)

To find the equilibrium vapor and liquid compositions, the mass balance is solved in an iterative fashion.

The total number of moles entering the condenser is equal to the sum of the liquid and vapor moles leaving the condenser.

Z = V + L (2.38)

Likewise for each component:

Zi = Vi + Li where Li = 0 for inerts (2.39)

or: Zi = (V*yi) + (L*xi) for volatile components (2.40)

Zi = (V*yi) for inert component (2.41)

Making the substitution of yi = Kideal * xi, for volatile components:

Zi = (V*xi*Kideal) + (L*xi) (2.42)

which can be arranged to yield:

Zi/{(V/L)Kideal + 1 } = Li (2.43)

To solve the mass balance for the number of moles in the liquid and vapor phases:

1. Assume a V/L ratio (where V is total molar volume including the inert gases)

2. Calculate the liquid moles of each volatile component by:

   Li= Zi/{(V/L)Kideal + 1 } (2.43)

3. Calculate the vapor moles of each volatile component by:

   Vi = Zi - Li (2.44)

4. The moles of inerts out of condenser is equal to the moles into the condenser, which has been calculated previously.

5. Sum the volatile component liquid moles (L) and the volatile and inert component vapor moles (V) and compute the ratio V/L.

6. The computed V/L is compared to the assumed V/L. If they are not equal a new iteration is performed using the calculated V/L.

PACMAN does this in the following fashion:

1. The mass of each component leaving the vessel (or leaving the previous condenser) is converted back to moles:

   N<i> = Mi<i> / mw<i> (2.45)

   and N<vm> = Mi<vm> / mw<vm> (2.46)

2. The "converge" function is used to do the iterative procedure outlined above. The vapor phase moles are the result of the calculation:

   V<vm> = converge(Kideal<vm>, N<vm>, N<i>) (2.47)

Step 3.

The mass of each component is related to its moles by:

Mi = Vi * MWi (3.20)

Mcondenser<vm> = V<vm> * mw<vm> (3.20.1)

Since the inerts do not condense:

Mout<i> = Mi<i> (3.20.2)

This iterative procedure is applied to all condensers, consecutively.

Step 4. - Optional

If the mass balance option has been chosen by the user, a comparison of the calculated vapor mass exiting the condenser is made against the initial liquid mass in the vessel. The calculated exiting amount is determined by steps 1 through 3.

If the calculated exiting vapor amount is greater than the vessel's initial liquid amount, the initial liquid amount is displayed in the output for the quantity per step.

For multiple condensers, this comparison is completed after each condenser.

The rate is determined by dividing the reported output value by the step time, giving the rate in pounds per hour:

mi = Mi / _ (min) * (60 min/ HR) (3.6)

Program Equations

<none given>

Final Control Devices

The theory of final control devices in PACMAN is addressed through these topics:

- Program background and assumptions
- Program structure
- Program theory and calculations
- Program equations

Program Background and Assumptions

The user can designate a final control device for each emission step calculation in the PACMAN program. The final control device calculation can only be used in conjunction with an emission step calculation and is not a stand-alone program.

This calculation determines the vapor composition leaving the final control device.

1. The program assumes that the inert is unchanged by the final control device.

2. Each volatile component has a unique control efficiency in the final control device.

Program Structure

The input information necessary to run the program is:

- Mass of each volatile component entering the final control device (LB)
- Volatile component control efficiency (_1)
- Step time (minutes)

The mass of each volatile component entering the final control device is the same as the mass of each volatile component leaving the previous control device or vessel. This is the result of the associated emission step calculation.

Program Theory and Calculations

The program calculation consists of a single step. The mass of each volatile entering the final control device is multiplied by 1 minus the control efficiency:

Mout,i = Mi * (1 - eff) (1.22)

The rate is determined by dividing the reported output value by the step time, giving the rate in pounds per hour:

mout,i = (Mout,i * (60 min/HR)) / _ (minutes) (1.23)

Program Equations

<none given>

PACMAN PROGRAM THEORY AND SAMPLE CALCULATIONS
FUGITIVE EMISSIONS

PROGRAM BACKGROUND

The fugitive emission program calculates the quantity of VOCs emitted from pump and agitator seals, connectors, liquid valve seals, vapor valve seals, and pressure relief valves. Fugitive emissions for process streams carrying hydrocarbon vapors and liquids are estimated by the use of emission factors, Lbs./Hr./Component. The emission rate of each VOC is determined by multiplying the emission factor by the number of components, and mass fraction of VOC within the component.

The program allows for the choice of emission factors. Four choices are available which are: 1) EPA SOCMI factors, 2) Lilly standard LDAR factors, 3) LeakDAS factors and 4)Ad hoc factors. The LeakDAS factors are not available from PACMAN at this time. The ad hoc factors enables the user to evaluate the emission rates using other factors.

Comparison of the emission factors are tabulated below:

EMISSION FACTORS LB/HR/COMPONENT

Method	Pumps & Agitators	Connectors	Liquid Valves	Gas Valves	Pressure Relief Valves
1	**0.108908**	**0.001830**	**0.015653**	**0.012346**	**0.229281**
2	**0.004969**	**0.000697**	**0.001459**	**0.000309**	**0.229281**
3					**0.229281**

Note: LeakDAS factors will be supplied by the LeakDAS program (at a later date and the Ad hoc factors are user generated.

PROGRAM STRUCTURE

The information necessary to run the program is:

Time in service per batch (Hrs. or Min.) - This is the time the component is in contact with the VOC.
10 Hours

Weight fraction of VOCs
Ethanol - 0.25
Methanol - 0.25
Methylene Chloride - 0.3

Number of components, ie; pumps/agitators, connectors, liquid valves, vapor valves, and pressure relief devices.
Pumps - 2
Agitators - 2
Connectors - 25
Liquid valves - 10
Gas valves - 5
Pressure relief valves - 2

Emission Factors
From table above (EPA SOCMI Factors)

Total hours per reporting period (needed to run Process Emission Summary Report, will be recorded in step note)
60 Hours

Number of batches per reporting period (needed to run Process Emission Summary Report, will be recorded in step note)
5 Batches

Building or equipment to which the fugitive emissions are attributed.
C66

The program calculations are broken down into four steps:

Step 1 - The Emission Rate (lbs. / hr.) - For each component type is calculated.

Step 2 - The Total Emission Rate (lbs. / hr.) - Sum of the emission rates from each components is calculated.

Step 3 - The Total Emissions (lbs.) - The total emission are calculated from the total emission rate and the step time.

Step 4 - The Emissions for Each Compound (lbs.) - Emissions based on weight fraction is calculated.

PROGRAM THEORY AND CALCULATIONS

This section explains the calculation methods for each step in the fugitive emission program.

The program allows for the choice of four sets of emission factors for the various components. If method 1 is chosen, the EPA supplied SOCMI numbers are used for the emission factors. If method 2 is chosen, the Lilly standard LDAR factors are used. If method 3 is chosen, the user supplies the factors for all the components except for pressure relief valves. Method 4 is currently unavailable, LeakDAS will supply these factors. The pressure relief valve factor can not be changed and is constant for all three methods.

Step 1

Emission Rate

The emission rate for each component is the total emissions for each component type, valve, connector, etc.

Emission Rate [lbs. / hr.] = Component Count * Emission Factor [(lbs. / hr.) / component] (1.0)

Note: for the purpose of this hand calculation the EPA SOCMI emission factors have been used.

*Emission Rate lbs. / hr. (Pumps) = 2 * 0.108908 lbs. / hr. / component*
= 0.218 lbs. / hr.

Emission Rate lbs. / hr. (Agitators) = 2 * 0.108908 lbs. / hr. / component
= 0.218 lbs. / hr.

Emission Rate lbs. / hr. (Connectors) = 25 * 0.001830 lbs. / hr. / component
= 0.0458 lbs. / hr.

Emission Rate lbs. / hr. (Liquid Valves) = 10 * 0.015653 lbs. / hr. / component
= 0.156 lbs. / hr.

Emission Rate lbs. / hr. (Gas Valves) = 5 * 0.012346 lbs. / hr. / component
= 0.0617 lbs. / hr.

Emission Rate lbs. / hr. (Press. Relief = 2 * 0.229281 lbs. / hr. / component
Valves) = 0.459 lbs. / hr.

Step 2

Total Emission Rate

The total emission rate is the sum of the individual emission rates for each component type during the step.

Total Emission Rate [lbs. / hr.] = Σ Emission Rate [lbs. / hr.] (2.0)
(for each component type)

Total Emission Rate lbs. / hr. = 0.217816 lbs. / hr. + 0.217816 lbs. / hr. + 0.04575 lbs. / hr. + 0.15653 lbs. / hr. + 0.06173 lbs. / hr. + 0.458562 lbs. / hr.

= *1.158 lbs. / hr.*

Step 3

Total Emissions

The total emissions are the total of all the emissions from all the component types based on the step time.

Total Emissions [lbs.] = Total Emission Rate [lbs. / hr.] * (3.0)
Time in service per batch [hr.]

*Total Emissions = 1.158 lbs. / hr. * 10 hrs.*
= 11.58 lbs

If the step time is entered in minutes a factor of 1 hr. / 60 min. will be used to obtain hours.

Step 4

Emission Quantity (by Compound)

The emissions for each compound is the total emissions multiplied by the mass fraction for that compound.

Emission Quantity $_i$ (by Compound) [lbs.] = Total Emissions [lbs.] * Mass Fraction $_i$ (4.0)

Emission Quantity (Ethanol) = 11.58 lbs. * 0.25
= 2.89 lbs.

Emission Quantity (Methanol). = 11.58204 lbs. * 0.25
= 2.89 lbs.

Emission Quantity = *11.58204 lbs. * 0.3*
(Methylene Chloride) = *3.47 lbs.*

The total hours per reporting period and the number of batches per reporting period are used to generate the Process Emission Summary Report in PACMAN. This report which, based on the number of lots and the total time in the reporting period, will list the emissions by material and material class in pounds and the average rate in pounds per hour.

TANK FARM WORKING LOSS EMISSIONS
SAMPLE CALCULATION

SUMMARY:

1. BASIS OF CALCULATION IS AP42.
2. THESE CALCULATIONS ARE FOR WORKING LOSS EMISSIONS WHEN LOADING TANKS WITH SOLVENTS

EMISSION FORMULA PER AP-42 :

$$L_w = (2.4 * 10^{-5})\ MW\ P_V\ V\ N\ K_N\ K_C$$

WHERE : L_w = Emission rate (lb/year)

mw = Vapor molecular weight (lb/lbmole)

F_V = Vapour pressure of the VOC (PSIA)

V = Tank Capacity (gal)

N = number of tank turnovers per year

$$= \frac{\text{Total Throughput per year(gal)}}{\text{Tank capacity (gal)}}$$

K_N = Turnover factor (see figure 4.3-7 of AP42)
= 1 for N < 30

K_C = Product factor
1 for all organic liquids other than crude oil

WORKING LOSS SAMPLE CALCULATION

ACETONE STORAGE TANK (TK-210)

ASSUME : STORAGE TEMPERATURE OF 25 ^{OC}
MW = 58.081
P_V = 4.34 PSIA AT 25 ^{OC}

HORIZONTAL TANK

TANK CAPACITY V = 38,500 GALLONS
TOTAL THROUGHPUT OF ACE = 894,373 GAL/YEAR
NO. OF TURNOVERS, N = $\frac{894,373}{38,500}$
= 23.23

EMISSION LOSS :

LW = (2.4 X $10^{-5)}$ (58.081)(4.34)(38,500)(23.23)(1)(1)
= 5410.6 LB/YEAR
= 2.70 TONS / YEAR

TANK FARM BREATHING LOSS EMISSIONS
SAMPLE CALCULATION

SUMMARY:

1. BASIS OF CALCULATION IS AP42.
2. CALCULATIONS ARE BASED ON ACETONE
2. THESE CALCULATIONS ARE FOR BREATHING LOSS EMISSIONS DUE TO TEMPERATURE VARIATIONS.

TANK LOCATION: INDOORS, HEATED IN WINTER TO MAINTAIN MINIMUM TEMPERATURE OF 40^0 F

TANK TYPE HORIZONTAL
HORIZONTAL TANKS : USE EQUIVALENT D_{eqv} AND H_{eqv}
D_{eqv} = $(4DL/Pi)^{0.5}$
H_{eqv} = (D*Pi/8)

WHERE : D = ACTUAL TANK DIAMETER (FT)
L = ACTUAL TANK LENGTH (FT)
Pi = 3.14

EMISSION FORMULA PER AP-42 :

$$\mathbf{Lb = (2.26 * 10^{-2)} MW (P_v/P_a\text{-}P_v)^{0.68} *D_{eqv}^{1.73}H_{eqv}^{0.51}\ T^{0.5}F_pCK_c}$$

WHERE:
Lb = EMISSION RATE (LB/YEAR)
MW = VAPOR MOLECULAR WEIGHT (LB/LBMOLE)
Pv = VAPOR PRESSURE OF THE VOC (PSIA)
Pa = ATMOSPHERIC PRESSURE (14.69 PSIA)
Deqv = EQUIVALENT DIAMETER (FT)
Heqv = EQUIVALENT HEIGHT (FT)
T = AVERAGE DIURNAL TEMPERATURE CHANGE (20^0 F)
Fp = PAINT FACTOR (ASSUME 1.0)
C = SMALL DIAMETER ADJUSTMENT FACTOR
Kc = PRODUCT FACTOR
1 FOR ALL ORGANIC LIQUIDS OTHER THAN CRUDE OIL

<u>BREATHING LOSS SAMPLE CALCULATION</u>

<u>ACETONE STORAGE TANK (TK-210)</u>

ASSUME = STORAGE TEMPERATURE OF 25^OC

MW = 58.081

P_V = 4.34 PSIA AT 25^OC

<u>HORIZONTAL TANK:</u>

TANK CAPACITY = 38,500 GALLONS

TANK DIMENSION = 12.75 ' OD X 42 ' L

D_{eqv} = $[\ 4(12.75)(42)/3.14\ ]^{0.5}$
= 26.118 ft

H_{eqv} = (3.14*12.75)/8
= 5.0 ft

BASED ON D_{eqv} 26.118 FT ; C FACTOR = 0.998

<u>EMISSION LOSS:</u>

Lb = $(2.26 \text{ X } 10^{-2})(58.081)[4.34/(14.69-4.34)]^{0.68}$
$(26.118)1.73\ (5.0)^{0.51}(20)^{0.5}\ (1.0)(0.998)(1.0)$
= 2084.00 LB/YEAR
=1.04 TONS/YEAR

SAMPLE FUGITIVE EMISSION CACULATIONS
BASED ON SOCMI EMISSION FACTORS

E_F = NFTW

WHERE:

N = NUMBER OF COMPONENTS IN SYSTEM (i.e. number of flanges, valves, & pumps)

F = SOCMI COMPONENTS EMISSION FACTOR, LB/HR/SOURCE

T = ANNUAL OPERATING TIME, HOURS

W = WEIGHT FRACTION OF VOC, (NOT APPLICABLE FOR VALVE CALCULATIONS AS A UNIQUE FACTOR EXISTS FOR VALVES IN VAPOR SERVICE)

SAMPLE CALCULATION BASED ON TANK 210-ACETONE :

FLANGE FUGITIVE EMISSIONS (LIQUID)

N = 79 CONNECTORS
F = 0.00183 LB/HR/SOURCE
T = 8760 HOURS
W = 1 FOR LIQUIDS
E_F = (79)(0.00183 LB/HR/SOURCE)(8760HR)(1)

E_F (liquid flanges) = 1266.43 LB

VALVE FUGITIVE EMISSIONS (LIQUID)

N = 9 VALVES
F = 0.015653 LB/HR/SOURCE
T = 8760 HOURS
W = NOT APPLICABLE
E_F = (9)(0.015653 LB/HR/SOURCE)(8760HR)

E_F(liquid valves)= 1234.08 LB

TOTAL FUGITIVE EMISSIONS (LIQUID)

E_F (total) = E_F (liquid flanges) + E_F (liquid valves)
E_F (total) = 1266.43 LB + 1234.08 LB
E_F (total) = 2500.51 LB

Indiana Department of Environmental Management
Office of Air Management

Addendum to the
Technical Support Document for New Construction and Operation

Source Name:	Eli Lilly and Company
Source Location:	10500 S. St. Rd. 63, Clinton, IN 47842
County:	Vermillion
Construction Permit No.:	CP 165-9135
SIC Code:	2833
Permit Reviewer:	Dr. T. P. Sinha

On December 17, 1997, the Office of Air Management (OAM) had a notice published in the Daily Clintonion, Clinton, Indiana, stating that Eli Lilly and Company had applied for a construction permit relating to the construction and operation of synthesized pharmaceutical manufacturing facilities, with regenerative thermal oxidizers, and condensers, as VOC emissions controls, involved in the production of three intermediate processes of the Cefaclor production process. The notice also stated that OAM proposed to issue a permit for this installation and provided information on how the public could review the proposed permit and other documentation. Finally, the notice informed interested parties that there was a period of thirty (30) days to provide comments on whether or not this permit should be issued as proposed.

On January 16, 1998, Eli Lilly and Company submitted comments on the proposed construction permit. The summary of the comments and corresponding responses is as follows:

Eli Lilly comments:

1. Comment

Construction Permit, Page 1:

Eli Lilly and Company (Lilly) is seeking a permit for the equipment, not the process or some combination of equipment and process. We suggest replacing the words"the three antibiotic intermediate processes L, I, and E," with the words "the equipment and operations listed in pages 3 through 8 of this permit".

1. OAM Response

The permit application Form A-C, No. 8 states “This application covers three intermediate processes of the Cefaclor production process. The three intermediate processes are E, L, and I. See the detailed list of equipment.” Since the Potential To Emit (PTE) is based on the process not the equipment, the permit must address the processes. Therefore, it is necessary to put these processes in the Construction Permit. However the permit has been revised to state “the three antibiotic intermediate processes L, I, and E, or other pharmaceutical products of equivalent or lower PTE.”

2. Comment

Construction Permit, Page 2, Paragraph 1:

We request removing C2TBFS001 from the paragraph. C2TBFS001 is a deminimis source not currently covered by any permit. It is an inaccurate statement to say that

Operation Permit 83-09-91-0078 no longer applies to this equipment.

2. OAM Response

Each piece of equipment will be covered by only one permit. The emissions from this equipment are included in calculating the overall emissions from this permit. When Title V permit is issued for this source, the Title V permit will supersede all the current operating permits. Therefore, this equipment will be covered by this construction permit.

3. Comment

Construction Permit, Pages 3 to 6:

The tank capacities included in our application are nominal capacity, not maximum capacity. We suggest the phrase "maximum" capacity be replaced with "nominal" capacity since this is a more accurate statement.

3. OAM Response

The tank capacities have been revised accordingly.

4. Comment

Construction Permit, Page 3, item (a)(9):

The capacity of the tote bag station is not 2000 gallons as listed in the draft. Also, the tote bag station is not a VOC source, and no emissions from the tote bag station are controlled. We suggest the following language”one (1) tote bag/drum filling station (C2TBFS001);”

4. OAM Response

The permit has been revised accordingly.

5. Comment

Construction Permit, Page 4, item (c)(6):

Since submission of the application Lilly determined a better description of C12TK27 would be an evaporator rather than a crystallizer. Please replace the word “crystallizer” with the word “evaporator”.

5. OAM Response

The permit has been revised accordingly.

6. Comment

Construction Permit, Page 5, item (c)(12):

Since submission of the application Lilly determined a better description of C12TK34B would be a hot well rather than a separating tank. Please replace the words “separating tank” with the words “hot well”.

6. OAM Response

The permit has been revised accordingly.

7. Comment

Construction Permit, Page 8 (Now page 7), Construction Condition 1:

Lilly requests IDEM delete the first sentence of Construction Condition 1. This sentence, which incorporates by reference the information in Lilly's construction permit application into the permit, creates an obligation where the specific requirements of the permittee are difficult to ascertain. It is not clear whether this provision renders all the statements made in the application as compliance obligations, or whether this provision creates any additional requirements on the permittee.

A permit should specifically identify all the compliance obligations on a source. If there are specific statements and information in the application that IDEM believes ought to be compliance obligations, then the permit should include specific conditions to address the information.

Moreover, including a blanket incorporation by reference statement in the permit is inconsistent with Title V permitting. (The terms of this permit will eventually need to be incorporated into the Title V permit IDEM issues for Clinton Laboratories.) 326 IAC 2-7-5(1)(B) discourages blanket incorporation by reference, and instead requires IDEM to include specific permit conditions to incorporate portions of a permit application.

In addition Lilly requests IDEM delete the second sentence of Construction Condition 1. This sentence is not necessary. Office of Air Management approval should be required only for changes that will increase allowable emissions, as required by 326 IAC 2-1-1.

7. OAM Response

The data and information supplied with the application are part of this permit. the permit decision is based on the data and information provided in the application. This condition will not be deleted.

The second sentence is revised to read: “Prior to any proposed change in construction which may increase allowable emissions, the change must be approved by the Office of Air Management (OAM).”

8. Comment

Construction Permit, Page 9 (Now page 8), Construction Condition 6(e):

This requirement is not clear whether IDEM is instructing Lilly to amend the Title V application or stating that the construction permit itself is amending the Title V application. Lilly suggests the following language: “The Permittee shall amend the Part 70 application to incorporate the equipment approved under this permit.”

8. OAM Response

Lilly does not have to amend the Title V permit application. The OAM will include this construction permit in Title V permit, when it is issued.

9. Comment

Construction Permit, Page 9 (Now page 8), Operation Condition 1:

Lilly requests IDEM modify this condition similar to the modifications suggested for Construction Condition 1.

9. OAM Response

The data and information supplied with the application are part of this permit. the permit decision is based on the data and information provided in the application. This condition will not be deleted.

10. Comment

Construction Permit, Page 9 (Now page 8), Operation Condition 4(a)

Lilly requests IDEM change the words "three antibiotic (Cefaclor) intermediate processes" to "the equipment identified in this permit".

10. OAM Response

The permit has been revised accordingly.

11. Comment

Construction Permit, Page 10, Operation Condition 7(a):

This requirement should require the use of the RTOs or condensers only when the listed equipment is in operation and emitting VOCs. Lilly suggests the phrase “the following equipment is in operation:” with the phrase “the following equipment is in operation and emitting VOCs:”

11. OAM Response

The permit has been revised accordingly.

12. Comment

Construction Permit, Page 11, Operation Condition 7(a), Process L (9):

The tote bag station is not a VOC source and emissions from the tote bag station are not controlled. Lilly suggests this item be deleted.

12. OAM Response

The permit has been revised accordingly.

13. Comment

Construction Permit, Page 11, Operation Condition 7(a) Process E (8):

Lilly suggests the word “percent” at the end of this item be deleted.

13. OAM Response

The typo has been corrected.

14. Comment

Construction Permit, Page 13, Operation Condition 7(e):

The forth line in the tank ID column lists C64BTK158, This should be C64BTK163.

14. OAM Response

The typo has been corrected.

15. Comment

Construction Permit, Page 14, Operation Condition 12(a):

For clarity Lilly requests the condition identify the tanks subject to the requirement. Lilly suggests the following language: “The Permittee shall keep readily accessible records showing the dimension and analysis showing the capacity of the following storage vessels: C64BTK163, C64BTK165, C64BTK167, C64BTK169, C64ETK158, C64ETK160, C64ETK162, C64ETK164, C64ETK174, and C64FTK203.”

15. OAM Response

The permit has been revised accordingly.

16. Comment

Construction Permit, Page 14, Operation Condition 12(b):

Condition 12(b) should include C64ETK162. It is subject to the same NSPS requirements as the other 4 tanks identified as being subject to the increase in vapor pressure requirement. In addition, Lilly suggests the words "increases above the specified vapor pressure" should be replaced by "exceeds the respective maximum true vapor pressure values for each volume range". This is the wording in the NSPS rule, and more accurately portrays the notification requirement.

16. OAM Response

The permit has been revised accordingly.

17. Comment

Construction Permit, Page 14, Operation Condition 12(c):

This condition, which applies only to TK162, should be deleted. It is not a requirement of the NSPS for solvent storage tanks. Lilly believes the condition was drafted with the intent of notifying IDEM if the provisions of 326 IAC 8-5-3(b)(3)(A) become applicable if the tank is ever used to store a solvent with a vapor pressure greater than 4.1 psia. Currently there is no requirement under 326 IAC 8-5-3 for such notification. Therefore, the condition should be deleted. If the condition must be included in the permit, Lilly suggests it be put under Operation Condition 8, which addresses compliance with 326 IAC 8-5-3.

17. OAM Response

The permit has been revised accordingly.

18. Comment

Construction Permit, Page 14, Operation Condition 13:

Lilly requests IDEM delete the limitation on the compounds we can produce in the equipment. We believe permits provide more flexibility if they apply to equipment, not processes. This limitation on the compounds produced severely restricts our future operational flexibility.

18. OAM Response

The limitation on the compounds which Lilly can produce, does not restrict the future operational flexibility to produce a different product as long as the potential to emit of the future product does not exceed the potential to emit of current products . It is necessary for Lilly to examine if the potential to emit increases any time a change in product or process occurs.

The condition has been reworded to clarify that the OAM's approval is only needed when PTE from the change in product or process exceeds the current allowable PTE. However, Lilly must evaluate the PTE resulting from the new product or process.

19. Comment

Construction Permit, Page 15 and 16, Operation Condition 15:

Lilly as previously submitted an Emergency Reduction Plan to IDEM. We do not believe we should be required to submit a new Emergency Reduction Plan, especially since it is unlikely this modification will result in any changes to our Plan. Lilly suggests this condition be modified to require Lilly to submit an amendment to our Emergency Reduction Plan only if this permit results in changes to the Plan, or a letter stating no amendment is necessary. In addition, the last word of paragraph(b) should be "permit", not "registration".

19. OAM Response

The permit has been revised accordingly.

20. Comment

Construction Permit, Page 16, Operation Condition 16:

Lilly requests the word "facility" in the first sentence should be changed to "source".

20. OAM Response

The permit has been revised accordingly.

21. Comment

Technical Support Document, Page 5, Stack Summary Table:

The second stack ID should be PVC70-BSCBR2, not PVC70-ASCBR2.

21. OAM Response

The second stack ID will be called PVC70-BSCBR2.

22. Comment

Technical Support Document, Page 8, Second Paragraph:

The paragraph currently states: “All the solvent storage tanks have been constructed and used prior to the submittal of this application.” Please note that C64HTK255 while not having been used was permitted and constructed under permit CP165-1951.

22. OAM Response

The permit now states that the solvent storage tank (C64HTK255) is no longer covered by the previous permit.

23. Comment

Technical Support Document, Page 8:

The discussion of SOCMI NSPS requirements: The rule does not apply because the equipment involved in the permit are not engaged in producing any of the synthetic organic chemicals that make a source subject to those requirements.

23. OAM Response

Lilly has not committed to produce a particular product from the equipment for flexibility reasons. At this time the SOCMI NSPS rule does not apply to the processes. Prior to manufacturing a NSPS listed product, OAM approval will be required.

24. Comment

Technical Support Document, Page 9, discussion of Rule 8-5-3, first paragraph:

(a) The permit lists C13CENT3B, centrifuge 3B is located in C12. Please replace “C13CENT3B” with “C12CENT3B”.

(b) Since submission of the application Lilly determined a better description of C63TK207 would be a neutralization tank rather than a waste extractor tank. Please replace the words “waste extractor tank” with the words “neutralization tank”. Also, please change the tag number of tank 207 from “C63SRTK207" to “C63TK207".

(c) The permit refers to “Building T27 standard operating procedures” . I believe the reference to Building T27 is a typographical error.

24. OAM Response

(a) The permit lists C12CENT3B, centrifuge 3B as located in C12. The correct ID for the centrifuge should be C12CENT3B.

(b) The waste extractor tank has been renamed as a neutralization tank. The ID is correctly stated in the permit in the list of equipment.

(c) The OAM agrees that it is a typographical error.

25. Comment

Technical Support Document, Page 9, discussion of Rule 8-4-3:

(a) The rule does not apply because the tanks are not storing petroleum liquids.

25. OAM Response

The OAM agrees with this.

26. Comment

Appendix A, Page 1, paragraph 4:

The second sentence of this paragraph implies we were operating the 35 pieces of existing equipment without any kind of permit. That is incorrect. The equipment has operated under operating permits or the equipment was deminimis. The second sentence should say"Instead the application covers only installation of 10 pieces of new equipment and 35 pieces of existing equipment that were not previously subject to enforceable VOC emission limitations."

26. OAM Response

The OAM agrees with this.

27. Comment

Appendix A, Page 2, paragraph 4:

The first sentence of this paragraph is incomplete. The complete sentence in the application stated "The Antibiotic Intermediate E process is a batch process which takes an antibiotic intermediate and through chemical transformation, converts it into another antibiotic intermediate."

27. OAM Response

The OAM agrees with this.