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Università di Corsica
Pasquale Paoli

Aix*Marseille université
iusti
UMR 7343

Groupement De Recherche Feux 2864

CSTB
le futur en construction

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france

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INSTITUT
DE RADIOPROTECTION
ET DE SÛRETÉ NUCLÉAIRE

Reaction to Fire of Liquids

coria
UMR 6614
CNRS - UNIVERSITE et INSA de ROUEN

UNIVERSITY OF MARYLAND
18 56

Stanislav I. Stoliarov

Fire Protection Engineering

Calyxis
PÔLE D'EXPERTISE DU RISQUE

Ecole Doctorale
ED 353
Sciences Pour l'Ingénieur

Ecole thématique du CNRS sur la Science des Incendies et ses Applications

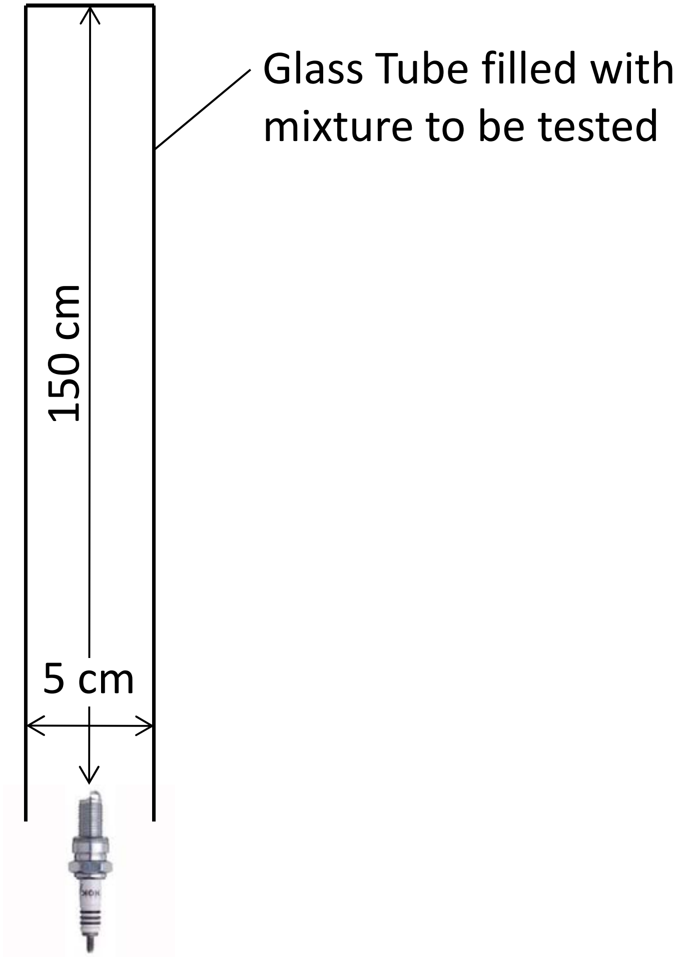
Porticcio, 30/05 – 04/06 2015

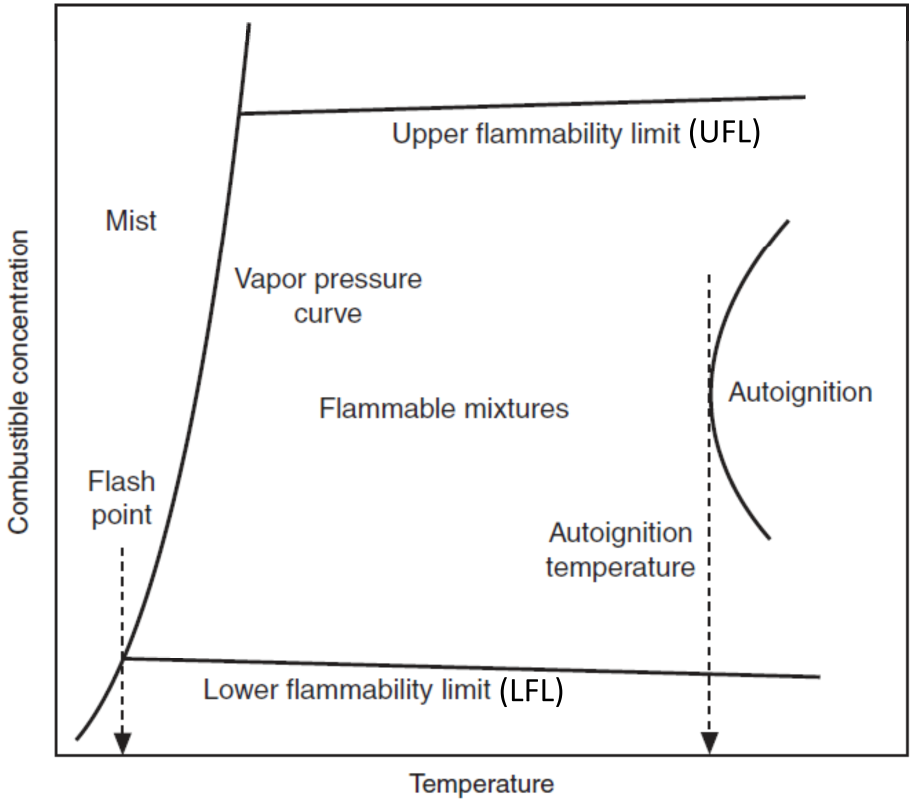
Piloted Ignition of Gases

- Ignitability of fuel/oxidizer gaseous mixtures is frequently characterized by lower and upper flammability limits (LFL and UFL).
- These limits are usually expressed as the minimum and maximum volumetric fraction (or concentration) of fuel in air capable of propagating self-sustained flame.
- The underling physics of these limits is associated with a competition between energy and active species (radicals) production in combustion reactions and energy and active species loss due to diffusion and radiation.
- The limits are typically measured experimentally using the Bureau of Mines Flammability Apparatus.

Piloted Ignition of Gases

Bureau of Mines Flammability Apparatus





Piloted Ignition of Gases

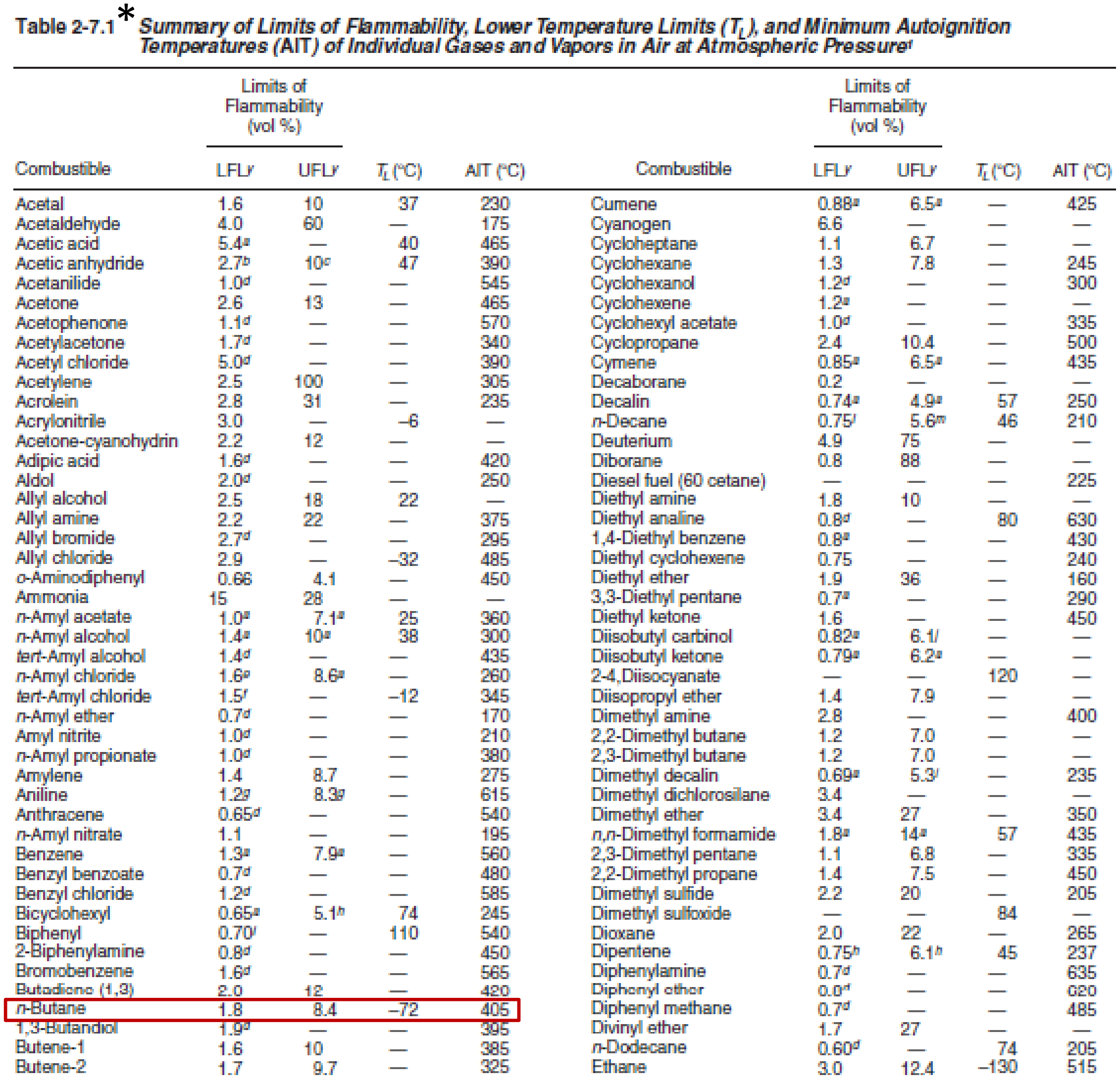


Table 2-7.1* *Summary of Limits of Flammability, Lower Temperature Limits (T_L), and Minimum Autoignition Temperatures (AIT) of Individual Gases and Vapors in Air at Atmospheric Pressure*^{t}

	Limits of Flammability (vol %)					Limits of Flammability (vol %)			
Combustible	LFL^{y}	UFL^{y}	T_L (°C)	AIT (°C)	Combustible	LFL^{y}	UFL^{y}	T_L (°C)	AIT (°C)
Acetal	1.6	10	37	230	Cumene	0.88^{a}	6.5^{a}	—	425
Acetaldehyde	4.0	60	—	175	Cyanogen	6.6	—	—	—
Acetic acid	5.4^{a}	—	40	465	Cycloheptane	1.1	6.7	—	—
Acetic anhydride	2.7^{b}	10^{c}	47	390	Cyclohexane	1.3	7.8	—	245
Acetanilide	1.0^{d}	—	—	545	Cyclohexanol	1.2^{d}	—	—	300
Acetone	2.6	13	—	465	Cyclohexene	1.2^{a}	—	—	—
Acetophenone	1.1^{d}	—	—	570	Cyclohexyl acetate	1.0^{d}	—	—	335
Acetylacetone	1.7^{d}	—	—	340	Cyclopropane	2.4	10.4	—	500
Acetyl chloride	5.0^{d}	—	—	390	Cymene	0.85^{a}	6.5^{a}	—	435
Acetylene	2.5	100	—	305	Decaborane	0.2	—	—	—
Acrolein	2.8	31	—	235	Decalin	0.74^{a}	4.9^{a}	57	250
Acrylonitrile	3.0	—	–6	—	*n*-Decane	0.75^{j}	5.6^{m}	46	210
Acetone-cyanohydrin	2.2	12	—	—	Deuterium	4.9	75	—	—
Adipic acid	1.6^{d}	—	—	420	Diborane	0.8	88	—	—
Aldol	2.0^{d}	—	—	250	Diesel fuel (60 cetane)	—	—	—	225
Allyl alcohol	2.5	18	22	—	Diethyl amine	1.8	10	—	—
Allyl amine	2.2	22	—	375	Diethyl analine	0.8^{d}	—	80	630
Allyl bromide	2.7^{d}	—	—	295	1,4-Diethyl benzene	0.8^{a}	—	—	430
Allyl chloride	2.9	—	–32	485	Diethyl cyclohexene	0.75	—	—	240
o-Aminodiphenyl	0.66	4.1	—	450	Diethyl ether	1.9	36	—	160
Ammonia	15	28	—	—	3,3-Diethyl pentane	0.7^{a}	—	—	290
n-Amyl acetate	1.0^{a}	7.1^{a}	25	360	Diethyl ketone	1.6	—	—	450
n-Amyl alcohol	1.4^{a}	10^{a}	38	300	Diisobutyl carbinol	0.82^{a}	6.1^{j}	—	—
tert-Amyl alcohol	1.4^{d}	—	—	435	Diisobutyl ketone	0.79^{a}	6.2^{a}	—	—
n-Amyl chloride	1.6^{e}	8.6^{e}	—	260	2-4,Diisocyanate	—	—	120	—
tert-Amyl chloride	1.5^{f}	—	–12	345	Diisopropyl ether	1.4	7.9	—	—
n-Amyl ether	0.7^{d}	—	—	170	Dimethyl amine	2.8	—	—	400
Amyl nitrite	1.0^{d}	—	—	210	2,2-Dimethyl butane	1.2	7.0	—	—
n-Amyl propionate	1.0^{d}	—	—	380	2,3-Dimethyl butane	1.2	7.0	—	—
Amylene	1.4	8.7	—	275	Dimethyl decalin	0.69^{a}	5.3^{j}	—	235
Aniline	1.2^{g}	8.3^{g}	—	615	Dimethyl dichlorosilane	3.4	—	—	—
Anthracene	0.65^{d}	—	—	540	Dimethyl ether	3.4	27	—	350
n-Amyl nitrate	1.1	—	—	195	*n*,*n*-Dimethyl formamide	1.8^{a}	14^{a}	57	435
Benzene	1.3^{a}	7.9^{a}	—	560	2,3-Dimethyl pentane	1.1	6.8	—	335
Benzyl benzoate	0.7^{d}	—	—	480	2,2-Dimethyl propane	1.4	7.5	—	450
Benzyl chloride	1.2^{d}	—	—	585	Dimethyl sulfide	2.2	20	—	205
Bicyclohexyl	0.65^{a}	5.1^{h}	74	245	Dimethyl sulfoxide	—	—	84	—
Biphenyl	0.70^{i}	—	110	540	Dioxane	2.0	22	—	265
2-Biphenylamine	0.8^{d}	—	—	450	Dipentene	0.75^{h}	6.1^{h}	45	237
Bromobenzene	1.6^{d}	—	—	565	Diphenylamine	0.7^{d}	—	—	635
Butadiene (1,3)	2.0	12	—	420	Diphenyl ether	0.8^{d}	—	—	620
n-Butane	1.8	8.4	–72	405	Diphenyl methane	0.7^{d}	—	—	485
1,3-Butandiol	1.9^{d}	—	—	395	Divinyl ether	1.7	27	—	—
Butene-1	1.6	10	—	385	*n*-Dodecane	0.60^{d}	—	74	205
Butene-2	1.7	9.7	—	325	Ethane	3.0	12.4	–130	515

* SFPE Fire Protection Engineering Handbook

Flammability Limits and Stoichiometry

For most simple hydrocarbons:

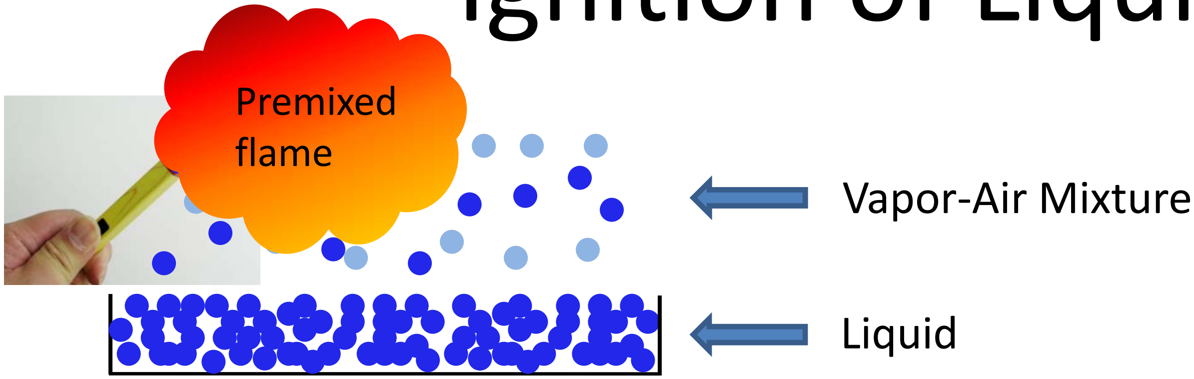
$$\mathrm{LFL} \approx \frac{1}{2}\left(\frac{V_{Fuel}}{V_{Air}+V_{Fuel}}\right)\Bigg|_{\mathrm{stoic}} = \frac{1}{2}\left(\frac{n_{Fuel}}{n_{Air}+n_{Fuel}}\right)\Bigg|_{\mathrm{stoic}} \qquad \mathrm{UFL} \approx 2\left(\frac{V_{Fuel}}{V_{Air}+V_{Fuel}}\right)\Bigg|_{\mathrm{stoic}} = 2\left(\frac{n_{Fuel}}{n_{Air}+n_{Fuel}}\right)\Bigg|_{\mathrm{stoic}}$$

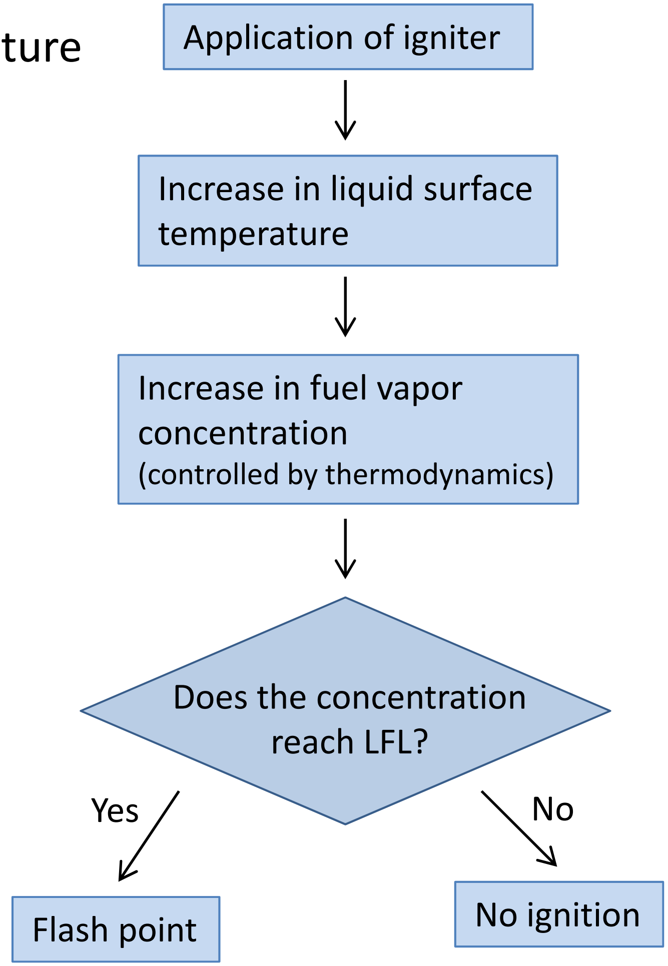
LFL of mixtures (Le Chatelier's) rule: Each gaseous fuel contribution to flammability is equal to the faction of its LFL.

In other words, the LFL of mixture is reached when: $\sum_i \frac{\left(\frac{V_i}{V_{total}}\right)}{\mathrm{LFL}_i} = 1$

$$V_{total} = \sum_i \frac{V_i}{\mathrm{LFL}_i}; \quad \mathrm{LFL}_{mix} = \sum_i \frac{V_i}{V_{total}} = \frac{1}{\sum_i \frac{V_i}{\mathrm{LFL}_i}} \sum_i V_i = \frac{1}{\sum_i \frac{\left(\frac{V_i}{V_{Fuels}}\right)}{\mathrm{LFL}_i}}$$

Ignition of Liquids





Application of igniter

Increase in liquid surface temperature

Increase in fuel vapor concentration
(controlled by thermodynamics)

Does the concentration reach LFL?

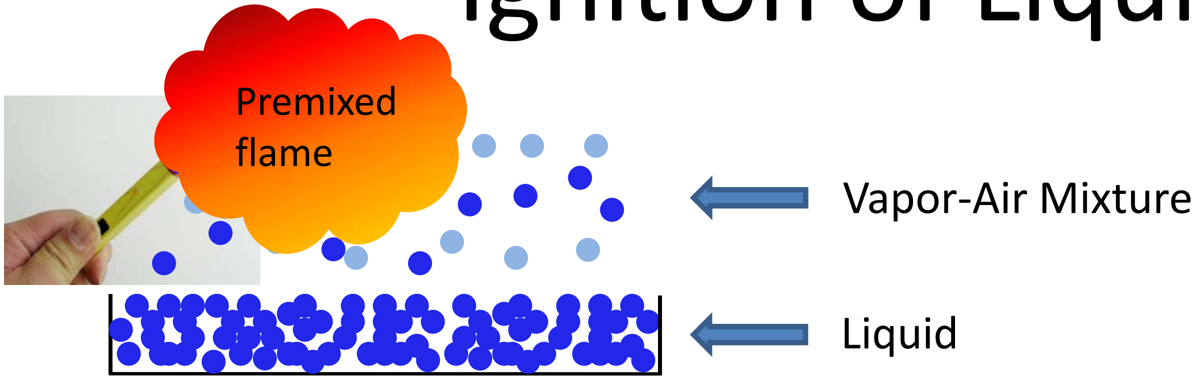
Yes

Flash point

No

No ignition

Ignition of Liquids



Flash point

Does the liquid produce enough gaseous fuel during the time between flashes to create UFL mixture in the space above it of the size of the flame quenching distance?

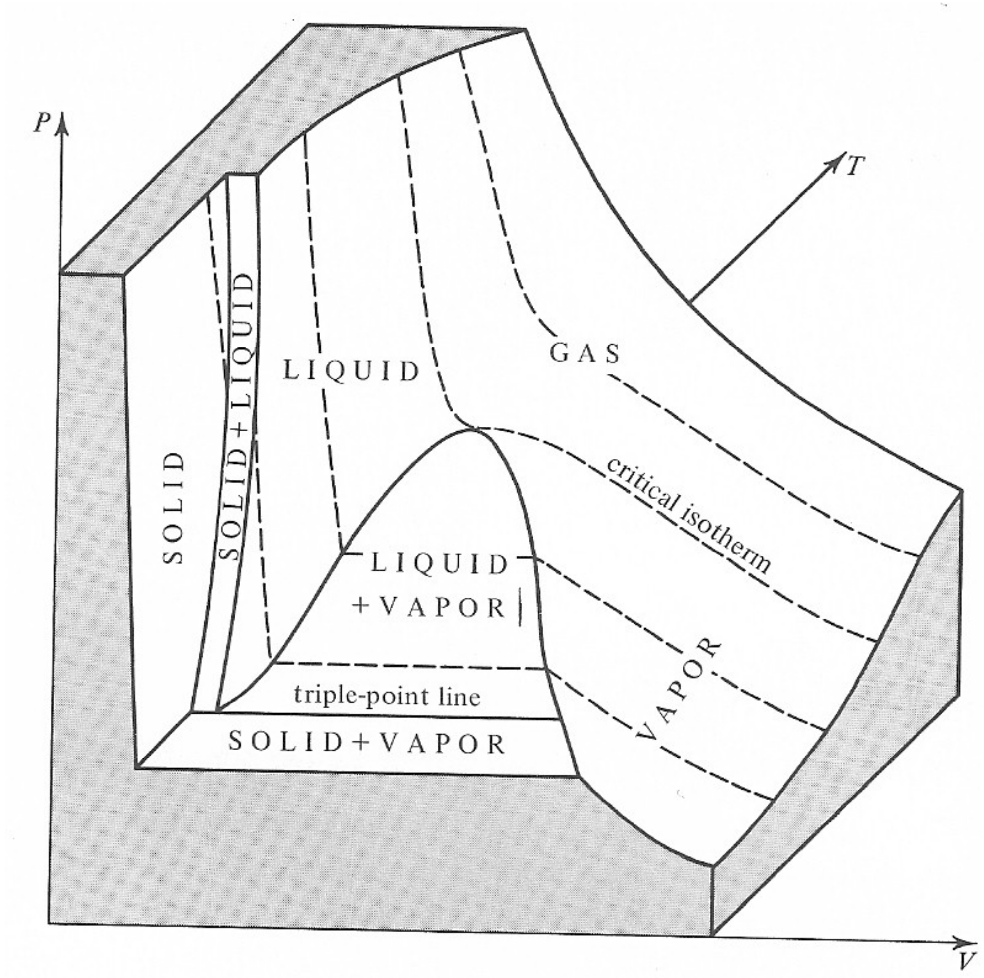
Yes

Potential transition to sustained diffusion flame - fire point

No

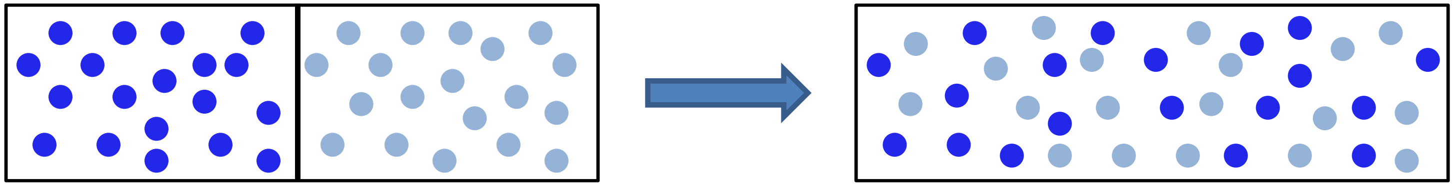
No ignition

States of Pure Substance



Second Law of Thermodynamics

Spontaneous process:



A function of state that defines randomness of a system is called entropy (S).

$S \propto \ln N$, where N is the number microstates comprising the system.

Second Law of Thermodynamics states that: $dS \geq \frac{dQ}{T}$

According to the First Law of Thermodynamics: $dQ = dU + PdV$

$$TdS \geq dU + PdV$$

$$dU + PdV - TdS \leq 0$$

If pressure and temperature are constant: $d\left(\underbrace{U + PV}_{\text{Enthalpy (function of state)}} - TS\right) = \overset{\text{Gibbs Free Energy}}{dG} \leq 0$

Clausius-Clapeyron Equation

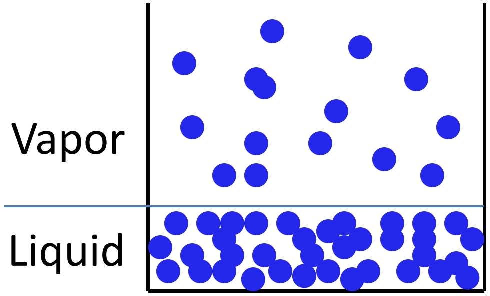
$$G = U + PV - TS$$

$$dG = dU + PdV + VdP - TdS - SdT$$

For reversible process: $TdS = dU + PdV \Rightarrow dU = TdS - PdV$

$$dG = \cancel{TdS} - \cancel{PdV} + \cancel{PdV} + VdP - \cancel{TdS} - SdT$$

$$dG = VdP - SdT$$



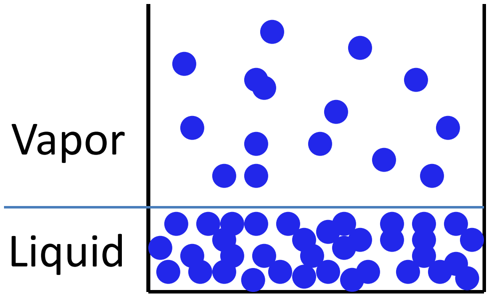
In equilibrium: $\frac{dG_L}{dn}dn + \frac{dG_V}{dn}(-dn) = 0 \Rightarrow \frac{dG_L}{dn} = \frac{dG_V}{dn}$

molar quantities

$$V_L dP - S_L dT = V_V dP - S_V dT$$

$$V_L \frac{dP}{dT} - S_L = V_V \frac{dP}{dT} - S_V$$

Clausius-Clapeyron Equation



$$V_L \frac{dP}{dT} - S_L = V_V \frac{dP}{dT} - S_V$$

$$\left(V_L - V_V\right)\frac{dP}{dT} = S_L - S_V$$

$$\frac{dP}{dT} = \frac{S_V - S_L}{V_V - V_L}$$

For reversible process: $dS = \frac{dQ}{T}$ or $\Delta S = \frac{\Delta Q}{T}$

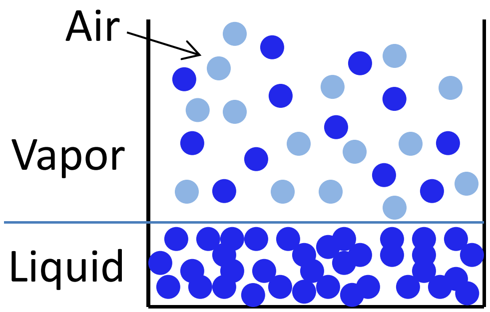
heat of vaporization, h_{fg}

$$\frac{dP}{dT} = \frac{\Delta Q}{T\left(V_V - V_L\right)}$$

$$V_V >> V_L \Rightarrow \frac{dP}{dT} = \frac{h_{\text{fg}}}{TV_V} = \frac{h_{\text{fg}}}{T\,\frac{RT}{P}}$$

$$\frac{dP}{P} = \frac{h_{\text{fg}}}{RT^2}\,dT$$

Clausius-Clapeyron Equation



$$\frac{dP}{P} = \frac{h_{\mathrm{fg}}}{RT^2}\,dT$$

boiling point

$$\int_{P}^{P_{\mathrm{b}}} \frac{dP}{P} = \int_{T}^{T_{\mathrm{b}}} \frac{h_{\mathrm{fg}}}{RT^2}\,dT$$

$$\ln P_{\mathrm{b}} - \ln P = -\frac{h_{\mathrm{fg}}}{R}\left(\frac{1}{T_{\mathrm{b}}} - \frac{1}{T}\right)$$

$$\ln\left(\frac{P}{P_{\mathrm{b}}}\right) = \frac{h_{\mathrm{fg}}}{R}\left(\frac{1}{T_{\mathrm{b}}} - \frac{1}{T}\right)$$

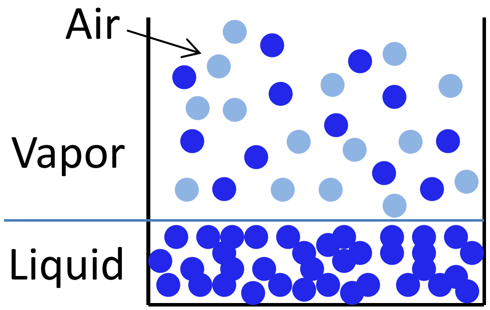
partial vapor pressure

atmospheric pressure
(101,325 Pa)

$$\frac{P}{P_{\mathrm{b}}} = \exp\left(\frac{h_{\mathrm{fg}}}{R}\left(\frac{1}{T_{\mathrm{b}}} - \frac{1}{T}\right)\right) = \frac{V_V}{V_{total}} = \chi_V$$

Key Result

Application to Ignition of Liquids



$$\chi_V = \exp\left(\frac{h_{\mathrm{fg}}}{R}\left(\frac{1}{T_{\mathrm{b}}} - \frac{1}{T}\right)\right)$$

$$\mathrm{LFL} = \exp\left(\frac{h_{\mathrm{fg}}}{R}\left(\frac{1}{T_{\mathrm{b}}} - \frac{1}{T_{\mathrm{L}}}\right)\right)$$

flash point

Cleveland Open Cup Tester (ASTM D92)

is used to measure:

flash point, T_{L}

temperature of onset of sustained burning (fire point)

Application to Ignition of Liquids

Fuel[a]	Formula	T_L (K) Closed	T_L (K) Open	T_b (K)	T_a (K)	$T_{f,ad}{}^a$ (K)	X_L (%)	h_{fg} (kJ/g)	Δh_c^b (kJ/g)
Methane	CH_4	—	—	111	910	2226	5.3	0.59	50.2
Propane	C_3H_8	—	169	231	723	2334	2.2	0.43	46.4
n-Butane	C_4H_{10}	—	213	273	561	2270	1.9	0.39	45.9
n-Hexane	C_6H_{14}	251	247	342	498	2273	1.2	0.35	45.1

$$\text{LFL} = \exp\left(\frac{h_{fg}}{R}\left(\frac{1}{T_b} - \frac{1}{T_L}\right)\right)$$

$$\text{LFL}_{\text{Hexane}} = \exp\left(\frac{0.35 \times 1000 \times \overset{\text{MW}_{\text{Hexane}}\ (\text{g mol}^{-1})}{\overset{\downarrow}{86.2}}}{8.314}\left(\frac{1}{342} - \frac{1}{\underset{\underset{\text{closed cup } T_L}{\uparrow}}{251}}\right)\right) = 0.021$$

$$\text{LFL}_{\text{Hexane}} = \exp\left(\frac{0.35 \times 1000 \times 86.2}{8.314}\left(\frac{1}{342} - \frac{1}{\underset{\underset{\text{open cup } T_L}{\uparrow}}{247}}\right)\right) = 0.017$$

$$\text{LFL}_{\text{Hexane}} = \exp\left(\frac{\overset{h_{fg}\text{ from NIST chemistry webbook}}{\overset{\downarrow}{31730}}}{8.314}\left(\frac{1}{342} - \frac{1}{247}\right)\right) = 0.014$$

Application to Ignition of Mixtures

Application of Raoult's law (the ratio is molar fraction in liquid mixture)

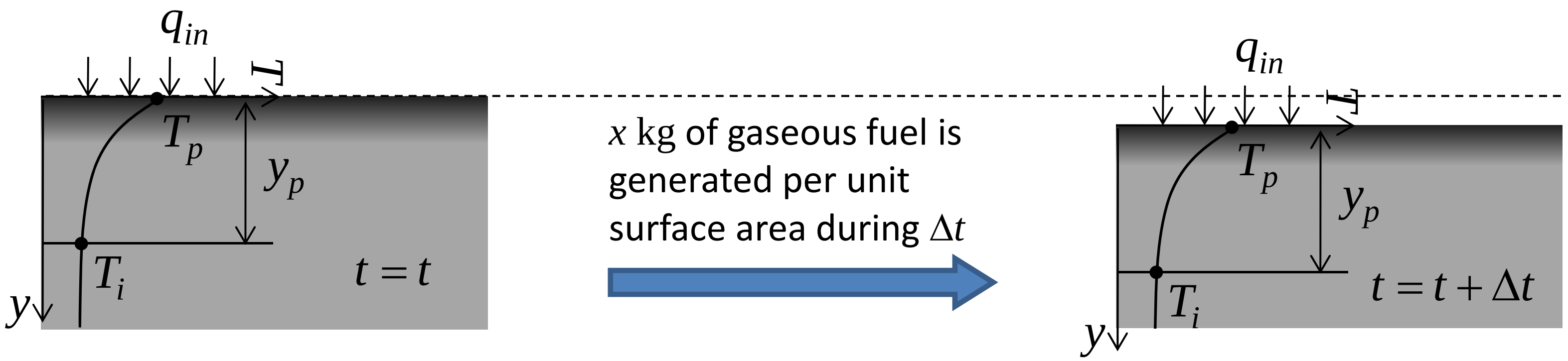
$$\sum_i \frac{\left(\frac{V_i}{V_{total}}\right)}{\mathrm{LFL}_i} = \sum_i \frac{\left(\frac{n_i}{\sum_j n_j}\frac{P_i}{P_\mathrm{b}}\right)}{\exp\left(\frac{h^i_{\mathrm{fg}}}{R}\left(\frac{1}{T^i_\mathrm{b}}-\frac{1}{T^i_\mathrm{L}}\right)\right)} = \sum_i \frac{\left(\frac{n_i}{\sum_j n_j}\exp\left(\frac{h^i_{\mathrm{fg}}}{R}\left(\frac{1}{T^i_\mathrm{b}}-\frac{1}{T}\right)\right)\right)}{\exp\left(\frac{h^i_{\mathrm{fg}}}{R}\left(\frac{1}{T^i_\mathrm{b}}-\frac{1}{T^i_\mathrm{L}}\right)\right)} \geq 1$$

indicates ignition
(Le Chatelier’s rule)

Burning Rate

Burning rate – the rate of mass loss or heat release per unit surface area of condensed-phase fuel.

Steady-State Burning of Solid or Liquid:



x kg of gaseous fuel is generated per unit surface area during Δt

$$\frac{x}{\Delta t} = mF_f = const$$

For steady-state to exist, x kg of fuel must be heated from T_i to T_p and vaporized during Δt:

$$x c_s (T_p - T_i) + x h_{fg} = q_{in} \Delta t$$

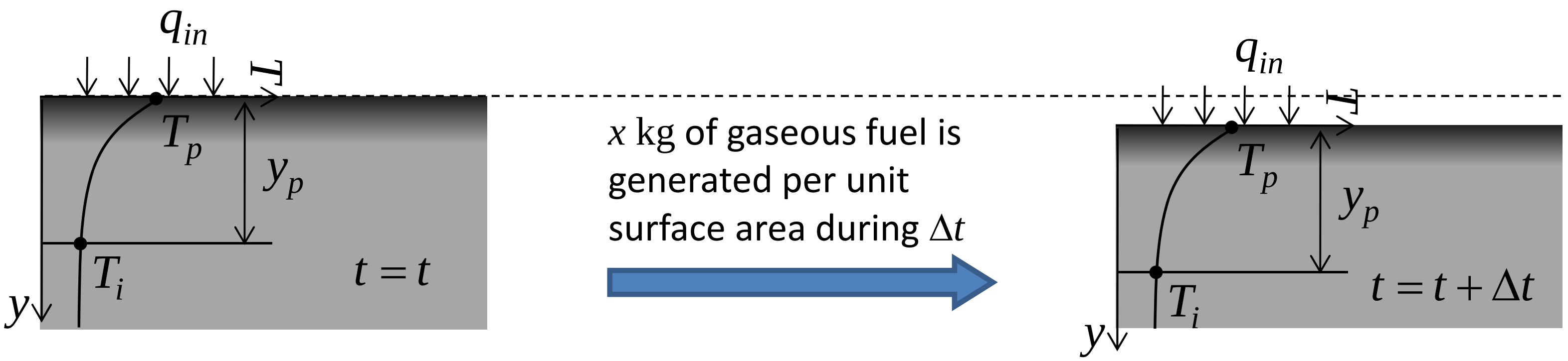
$$\frac{x}{\Delta t} = \frac{q_{in}}{c_s (T_p - T_i) + h_{fg}}$$

- h_{fg} may represent heat of decomposition or vaporization;
- T_p may represent pyrolysis temperature or boiling point.

Burning Rate

Burning rate – the rate of mass loss or heat release per unit surface area of condensed-phase fuel.

Steady-State Burning of Solid or Liquid:



x kg of gaseous fuel is generated per unit surface area during Δt

$$mF_f = \frac{q_{in}}{c_s\left(T_p - T_i\right) + h_{fg}}$$

If c_s is a function of T: $$mF_f = \frac{q_{in}}{\boxed{\int_{T_i}^{T_p} c_s\,dT + h_{fg}}}$$

$= L$ - heat of gasification

Pool Fire Analysis

Spalding *B* number

Convection from flame only: $q_{in} = \frac{h}{c_g}\ln(1+B)L$

Mean beam length

Convection and radiation from flame: $q_{in} = \frac{h}{c_g}\ln(1+B')L + \varepsilon_s\left(1-e^{-kD}\right)\sigma T_{flame}^4 - \varepsilon_s \sigma T_p^4$

Fraction of combustion energy that is radiated out

where $B' = \dfrac{\dfrac{\Delta H_c}{s} Y_{oxid}^{\infty}(1-X_r) - c_g(T_p - T_\infty)}{L}$

Mass of oxidizer consumed per unit mass of fuel

$$mF_f(\text{steady}) = \frac{q_{in}}{L} = \frac{h}{c_g}\ln(1+B') + \frac{\varepsilon_s\left(1-e^{-kD}\right)\sigma T_{flame}^4}{L} - \frac{\varepsilon_s \sigma T_p^4}{L}$$

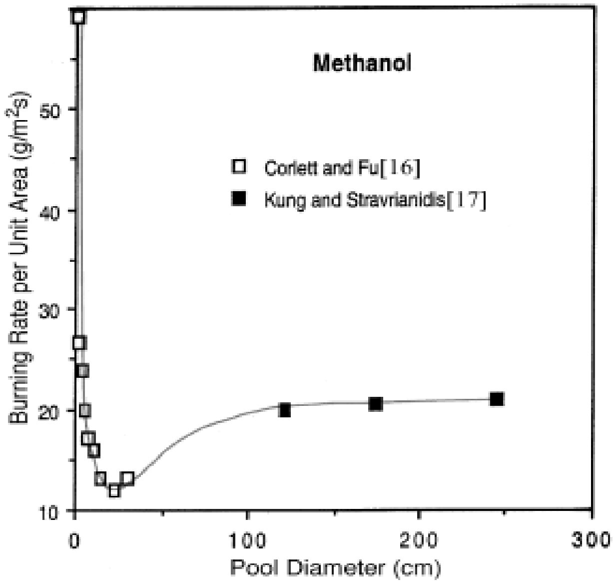


Figure 9.15 Regimes of the steady burning rate for methanol: $D < 25$ cm laminar, turbulent, $D > 100$ cm radiation saturated [16, 17]*

*Figure from Quintiere, *Fundamentals of Fire …*

Case Study*

The US Attorney General authorizes the use of 'nonpyrotechnic tear gas' to force cult members from a building under siege. She is assured the tear gas is not flammable. The teargas (CS) is delivered in a droplet of methylene chloride (dichloromethane, CH_2Cl_2) as an aerosol. Twenty canisters of the tear gas are simultaneously delivered, each containing 0.5 liters of methylene chloride. The properties of the CH_2Cl_2 are listed below:

Properties of CH_2Cl_2:

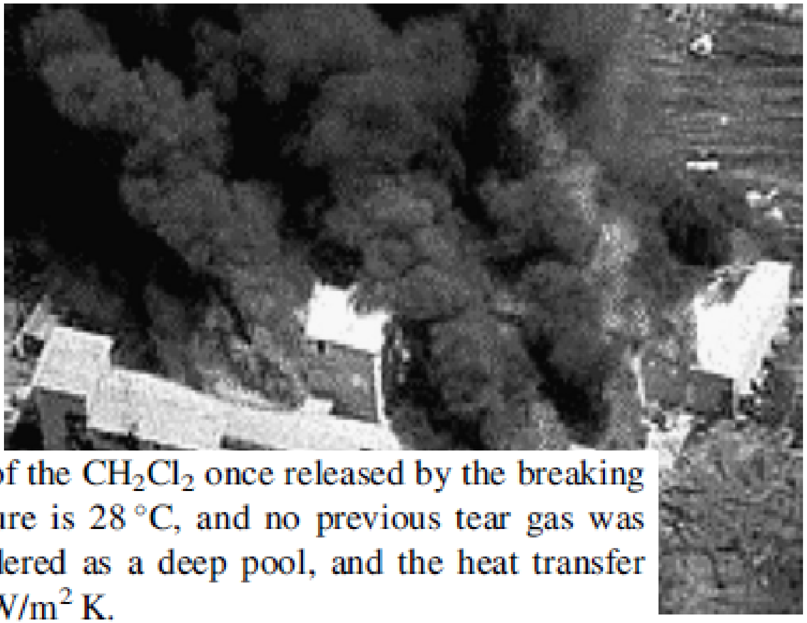
Liquid specific heat = 2 J/g K

Boiling point = 40 °C

Liquid density = 1.33 g/cm^3

Heat of vaporization = 7527 cal/g mole

Lower flammability limit = 12 % (molar)



Questions need to be answered:

Compute the evaporation rate per unit area of the CH_2Cl_2 once released by the breaking canisters in the building. The air temperature is 28 °C, and no previous tear gas was introduced. Assume the spill can be considered as a deep pool, and the heat transfer coefficient between the floor and air is 10 W/m^2 K.

What is the maximum concentration of CH_2Cl_2 gas in the building assuming it is well mixed. The building is 60 ft × 30 ft × 8 ft high, and has eight broken windows 3 ft × 5 ft high. Each canister makes a 1 m diameter spill, and the air flow rate into the building can be taken as $0.05\, A_0 H_0^{1/2}$ in kg/s, where A_0 is the total area of the windows and H_0 is the height of a window.

*From Quintiere, *Fundamentals of Fire …*

Case Study

$$L \approx h_{\text{fg}}$$

$$mF_{\text{evap}}(\text{steady}) = \frac{q_{in}}{L} \qquad q_{in} = h(T_{surf} - T_{air})$$

Lewis number

$$mF_{\text{evap}} = K\left(Y_{surf}^{CH_2Cl_2} - Y_{air}^{CH_2Cl_2}\right) \quad \text{If Le} \approx 1 \Rightarrow mF_{\text{evap}} \approx \frac{h}{c_{air}}\left(Y_{surf}^{CH_2Cl_2} - Y_{air}^{CH_2Cl_2}\right)$$

$$Y_{surf}^{CH_2Cl_2} >> Y_{air}^{CH_2Cl_2} \Rightarrow mF_{\text{evap}} \approx \frac{h}{c_{air}} Y_{surf}^{CH_2Cl_2} \approx \frac{h}{c_{air}} \frac{MW_{CH_2Cl_2}}{MW_{air}} \exp\left(\frac{h_{\text{fg}}}{R}\left(\frac{1}{T_{\text{b}}} - \frac{1}{T_{surf}}\right)\right)$$

$$\frac{h}{c_{air}} \frac{MW_{CH_2Cl_2}}{MW_{air}} \exp\left(\frac{h_{\text{fg}}}{R}\left(\frac{1}{T_{\text{b}}} - \frac{1}{T_{surf}}\right)\right) = \frac{h(T_{surf} - T_{air})}{h_{\text{fg}}} \Rightarrow T_{surf} \approx -20\ ^{\text{o}}\text{C}$$

Mass conservation for CH_2Cl_2:

$$\left.\begin{array}{l} \dfrac{d}{dt}\left(Y^{CH_2Cl_2}\rho_{air}V_{\text{bldg}}\right) = mF_{\text{evap}}A_{\text{spills}} - Y^{CH_2Cl_2}\left(0.05A_0H_0^{1/2}\right) \\ \displaystyle\int_0^{\infty} mF_{\text{evap}}A_{\text{spills}}\,dt = N_{\text{cans}}V_{\text{can}}\rho_{CH_2Cl_2} \end{array}\right\} \Rightarrow Y_{\max}^{CH_2Cl_2} \approx 0.02$$

Result: LFL is not reached