

# Introduction to natural gas plant LPG Technology



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## Appendix 1

### Important Conversion Factors (\*SI Units)

<i>Length</i>	$1 \text{ cm} = 10 \text{ mm} = 0.01 \text{ m}^*$ $= 0.0328 \text{ ft}$ $= 0.3937 \text{ in}$ $1 \text{ ft} = 12 \text{ in} = 0.333 \text{ yd}$ $= 30.48 \text{ cm}$ $= 304.8 \text{ mm}$ $= 0.3048 \text{ m}$
<i>Area</i>	$1 \text{ cm}^2 = 100 \text{ mm}^2 = 10^{-4} \text{ m}^{2*}$ $= 1.076 \times 10^{-3} \text{ ft}^2$ $= 0.155 \text{ in}^2$ $1 \text{ ft}^2 = 144 \text{ in}^2 = 0.1111 \text{ yd}^2$ $= 0.92903 \times 10^3 \text{ cm}^2$ $= 0.92903 \times 10^5 \text{ mm}^2$
<i>Volume</i>	$1 \text{ cm}^3 = 10^3 \text{ mm}^3 = 10^{-6} \text{ m}^{3*}$ $= 35.315 \times 10^{-6} \text{ ft}^3$ $= 6.1024 \times 10^{-2} \text{ in}^3$ $1 \text{ ft}^3 = 1728 \text{ in}^3 = 0.03704 \text{ yd}^3$ $= 28.3167 \times 10^3 \text{ cm}^3$ $= 28.3167 \times 10^6 \text{ mm}^3 = 0.02832 \text{ m}^3$ also $1 \text{ Imp. gal} = 1.201 \text{ U.S. gal} = 0.16055 \text{ ft}^3$ $= 4.54596 \text{ l.}$ $1 \text{ U.S. gal} = 0.83267 \text{ Imp. gal} = 0.1337 \text{ ft}^3$ $= 3.7853 \text{ l.}$ $1 \text{ ft}^3 = 7.481 \text{ U.S. gal} = 6.24 \text{ I.G.}$
<i>Density</i>	$1 \text{ g/cm}^3 = 1.000028 \text{ kg/l} = 10^3 \text{ kg/m}^{3*}$ $= 62.43 \text{ lb/ft}^3$ $1 \text{ lb/ft}^3 = 0.13366 \text{ lb/U.S. gal} = 0.16053 \text{ lb/Imp. gal}$ $= 0.01602 \text{ g/cm}^3$ $= 16.0185 \text{ kg/m}^{3*}$
<i>Pressure</i>	$1 \text{ lb/in}^2 \text{ abs.} = 27.68 \text{ in w.c.} = 2.307 \text{ ft w.c.}$ $= 2.0367 \text{ in Hg} = 51.715 \text{ mmHg (torr)}$ $= 0.070306 \text{ kg/cm}^2$ $= 0.068047 \text{ atm}$ $= 0.068948 \text{ bar}$ $= 0.68948 \text{ N/cm}^{2*}$ $1 \text{ bar} = 1.01972 \text{ kg/cm}^2 = 750.06 \text{ torr}$ $= 0.98692 \text{ atm} = 10 \text{ N/cm}^{2*}$ $= 14.50 \text{ lb/in}^2 \text{ abs.}$ $= 401.47 \text{ in w.c.} = 29.53 \text{ in Hg}$



## Appendix 1 (Continued)

<i>Energy</i>	1 Btu	= $2.93 \times 10^{-4}$ kWh = $1 \times 10^{-5}$ therm
		= $3.93 \times 10^{-4}$ HPh
		= 0.251996 kcal
		= 1.05506 kJ*
	1 kcal	= $1.1628 \times 10^{-3}$ kWh
		= 3.9683 Btu
		= $39.68 \times 10^{-6}$ therm
		= 4.1868 kJ*
<i>Gas volume</i>	1 SCF (Standard cubic foot) (60°F, 30 in. sat.)	= 0.02641 N m <sup>3</sup>
		(15°C, 760 mmHg, dry)
	1 Nm <sup>3</sup>	= 37.875 SCF
<i>Gas density</i>	1 lb/SCF	= 17.187 kg/N m <sup>3</sup> *
	1 kg/N m <sup>3</sup>	= 0.05818 lb/SCF
<i>Gas calorific Value</i>	1 Btu/SCF	= 1.018 Btu/ft <sup>3</sup> (60°F, 14.7 lb/in <sup>2</sup> abs., dry)
		= 9.548 kcal/N m <sup>3</sup>
		= 39.978 kJ/N m <sup>3</sup> *
	1 kcal/N m <sup>3</sup>	= 0.948 kcal/m <sup>3</sup> (15°C, 760 mmHg, dry)
		= 0.10473 Btu/SCF
		= 0.10661 Btu/ft <sup>3</sup> (60°F, 14.7 lb/in <sup>2</sup> abs., dry)
		= 4.187 kJ/N m <sup>3</sup> *

## Appendix 2

### Liquid Volume Correction Factors

Specific gravities at 60°F/ 60°F (15.6°C/15.6°C)

Observed temp., °F	0-500	Propane 0-5079	0-510	0-520	0-530	0-540	0-550	0-560	Isobutane 0-5631	0-570	0-580	n-butane 0-5844	0-590	Observed temp., °C
<i>Volume correction figures</i>														
-50	1-160	1-155	1-153	1-146	1-140	1-133	1-127	1-122	1-120	1-116	1-111	1-108	1-106	-45.6
-45	1-153	1-148	1-146	1-140	1-134	1-128	1-122	1-117	1-115	1-111	1-106	1-103	1-101	-42.8
-40	1-147	1-142	1-140	1-134	1-128	1-122	1-117	1-111	1-110	1-106	1-101	1-099	1-097	-40
-35	1-140	1-135	1-134	1-128	1-122	1-116	1-112	1-106	1-105	1-101	1-096	1-094	1-092	-37.2
-30	1-134	1-129	1-128	1-122	1-116	1-111	1-106	1-101	1-100	1-096	1-092	1-090	1-088	-34.4
-25	1-127	1-122	1-121	1-115	1-110	1-105	1-100	1-095	1-094	1-091	1-087	1-085	1-083	-31.7
-20	1-120	1-115	1-114	1-109	1-104	1-099	1-095	1-090	1-089	1-086	1-082	1-080	1-079	-28.9
-15	1-112	1-109	1-107	1-102	1-097	1-093	1-089	1-084	1-083	1-080	1-077	1-075	1-074	-26.1
-10	1-105	1-102	1-100	1-095	1-091	1-087	1-083	1-079	1-078	1-075	1-072	1-071	1-069	-23.3
-5	1-098	1-094	1-094	1-089	1-085	1-081	1-077	1-074	1-073	1-070	1-067	1-066	1-065	-20.6
0	1-092	1-088	1-088	1-084	1-080	1-076	1-073	1-069	1-068	1-066	1-063	1-063	1-061	-17.8
2	1-089	1-086	1-085	1-081	1-077	1-074	1-070	1-067	1-066	1-064	1-061	1-060	1-059	-16.7
4	1-086	1-083	1-082	1-079	1-075	1-071	1-068	1-065	1-064	1-062	1-059	1-058	1-057	-15.6
6	1-084	1-080	1-080	1-076	1-072	1-069	1-065	1-062	1-061	1-059	1-057	1-055	1-054	-14.4
8	1-081	1-078	1-077	1-074	1-070	1-066	1-063	1-060	1-059	1-057	1-055	1-053	1-052	-13.3
10	1-078	1-075	1-074	1-071	1-067	1-064	1-061	1-058	1-057	1-055	1-053	1-051	1-050	-12.2
12	1-075	1-072	1-071	1-068	1-064	1-061	1-059	1-056	1-055	1-053	1-051	1-049	1-048	-11.1
14	1-072	1-070	1-069	1-066	1-062	1-059	1-056	1-053	1-053	1-051	1-049	1-047	1-046	-10.0
16	1-070	1-067	1-066	1-063	1-060	1-056	1-054	1-051	1-050	1-048	1-046	1-045	1-044	-8.9
18	1-067	1-065	1-064	1-061	1-057	1-054	1-051	1-049	1-048	1-046	1-044	1-043	1-042	-7.8
20	1-064	1-062	1-061	1-058	1-054	1-051	1-049	1-046	1-046	1-044	1-042	1-041	1-040	-6.7
22	1-061	1-059	1-058	1-055	1-052	1-049	1-046	1-044	1-044	1-042	1-040	1-039	1-038	-5.6
24	1-058	1-056	1-055	1-052	1-049	1-046	1-044	1-042	1-042	1-040	1-038	1-037	1-036	-4.4



## Appendix 2 (Continued)

### Liquid Volume Correction Factors

Specific gravities at 60°F/ 60°F (15.6°C/15.6°C)

Observed temp., °F	0-500	Propane 0-5079	0-510	0-520	0-530	0-540	0-550	0-560	Isobutane 0-5631	0-570	0-580	n-butane 0-5844	0-590	Observed temp., °C
<i>Volume correction figures</i>														
26	1-055	1-053	1-052	1-049	1-047	1-044	1-042	1-039	1-039	1-037	1-036	1-036	1-034	-3.3
28	1-052	1-050	1-049	1-047	1-044	1-041	1-039	1-037	1-037	1-035	1-034	1-034	1-032	-2.2
30	1-049	1-047	1-046	1-044	1-041	1-038	1-036	1-035	1-035	1-033	1-032	1-032	1-030	-1.1
32	1-046	1-044	1-043	1-041	1-038	1-036	1-035	1-033	1-033	1-031	1-030	1-030	1-028	0
34	1-043	1-041	1-040	1-038	1-036	1-034	1-032	1-031	1-030	1-029	1-028	1-028	1-026	1.1
36	1-039	1-038	1-037	1-035	1-033	1-031	1-030	1-028	1-028	1-027	1-025	1-025	1-024	2.2
38	1-036	1-035	1-034	1-032	1-031	1-029	1-027	1-026	1-025	1-025	1-023	1-023	1-022	3.3
40	1-033	1-032	1-031	1-029	1-028	1-026	1-025	1-024	1-023	1-023	1-021	1-021	1-020	4.4
42	1-030	1-029	1-028	1-027	1-025	1-024	1-023	1-022	1-021	1-021	1-019	1-019	1-018	5.6
44	1-027	1-026	1-025	1-023	1-022	1-021	1-020	1-019	1-019	1-018	1-017	1-017	1-016	6.7
46	1-023	1-022	1-022	1-021	1-020	1-018	1-018	1-017	1-016	1-016	1-015	1-015	1-014	7.8
48	1-020	1-019	1-019	1-018	1-017	1-016	1-015	1-014	1-014	1-013	1-013	1-013	1-012	8.9
50	1-017	1-016	1-016	1-015	1-014	1-013	1-013	1-012	1-012	1-011	1-011	1-011	1-010	10.0
52	1-014	1-013	1-012	1-012	1-011	1-010	1-010	1-009	1-009	1-009	1-009	1-009	1-008	11.1
54	1-011	1-010	1-009	1-009	1-008	1-008	1-007	1-007	1-007	1-007	1-006	1-006	1-006	12.2
56	1-007	1-007	1-006	1-006	1-005	1-005	1-005	1-005	1-005	1-005	1-004	1-004	1-004	13.3
58	1-003	1-003	1-003	1-003	1-003	1-003	1-002	1-002	1-002	1-002	1-002	1-002	1-002	14.4
60	1-000	1-000	1-000	1-000	1-000	1-000	1-000	1-000	1-000	1-000	1-000	1-000	1-000	15.6
62	0-997	0-997	0-997	0-997	0-997	0-997	0-997	0-998	0-998	0-998	0-998	0-998	0-998	16.7
64	0-993	0-993	0-994	0-994	0-994	0-994	0-995	0-995	0-995	0-995	0-996	0-996	0-996	17.8
66	0-990	0-990	0-990	0-990	0-991	0-992	0-992	0-993	0-993	0-993	0-993	0-993	0-993	18.9
68	0-986	0-986	0-987	0-987	0-988	0-989	0-990	0-990	0-990	0-990	0-991	0-991	0-991	20.0
70	0-983	0-983	0-984	0-984	0-985	0-986	0-987	0-988	0-988	0-988	0-989	0-989	0-989	21.1
72	0-979	0-980	0-981	0-981	0-982	0-983	0-984	0-985	0-986	0-986	0-987	0-987	0-987	22.2

## Appendix 2 (Continued)

### Liquid Volume Correction Factors

Specific gravities at 60°F/60°F (15.6°C/15.6°C)

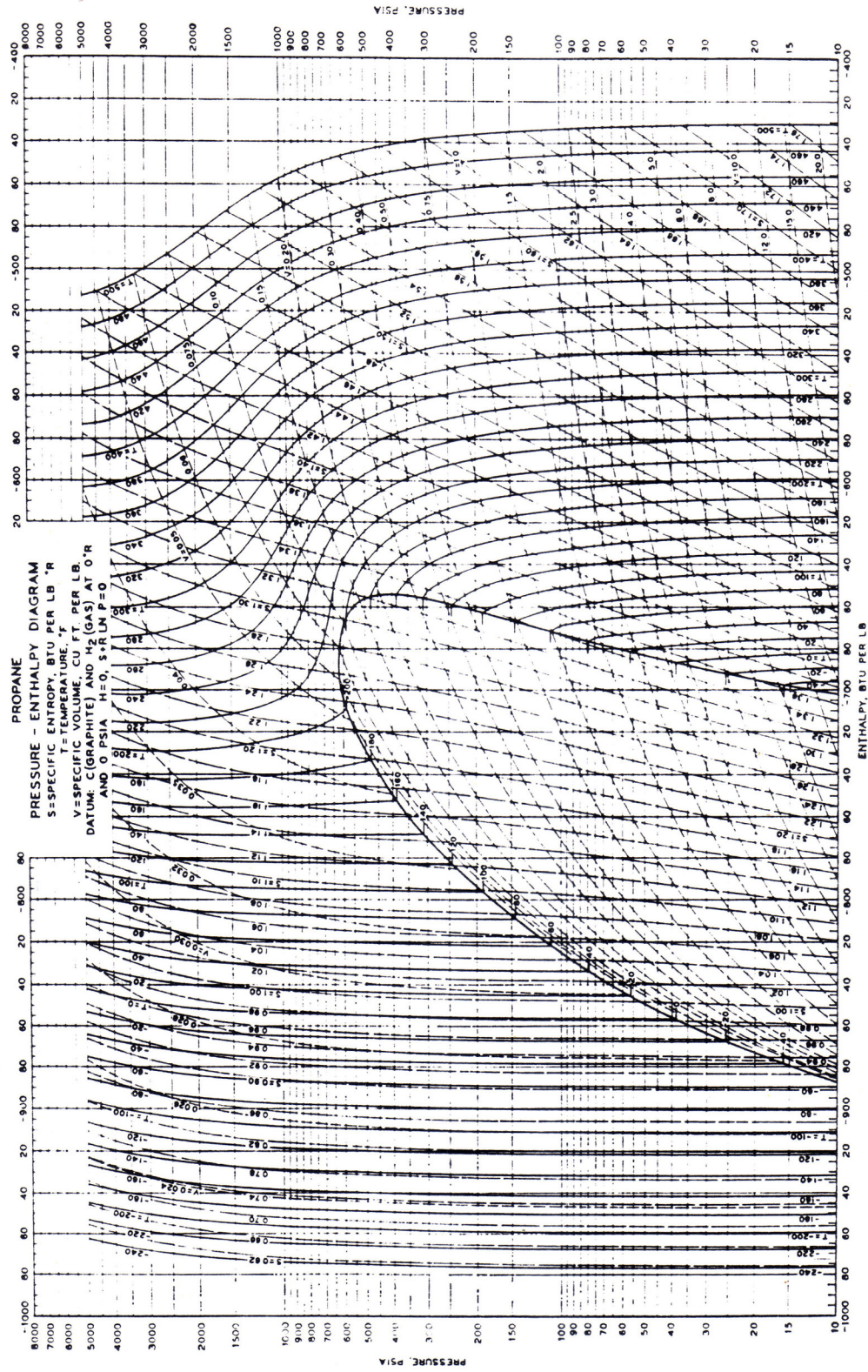
Observed temp., °F	0-500	Propane 0-5079	0-510	0-520	0-530	0-540	0-550	0-560	Isobutane 0-5631	0-570	0-580	n-butane 0-5844	0-590	Observed temp., °C
<i>Volume correction figures</i>														
74	0-976	0-976	0-977	0-978	0-980	0-980	0-982	0-983	0-983	0-984	0-985	0-985	0-985	23.3
76	0-972	0-973	0-974	0-975	0-977	0-978	0-979	0-980	0-981	0-981	0-982	0-982	0-983	24.4
78	0-969	0-970	0-970	0-972	0-974	0-975	0-977	0-978	0-978	0-979	0-980	0-980	0-981	25.6
80	0-965	0-967	0-967	0-969	0-971	0-972	0-974	0-975	0-976	0-977	0-978	0-978	0-979	26.7
82	0-961	0-963	0-963	0-966	0-968	0-969	0-971	0-972	0-973	0-974	0-976	0-976	0-977	27.8
84	0-957	0-959	0-960	0-962	0-965	0-966	0-968	0-970	0-971	0-972	0-974	0-974	0-975	28.9
86	0-954	0-956	0-956	0-959	0-961	0-964	0-966	0-967	0-968	0-969	0-971	0-971	0-972	30.0
88	0-950	0-950	0-953	0-955	0-958	0-961	0-963	0-965	0-966	0-967	0-969	0-969	0-970	31.1
90	0-946	0-949	0-949	0-952	0-955	0-958	0-960	0-962	0-963	0-964	0-967	0-967	0-968	32.2
92	0-942	0-945	0-946	0-949	0-952	0-955	0-957	0-959	0-960	0-962	0-964	0-965	0-966	33.3
94	0-938	0-941	0-942	0-946	0-949	0-952	0-954	0-957	0-958	0-959	0-962	0-962	0-964	34.4
96	0-935	0-938	0-939	0-942	0-946	0-949	0-952	0-954	0-955	0-957	0-959	0-960	0-961	35.6
98	0-931	0-934	0-935	0-939	0-943	0-946	0-949	0-952	0-953	0-954	0-957	0-957	0-959	36.7
100	0-927	0-930	0-932	0-936	0-940	0-943	0-946	0-949	0-950	0-952	0-954	0-955	0-957	37.8
105	0-917	0-920	0-923	0-927	0-931	0-935	0-939	0-943	0-943	0-946	0-949	0-949	0-951	40.6
110	0-907	0-911	0-913	0-918	0-923	0-927	0-932	0-936	0-937	0-939	0-943	0-944	0-946	43.3
115	0-897	0-902	0-904	0-909	0-915	0-920	0-925	0-930	0-930	0-933	0-937	0-938	0-940	46.1
120	0-887	0-892	0-894	0-900	0-907	0-912	0-918	0-923	0-924	0-927	0-931	0-932	0-934	48.9
125	0-876	0-881	0-884	0-890	0-898	0-903	0-909	0-916	0-916	0-920	0-925	0-927	0-928	51.7
130	0-865	0-871	0-873	0-880	0-888	0-895	0-901	0-908	0-909	0-913	0-918	0-921	0-923	54.4
135	0-854	0-861	0-863	0-871	0-879	0-887	0-894	0-901	0-902	0-907	0-912	0-914	0-916	57.2
140	0-842	0-850	0-852	0-861	0-870	0-879	0-886	0-893	0-895	0-900	0-905	0-907	0-910	60.0



# Appendix 3

## Pressure-Enthalpy Diagrams for Propane and n-Butane

Figure A.3a Propane



S = specific entropy, Btu/lb°R  
 T = temperature, °F  
 Datum: C (graphite) and H<sub>2</sub> (gas) at 0° R and 0 lb/in<sup>2</sup> abs

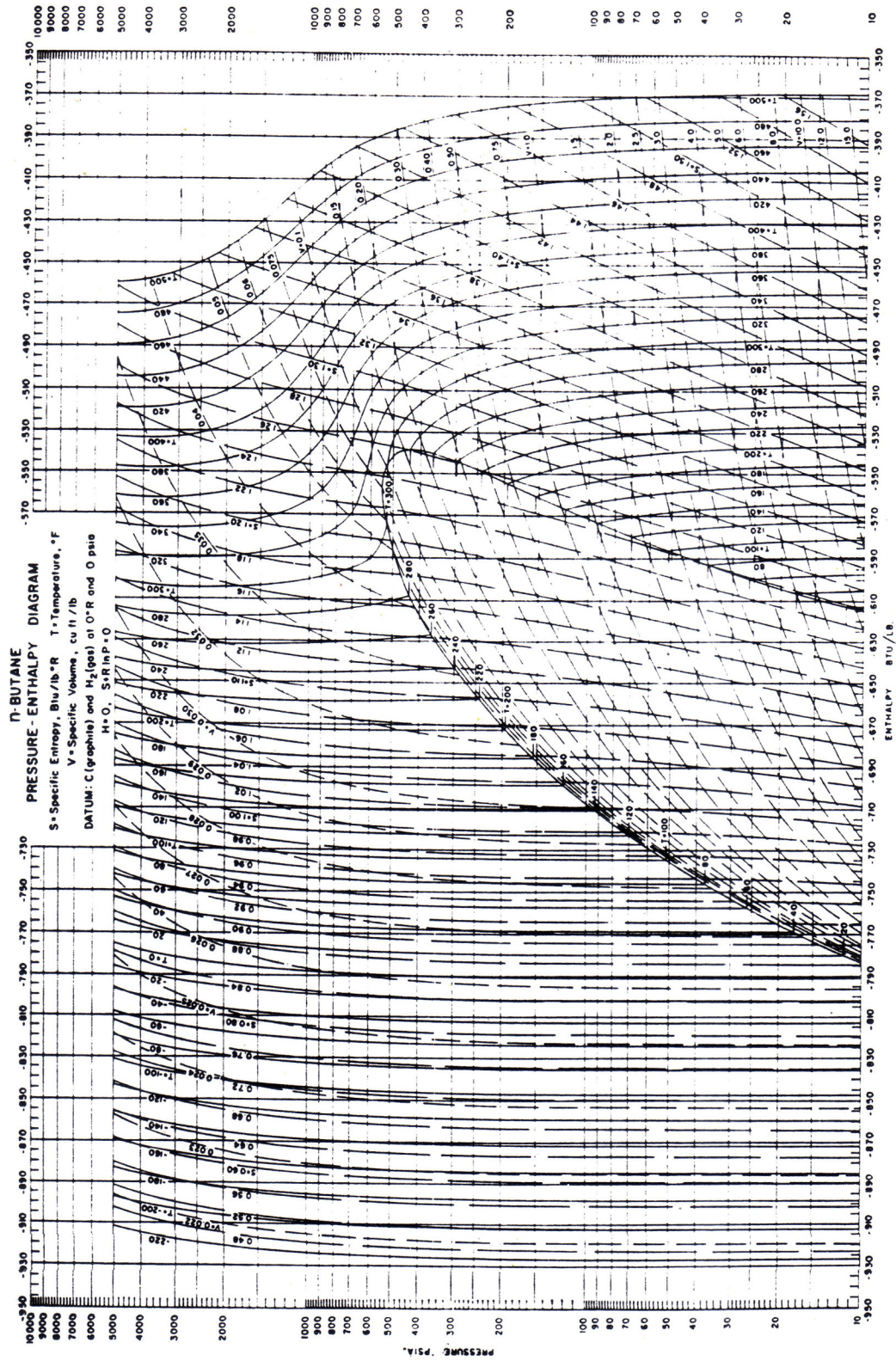
V = specific volume, ft<sup>3</sup>/lb  
 H = O, S + R ln P=0



# Appendix 3 (Continued)

## Pressure-Enthalpy Diagrams for Propane and n-Butane

Figure A.3b n-Butane



$S$  = specific entropy, Btu/lb·°R     $T$  = temperature, °F  
 Datum: C (graphite) and  $H_2$  (gas) at 0° R and 0 lb/in<sup>2</sup> abs  
 $V$  = specific volume, ft<sup>3</sup>/lb  
 $H = 0$ ,  $S = R \ln P + O$



## Appendix 4

### Specifications for Propanes and Butanes

Table A. 4(a) *Propanes*

	(a)	(b)	(c)	(d)	(e)
<i>Composition, mol %</i>					
Acetylenes, max	(n.s.)	(n.s.)	2	(n.s.)	(n.s.)
C <sub>2</sub> 's, max	(n.s.)	(n.s.)	5	(n.s.)	(n.s.)
Ethylene, max	(n.s.)	(n.s.)	1	(n.s.)	(n.s.)
Propylene, max	(n.s.)	≥5	(n.s.)	(n.s.)	(n.s.)
Propane, min	(n.s.)	≤90	(n.s.)	(n.s.)	(n.s.)
Propane + propylene, min	(n.s.)	(n.s.)	(n.s.)	95% wt	(n.s.)
C <sub>4</sub> and higher, max	2.5	2.5	10	(n.s.)	(n.s.)
C <sub>5</sub> and higher, max	(n.s.)	(n.s.)	2	(n.s.)	(n.s.)
<i>Vapour pressure, kg cm<sup>-2</sup> gauge, max</i>					
38.8°C	14.1	14.1	17.9		14.4
45					
70				30	(n.s.)
95% Evaporated, °C, max	-38.3	-38.3	(n.s.)	(n.s.)	2(f)
<i>Residual matter, max</i>					
ml/100 ml	0.05	0.05	(n.s.)		
Oil stain number (f)	30	30	(n.s.)		
ppm wt				50	
<i>Corrosion, copper strip, max</i>					
ASTM scale	1	1	(n.s.)	(n.s.)	1 B
<i>Sulphur compounds, max</i>					
H <sub>2</sub> S, ppm vol. on gas	(n.s.)	(n.s.)	(f)	Negative	(n.s.)
Volatile sulphur, ppm wt	180	120	200	50	50
Elemental sulphur, ppm wt	(n.s.)	(n.s.)	(n.s.)	1.5	(n.s.)
Elemental sulphur and carbonyl sulphide, ppm wt	(n.s.)	(n.s.)	(n.s.)	5.0	(n.s.)
<i>Other impurities, max</i>					
Free water			None visible		
Ammonia	(n.s.)	(n.s.)	(n.s.)	Negative	(n.s.)
Alkali	(n.s.)	(n.s.)	(n.s.)	Negative	(n.s.)
Hydrogen + nitrogen + oxygen + methane, % wt	(n.s.)	(n.s.)	(n.s.)	0.2	(n.s.)

(n.s) not specified, (a) Natural Gas Processors' Association (NGPA), U.S.A.: Commercial.  
 (c) British Standard Specification 4250. (d) Deutsche Normen 51622.  
 (e) French Ministry of Industry and Agriculture N.F.M. 41010  
 (f) Refer Method, † Pass on 'Doctor test'.

# Appendix 4 (Continued)

## Specifications for Propanes and Butanes

Table A. 4(b) *Butanes*

	(a)	(b)	(c)	(d)	(e)
<i>Composition, mol %</i>					
Acetylenes	(n.s.)		2	(n.s.)	(n.s.)
Propane, max	(n.s.)		(n.s.)	(n.s.)	
Butanes + butenes, min	(n.s.)		(n.s.)	95% wt	
C <sub>6</sub> 's and above, max	2.0		2.0	(n.s.)	
Dienes, max	(n.s.)		10	(n.s.)	
<i>Vapour pressure, kg cm<sup>-2</sup> gauge</i>					
38.8°C, max	4.9				
45, max			5.9		
45, min			4.9		
50, max					7.5
70, max					
95% Evaporated, °C, max	+2.2		+2.2	12.0	+1.0
<i>Residual Matter</i>					
ml/100 ml, max	(n.s.)		(n.s.)		
ppm wt	—		—	50	
<i>Doctor test</i>	(n.s.)		(n.s.)	(n.s.)	Pass
<i>Corrosion, copper strip, max</i>					
ASTM scale	1		(n.s.)	(n.s.)	1 B
<i>Sulphur compounds, max</i>					
H <sub>2</sub> S, ppm vol. on gas	(n.s.)		(f)	Negative	Negative†
Volatile sulphur, ppm wt	180		200	50	(n.s.)
Elemental sulphur, ppm wt	(n.s.)		(n.s.)	1.5	(n.s.)
Elemental sulphur + carbonyl sulphide, ppm wt	(n.s.)		(n.s.)	5	(n.s.)
<i>Other impurities, max</i>					
Free water	None		None	Negative	None
Ammonia	(n.s.)		(n.s.)	Negative	(n.s.)
Alkali	(n.s.)		(n.s.)	Negative	(n.s.)
Hydrogen + nitrogen + oxygen + methane, % wt max	(n.s.)		(n.s.)	0.2	(n.s.)

(n.s) not specified, (a) Natural Gas Processors' Association (NGPA), U.S.A.: Commercial.

(c) British Standard Specification 4250. (d) Deutsche Normen 51622.

(e) French Ministry of Industry and Agriculture N.F.M. 41010

(f) Refer Method, † Pass on 'Doctor test'.

## Appendix 5

### LPG Orifice Capacity

At sea level-Gas pressure 280 mm H<sub>2</sub>O

Orifice dimensions			Throughout capacity, kcal/hr		
Drill size No.	Diameter, mm	Area, mm <sup>2</sup>	Propane	Butane	60/40 C <sub>4</sub> /C <sub>3</sub>
80	0.343	0.0922	314	361	338
75	0.534	0.223	789	891	850
70	0.711	0.397	1442	1608	1533
69	0.742	0.432	1550	1750	1670
68	0.797	0.487	1748	1972	1880
67	0.813	0.518	1862	2100	2040
66	0.839	0.552	1978	2235	2135
65	0.889	0.620	2230	2520	2405
64	0.915	0.656	2360	2665	2540
63	0.940	0.694	2495	2815	2685
62	0.965	0.732	2625	2970	2830
61	0.990	0.770	2770	3130	2985
60	1.015	0.810	2920	3290	3140
59	1.041	0.851	3060	3455	3300
58	1.068	0.894	3215	3630	3460
57	1.091	0.937	3365	3800	3630
56	1.181	1.093	3960	4440	4250
55	1.320	1.368	4920	5550	5290
54	1.398	1.535	5520	6220	5940
53	1.512	1.792	6435	7280	6930
52	1.613	2.045	7355	8300	7930
51	1.702	2.275	8225	9280	8870
50	1.779	2.480	9000	10,160	9670
49	1.855	2.705	9810	11,090	10,580
48	1.930	2.915	10,720	12,100	11,520
47	1.995	3.125	11,450	12,950	12,350
46	2.060	3.320	12,250	13,820	13,200
45	2.085	3.405	12,670	14,280	13,650
44	2.185	3.750	14,020	15,820	15,090
43	2.262	4.010	14,980	16,900	16,130
42	2.375	4.43	16,550	18,680	17,800
41	2.440	4.67	17,420	19,700	18,800
40	2.435	4.86	18,150	20,500	19,570
39	2.525	5.02	18,720	21,150	20,200
38	2.575	5.22	19,500	22,000	21,000
37	2.640	5.47	20,450	23,070	22,030
36	2.705	5.74	21,450	24,200	23,120
35	2.795	6.01	22,850	25,620	24,650
34	2.820	6.24	23,300	26,400	25,120
33	2.870	6.45	24,130	27,300	26,150
32	2.945	6.81	25,450	28,750	27,500
31	3.050	7.29	27,250	30,750	29,400
30	3.265	8.35	31,250	35,300	33,650
25	3.80	11.30	42,300	47,800	45,600
20	4.09	13.15	49,100	55,450	52,900
15	4.60	16.58	61,800	69,900	66,800



## Appendix 6

### Some World Manufacturers of Combustion Equipment

#### (a) LPG Burners

(N.B. Equipment made by these firms is frequently produced under licence. If known, this is indicated in brackets.)

<i>United States</i>	Aeroil Products Brunner Engineering Burners Inc. Coen Liptak Eclipse Fuel Engineering Flame Engineering Flynn Burner Co. Gordon & Piatt	Hauck Manufacturing Maxon Burner Co. North American LP Gas Equipment Corp. Peabody Engineering Co. Pyronics Selas Corporation
<i>United Kingdom</i>	Aeromatic Co. British Oxygen Co. Bray, Geo. Calor Gas Davis/Wayne Hamworthy Engineering (Schieldrop etc.) Keith Blackman Laidlaw Drew Maywick Morganite (Blu Surf)	Nuway (Eclipse) Radiant Heating W. H. Rowe Stordy Combustion (Hauck) John Thurley (Maxon) Urquhart Engineering Wellman Engineering (Selas)
<i>W. Germany</i>	Balcke Citex-Gastechnik Demat (MAT) Elco Flameco (Eclipse) Fulmina GFG Junkers Kraft	Küpersbusch Maile H. Saacke Maxon G.m.b.H. (Maxon) Schwank Selas Wärmetechnik (Selas) Weisshaupt Widekind (Hauck)
<i>France</i>	Air Liquide Chaffoteaux S.B.M.	Stein Surface (Maxon) Sucmanu U.R.G.
<i>Denmark</i>	Kosangas Internat.	Danfoss
<i>Japan</i>	Katsura	Rinai
<i>India</i>	Bombay Foods	
<i>Sweden</i>	Primus-Sievert	
<i>Netherlands</i>	Duiker	Schildrop
<i>Belgium</i>	M.A.T.	Hanrez
<i>Australia</i>	Bulgin	C.I.G.

## **Appendix 6 (Continued)**

### **Some World Manufacturers of Combustion Equipment**

#### **(b) Flame Supervision Equipment**

<i>Country</i>	<i>Organization</i>	<i>Detection method</i>
United States	Electronics Corp. of America (Fireye)	Ultraviolet, Rectification
	Honeywell	Rectification
	Peabody	Infra-red Pulsation
United Kingdom	Black Automatic Controls (G.E.C.)	Rectification
	Ronald Trist Controls	Ultraviolet
	Radiovisor Parent	Rectification
Denmark	Danfoss	Ultraviolet
Switzerland	Landis and Gyr	Rectification or Ultraviolet
Belgium	J.M.G. Controls	Rectification

## Appendix 7

### Common Properties of Commercial LPG's

	<i>Commercial Propane</i>	<i>Commercial Butane</i>
Boiling point, °C	-45	-7
Freezing point, °C	-186	-150
(a) <i>Liquid at vapour pressure, 15.5°C</i>		
Density		
lb/U.S. gal	4.2	4.8
lb/Imp. gal	5.1	5.75
lb/ft <sup>3</sup>	31.9	35.9
kg./l.	0.51	0.575
Specific volume		
U.S. gal/lb	0.24	0.21
Imp. gal/lb	0.20	0.175
ft <sup>3</sup> /lb	0.031	0.028
l./kg	1.96	1.73
Imp. gal/long ton	440	390
Specific gravity (w.r.t. water = 1)	0.510	0.575
Vapour pressure		
psig	95	20
kg/cm <sup>-2</sup> g	6.65	1.40
Viscosity, cP	0.10	0.15
Latent heat		
Btu/lb	170	160
kcal/kg	95	90
Specific heat, Btu/lb °F (kg/kg °C)	0.60	0.57
Calorific value, gross		
Btu/lb	21,500	21,200
Btu/U.S. gal	91,550	101,000
Btu/Imp. gal	110,000	122,000
Therms/Imp. gal	1.10	1.22
Therms/long ton	480	475
kcal/kg	11,900	11,800
Calorific value, nett		
Btu/lb	20,000	19,800
kcal/kg	11,000	10,900
(b) <i>Saturated vapour, 15.5°C</i>		
Density		
lb/ft <sup>3</sup>	0.95	0.35
kg/m <sup>3</sup>	15.3	5.62
Specific volume		
ft <sup>3</sup> /lb	1.1	2.85
m <sup>3</sup> /tonne	65.0	178



## Appendix 7 (Continued)

### Common Properties of Commercial LPG's

	<i>Commercial Propane</i>	<i>Commercial Butane</i>
(c) <i>Vapour at 1 atmosphere, 15.5°C</i>		
Density		
lb/ft <sup>3</sup>	0.115	0.155
kg/m <sup>3</sup>	2.0	2.6
Specific volume		
ft <sup>3</sup> /lb	8.6	6.5
ft <sup>3</sup> /ft <sup>3</sup> of liquid	274	233
m <sup>3</sup> /kg	0.5	0.38
Specific gravity (air = 1)	1.5	2.0
Specific heat, Btu/lb °F ( kcal/kg °C)		
<i>c<sub>p</sub></i>	0.38	0.39
<i>c<sub>v</sub></i>	0.34	0.35
Calorific value, gross		
Btu/ft <sup>3</sup> (dry)	2500	3200
kcal/N m <sup>3</sup>	24,000	30,700
Calorific value, nett.		
Btu/ft <sup>3</sup>	2300	3000
kcal/N m <sup>3</sup>	22,600	29,000
Ignition temperature, in air, °C	450–500	420–490
Flame temperature, in air, °C, max.	1970	1975
Combustion air required,		
stichiometric proportion		
ft <sup>3</sup> /ft <sup>3</sup> (m <sup>3</sup> /m <sup>3</sup> )	24	30
Max. CO <sub>2</sub> at stoichiometric air	13.8	13.9
Burning velocity, max.		
ft/sec	1.3	1.3
cm/sec	38.5	38
Limits of flammability,		
vol % of vapour in air–gas mixture		
lower	2.0	1.8
upper	10.0	8.5

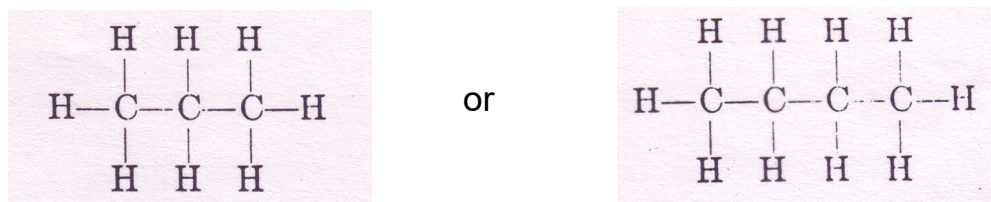
## Appendix 8

### Nomenclature of Hydrocarbons

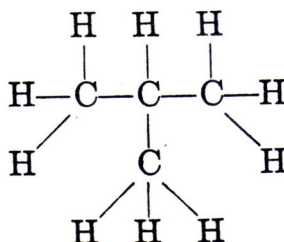
As the name implies, hydrocarbons are chemical compounds composed of hydrogen and carbon atoms. Each hydrogen atom has one electron that it shares with another atom; each carbon atom has four such electrons. A chemical linkage is formed between two atoms when each contributes an electron to make a pair that is shared by the two atoms: the pair of shared electrons is called a "bond." Because a hydrogen atom has only one sharable electron, it forms only one bond.<sup>^</sup> With four sharable electrons, a carbon atom forms four bonds. Sometimes two carbon atoms share two pairs of electrons, which constitute a "double bond," or three pairs of electrons, which constitute a "triple bond."

Hydrocarbons are classified according to the manner in which their carbon atoms are linked together. Depending upon their hydrocarbon skeletons, hydrocarbons are classified as paraffins, naphthenes, olefins, diolefines, acetylenes, and aromatics.

**Paraffins:** Paraffins are hydrocarbons whose carbon atoms form chains, like C—C—C or C—C—C—C, with only single bonds between each pair of carbon atoms. Hydrogen atoms satisfy the remaining linkages of each carbon atom, and the complete molecules are, for example:



If the chain has no branches, the molecule is classified as normal paraffin (n-paraffin). If the chain is branched, the molecule is classified as an i-paraffin. The simplest i-paraffin contains four carbon atoms. Its carbon skeleton is C—C—C, and the complete molecule is:



The chemical formulas of all paraffins can be represented by  $C_nH_{2n+2}$ , where  $n$  is any whole number. Some of the lower-boiling paraffins are listed in Table A.8-1.

**Naphthenes:** Naphthenic hydrocarbons are similar to paraffins, except that all or parts of the carbon atoms are joined to form a ring. As shown in Table A.8-2, a naphthenic ring usually contains five or six carbon atoms, although more or fewer are possible. The formation of a ring requires one more carbon-to-carbon bond than does the formation of a chain. Consequently, naphthenes contain less hydrogen than do paraffins. The general formula of single-ring naphthenes is  $C_nH_{2n}$ . Chemically, naphthenes are somewhat more reactive than paraffins.

**Olefins:** An ordinary olefin is similar to paraffin, except that two of its carbon atoms are connected by a double bond; thus, it has two less hydrogen atoms than the corresponding paraffin, and the general formula is the same as for single-ring naphthenes,  $C_nH_{2n}$ . Some lower-boiling olefins are listed in Table A.8-3.

A cyclic olefin is like a naphthene, although it also has a double bond. The general formula for a single-ring cyclic olefin is  $C_nH_{2n-2}$ . Various chemicals add readily to a double bond. Thus, olefins are much more reactive than paraffins or naphthenes, both of which are relatively inert chemically. Their reactivity often makes olefins more valuable than paraffins or naphthenes.

**Diolefins:** As illustrated in Table A.8-3, a diolefine contains two double bonds. Diolefins are very reactive chemically and, in high concentrations, are valuable chemicals. When they are present in low concentrations, their high reactivities often make them harmful to product quality, inasmuch as they institute undesirable reactions, such as gum formation in gasoline. The general formula for straight-chain diolefines is  $C_nH_{2n-2}$ . For single-ring cyclic diolefines, the general formula is  $C_nH_{2n-4}$ .

**Acetylenic Hydrocarbons:** Acetylenic hydrocarbons are illustrated in Table A.8-4; they contain triple bonds between two carbon atoms. Like diolefines they are highly reactive, and their reactivity makes them valuable in high concentrations, but usually deleterious in low concentrations. The general formula for acetylenic hydrocarbons is the same as for diolefines, i.e.,  $C_nH_{2n-2}$  for straight-chain compounds,  $C_nH_{2n-4}$  for single-ring cyclic compounds.



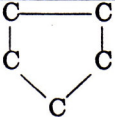
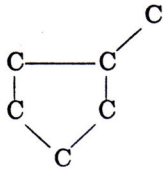
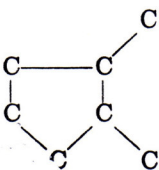
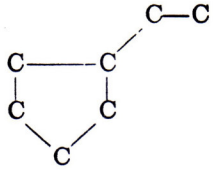
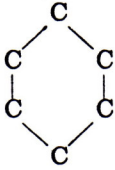
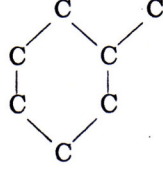
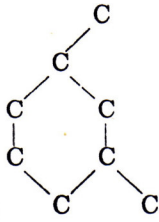
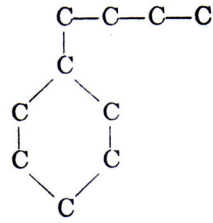
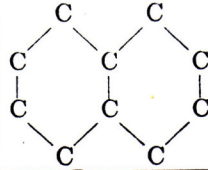
**Aromatics:** Aromatics are compounds that contain at least one six-carbon ring with three double bonds. As illustrated in Table A.8-6, the rings may be joined together. Aromatics are intermediate in chemical reactivity, and they are often used as chemical building blocks. They are much less reactive, however, than diolefines or acetylenic hydrocarbons, and their chemical reactivity is seldom great enough to constitute a product-quality problem.

## A.8-1 Some Paraffinic Hydrocarbons

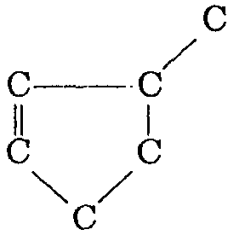
Carbon atoms	Name	Carbon skeleton	Boiling point, °F
1	Methane	C	-259
2	Ethane	C—C	-128
3	Propane	C—C—C	-44
4	<i>n</i> -Butane	C—C—C—C	31
5	<i>n</i> -Pentane	C—C—C—C—C	97
6	<i>n</i> -Hexane	C—C—C—C—C—C	156
7	<i>n</i> -Heptane	C—C—C—C—C—C—C	209
8	<i>n</i> -Octane	C—C—C—C—C—C—C—C	258
9	<i>n</i> -Nonane	C—C—C . . . .C—C	303
10	<i>n</i> -Decane	C—C—C . . . .C—C	345
11	<i>n</i> -Undecane	C—C—C . . . .C—C	385
12	<i>n</i> -Dodecane	C—C—C . . . .C—C	421
16	Cetane	C—C—C . . . .C—C	547
4	<i>i</i> -Butane	C—C—C   C	11
5	<i>i</i> -Pentane	C—C—C—C   C	82
6	2-Methylpentane	C—C—C—C—C   C	141
6	3-Methylpentane	C—C—C—C—C   C	146
6	Neohexane	C   C—C—C—C   C	122
6	Diisopropyl	C—C—C—C       C   C	136
8	<i>i</i> -Octane	C   C—C—C—C—C          C      C	211



## A.8-2 Some Naphthenic Hydrocarbons

Carbon atoms	Name	Carbon skeleton	Boiling point, °F
5	Cyclopentane		121
6	Methylcyclopentane		161
7	1,2-Dimethylcyclopentane		
7	Ethylcyclopentane		218
6	Cyclohexane		177
7	Methylcyclohexane		214
8	1-3-Dimethylcyclohexane		254
10	n-Butylcyclohexane		
10	Decalin		373

## A.8-3 Some Olefinic Hydrocarbons

Carbon atoms	Name	Carbon skeleton	Boiling point, °F
2	Ethylene	$C=C$	-155
3	Propene	$C=C-C$	-54
4	<i>n</i> -Butene-1	$C=C-C-C$	21
4	<i>n</i> -Butene-2	$C-C=C-C$	36
5	<i>n</i> -Pentene-1	$C=C-C-C-C$	86
5	<i>n</i> -Pentene-2	$C-C=C-C-C$	98
6	<i>n</i> -Hexene-1	$C=C-C-C-C-C$	146
6	<i>n</i> -Hexene-3	$C-C-C=C-C-C$	154
4	<i>i</i> -Butene	$  \begin{array}{c}  C=C-C \\    \\  C  \end{array}  $	20
5	<i>i</i> -Pentene-1	$  \begin{array}{c}  C=C-C-C \\    \\  C  \end{array}  $	88
5	<i>i</i> -Pentene-2	$  \begin{array}{c}  C-C=C-C \\    \\  C  \end{array}  $	101
6	2-Methylpentene-1	$  \begin{array}{c}  C=C-C-C-C \\    \\  C  \end{array}  $	144
6	2-Methylpentene-3	$  \begin{array}{c}  C-C-C=C-C \\    \\  C  \end{array}  $	134
6	Methylcyclopentene		

## A.8-4 Some Diolefinic Hydrocarbons

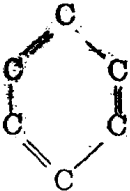
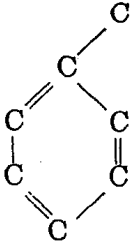
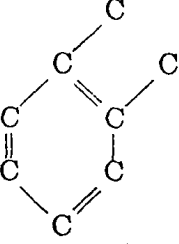
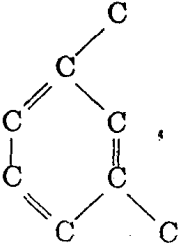
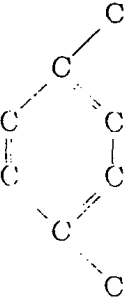
Carbon atoms	Name	Carbon skeleton	Boiling point, °F
4	Butadiene	$C=C-C=C$	24
5	Pentadiene-1,3	$C=C-C=C-C$	100
5	Pentadiene-1,4	$C=C-C-C=C$	
5	Isoprene	$  \begin{array}{c}  C=C-C=C \\    \\  C  \end{array}  $	98

## A.8-5 Some Acetylenic Hydrocarbons

Carbon atoms	Name	Carbon skeleton	Boiling point, °F
2	Acetylene	$C\equiv C$	-10
3	Propine	$C\equiv C-C$	
4	Butine-1	$C\equiv C-C-C$	47
4	Butine-2	$C-C\equiv C-C$	81



## A.8-6 Some Aromatic Hydrocarbons

Carbon atoms	Name	Carbon skeleton	Boiling point, °F
6	Benzene		176
7	Toluene		231
8	<i>o</i> -Xylene		292
8	<i>m</i> -Xylene		282
8	<i>p</i> -Xylene		281

## A.8-6 Some Aromatic Hydrocarbons (Continued)

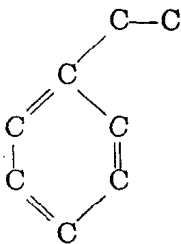
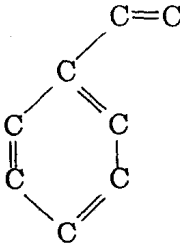
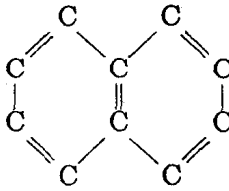
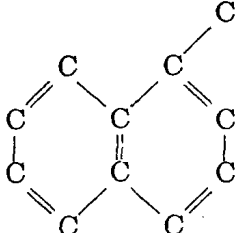
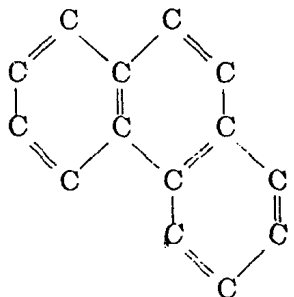
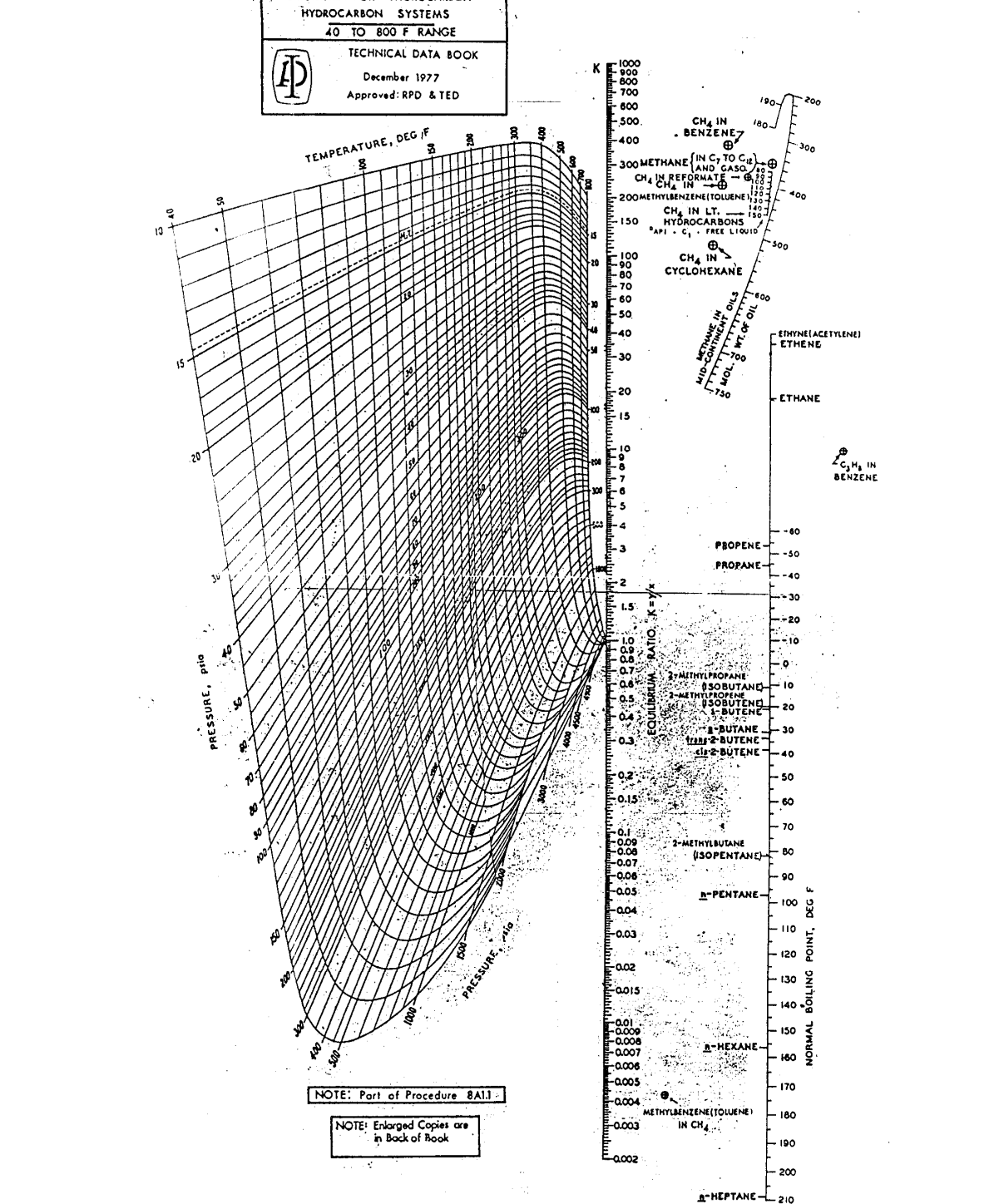
Carbon atoms	Name	Carbon skeleton	Boiling point, °F
8	Ethylbenzene		277
8	Styrene		293
10	Naphthalene		424
11	1-Methylnaphthalene		467
14	Phenanthrene		644

FIGURE 8A1.17  
HIGH-TEMPERATURE VAPOR-LIQUID





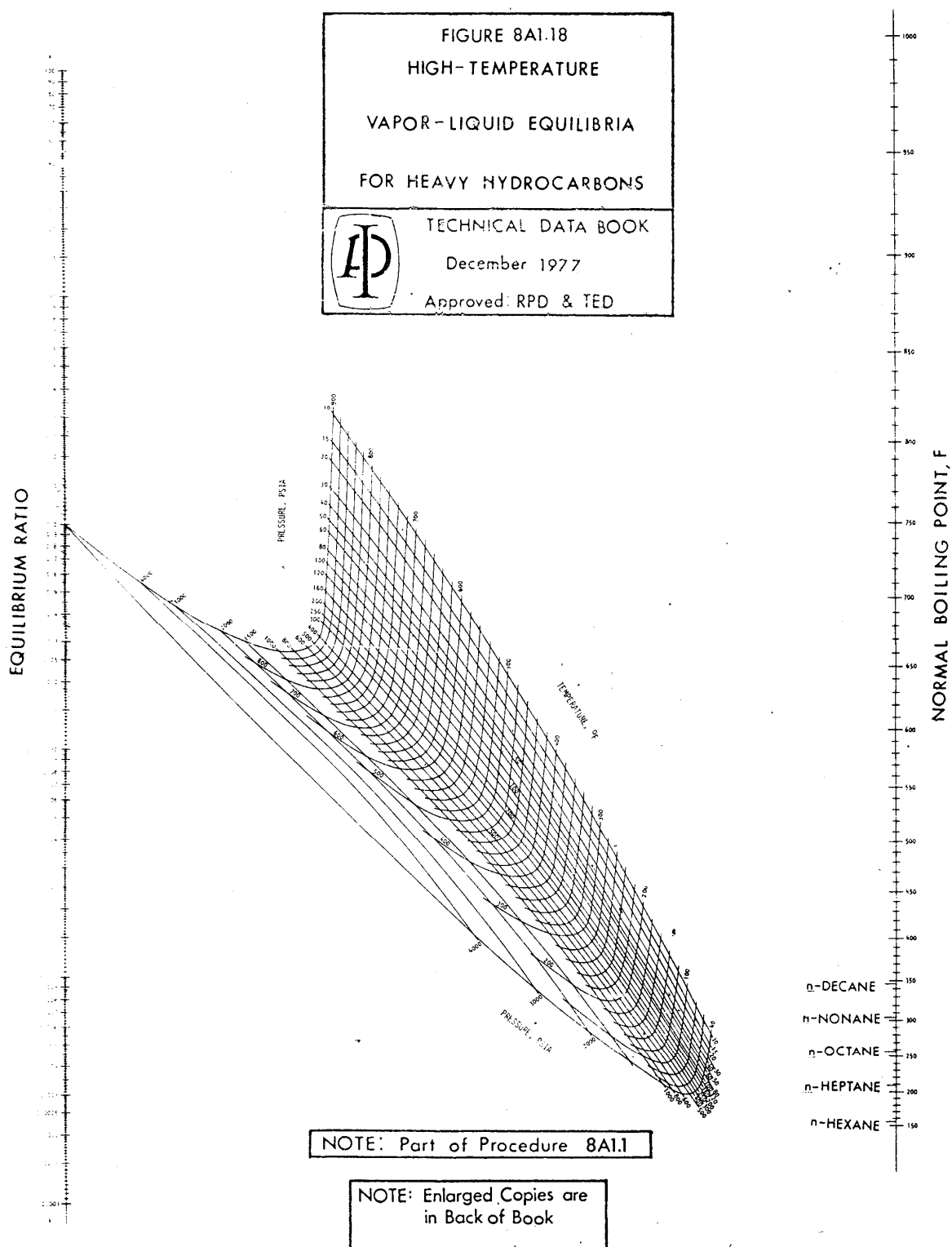


Figure A.9-1b Vapor – Liquid Equilibria for Heavy Hydrocarbons

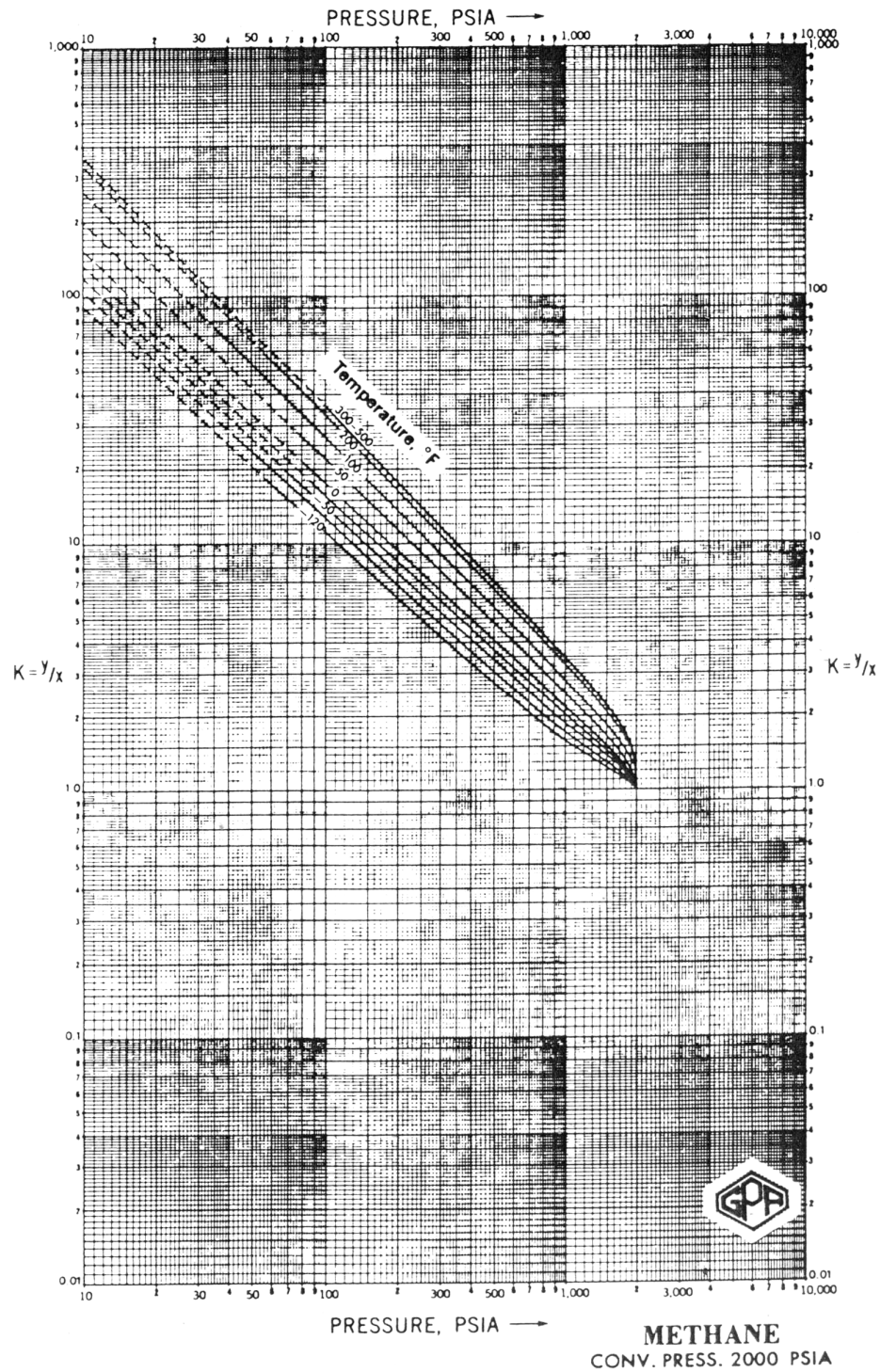


Figure A.9-2 “K” Values for Methane

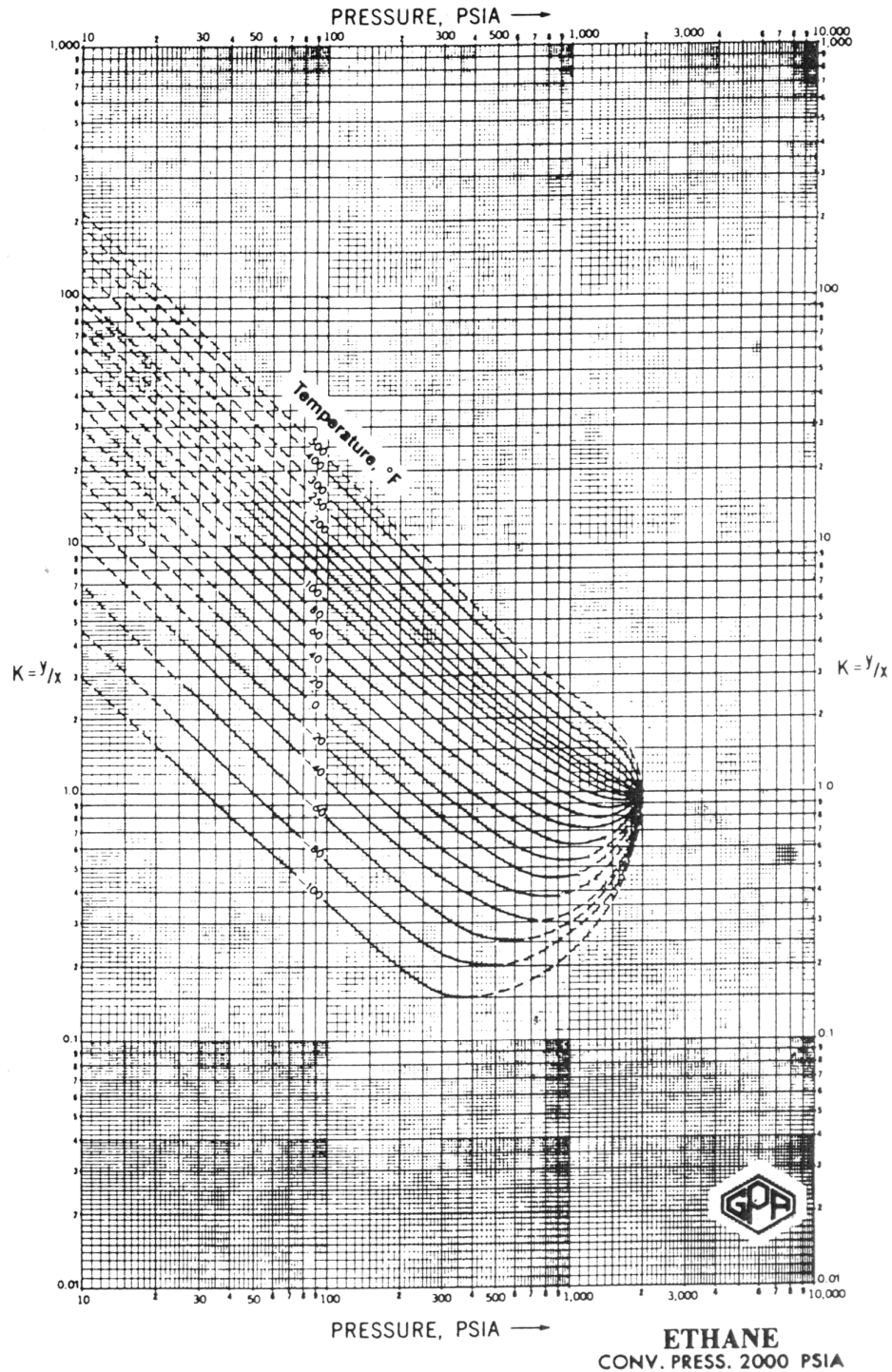


Figure A.9-3 “K” Values for Ethane



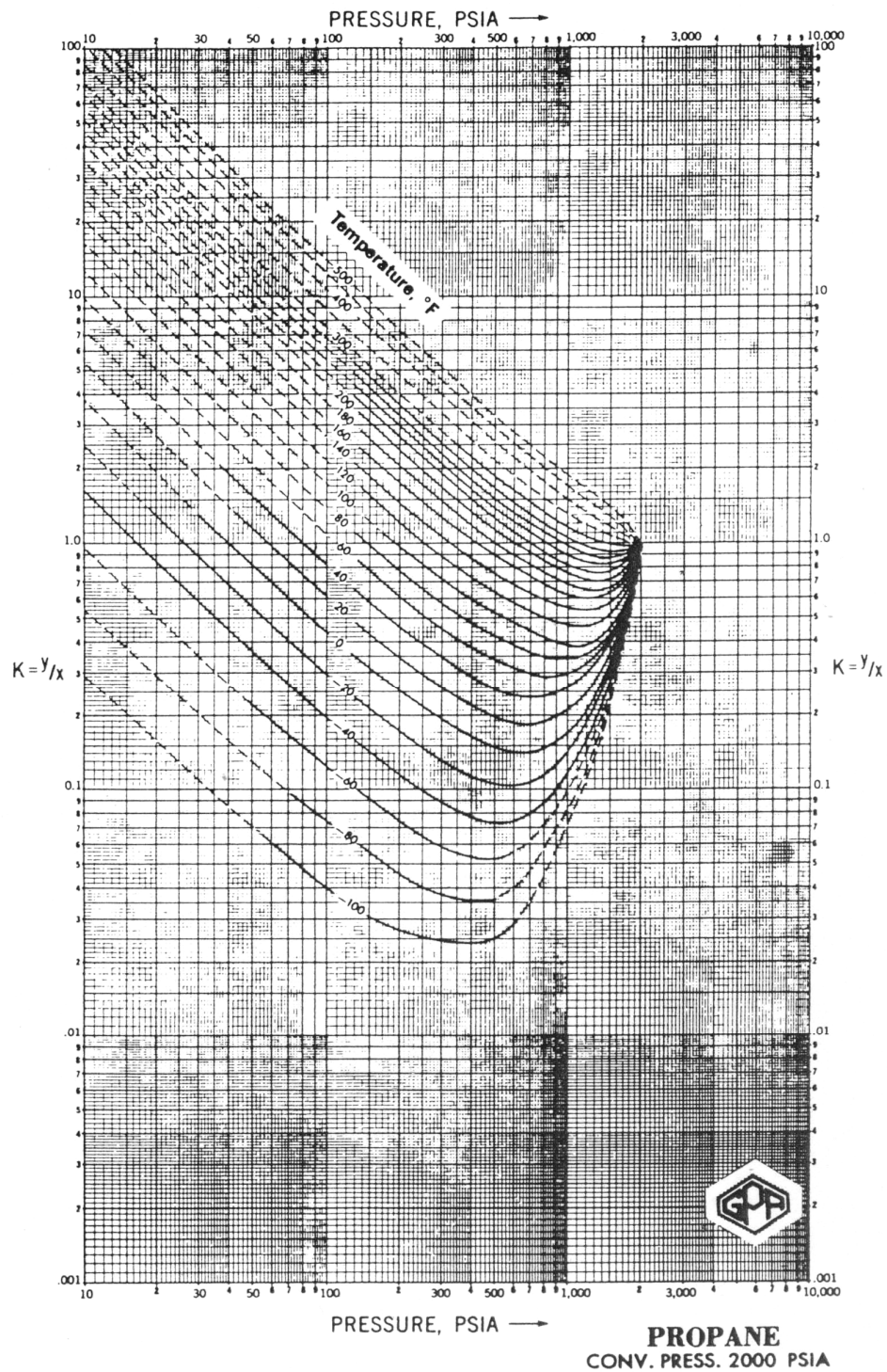


Figure A.9-4 “K” Values for Propane

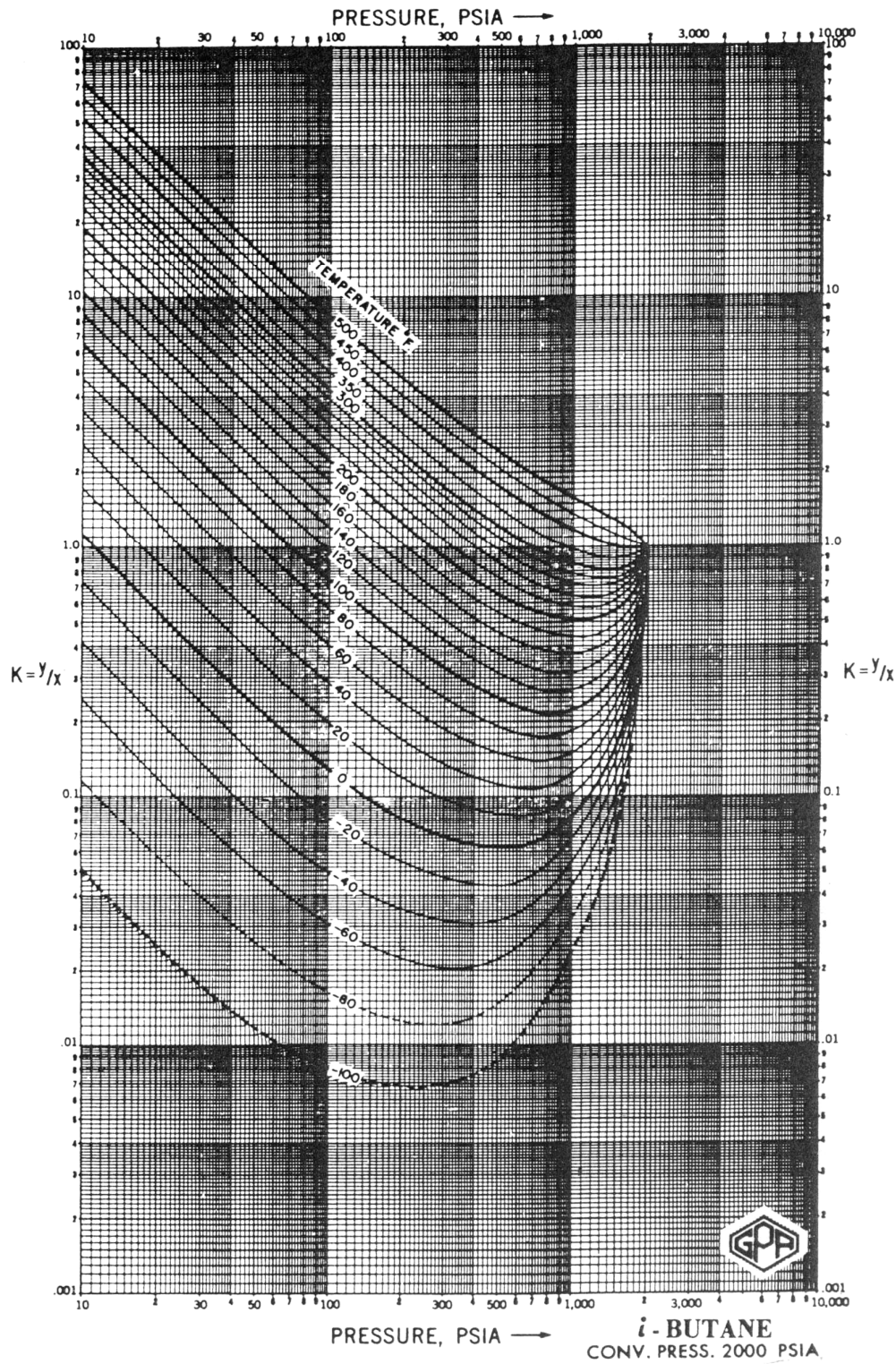


Figure A.9-5 "K" Values for i-Butane

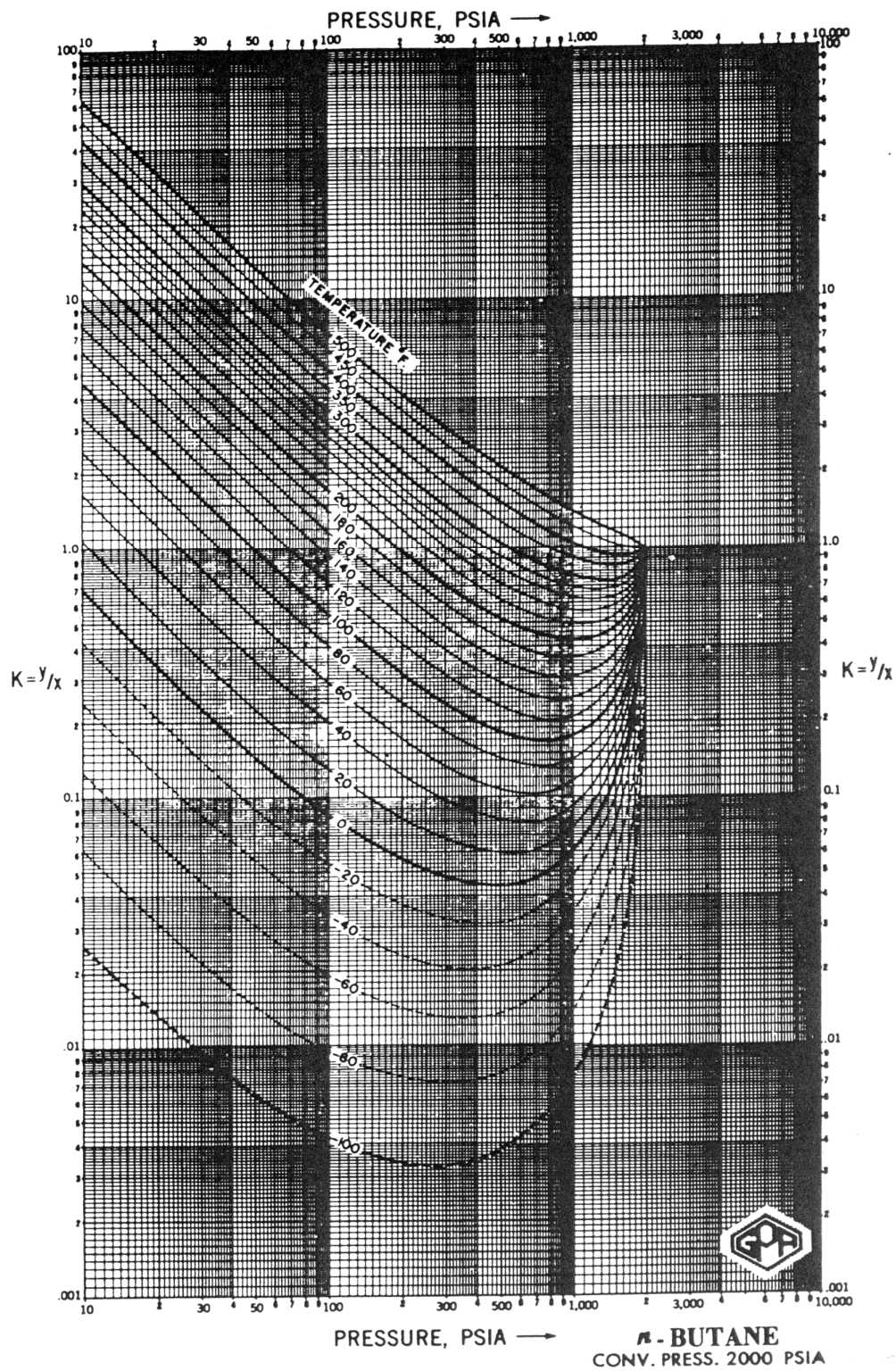


Figure A.9-6 “K” Values for n-Butane





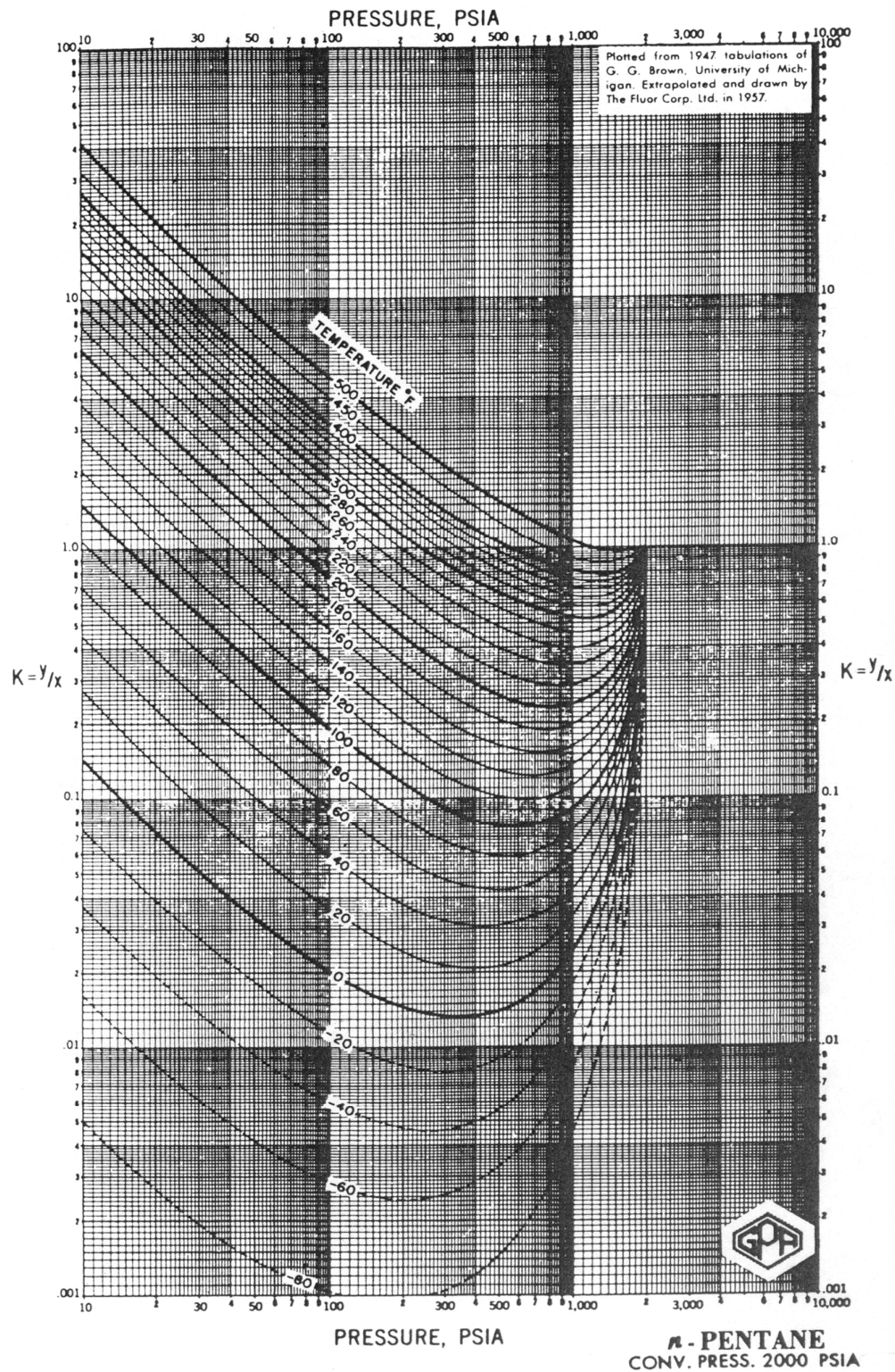


Figure A.9-8 "K" Values for n-Pentane

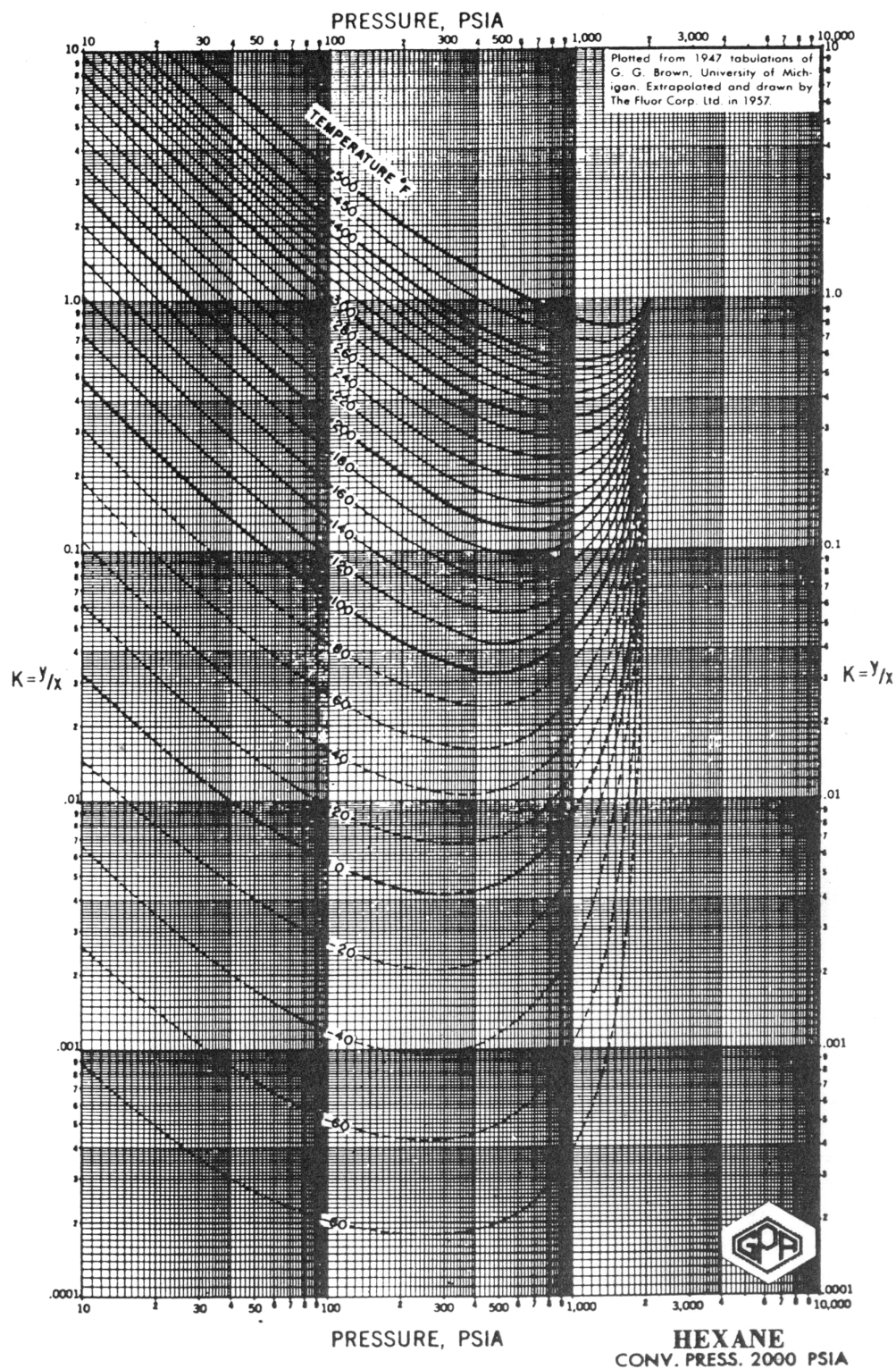


Figure A.9-9 “K” Values for Hexane

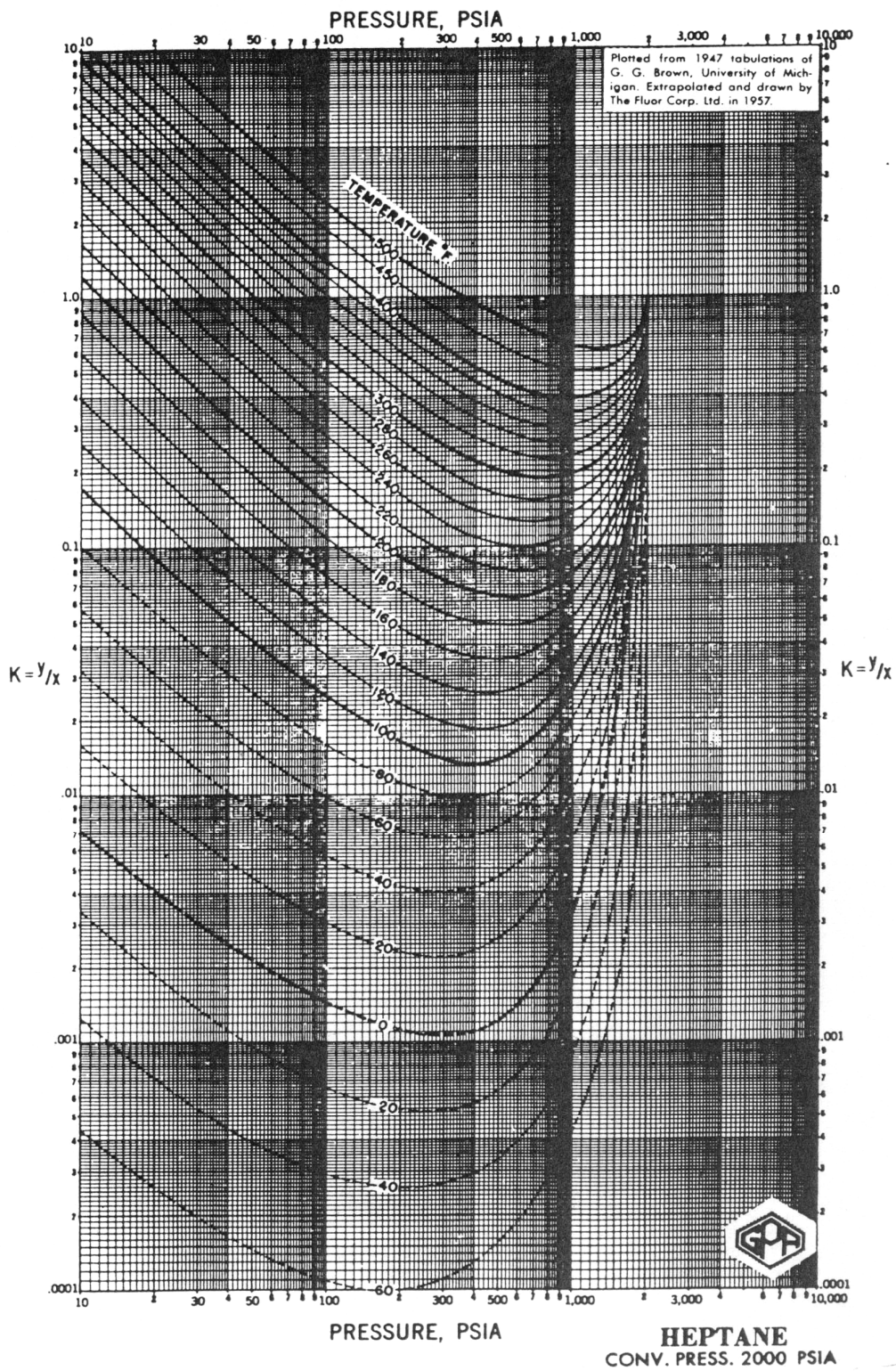


Figure A.9-10 “K” Values for Heptane







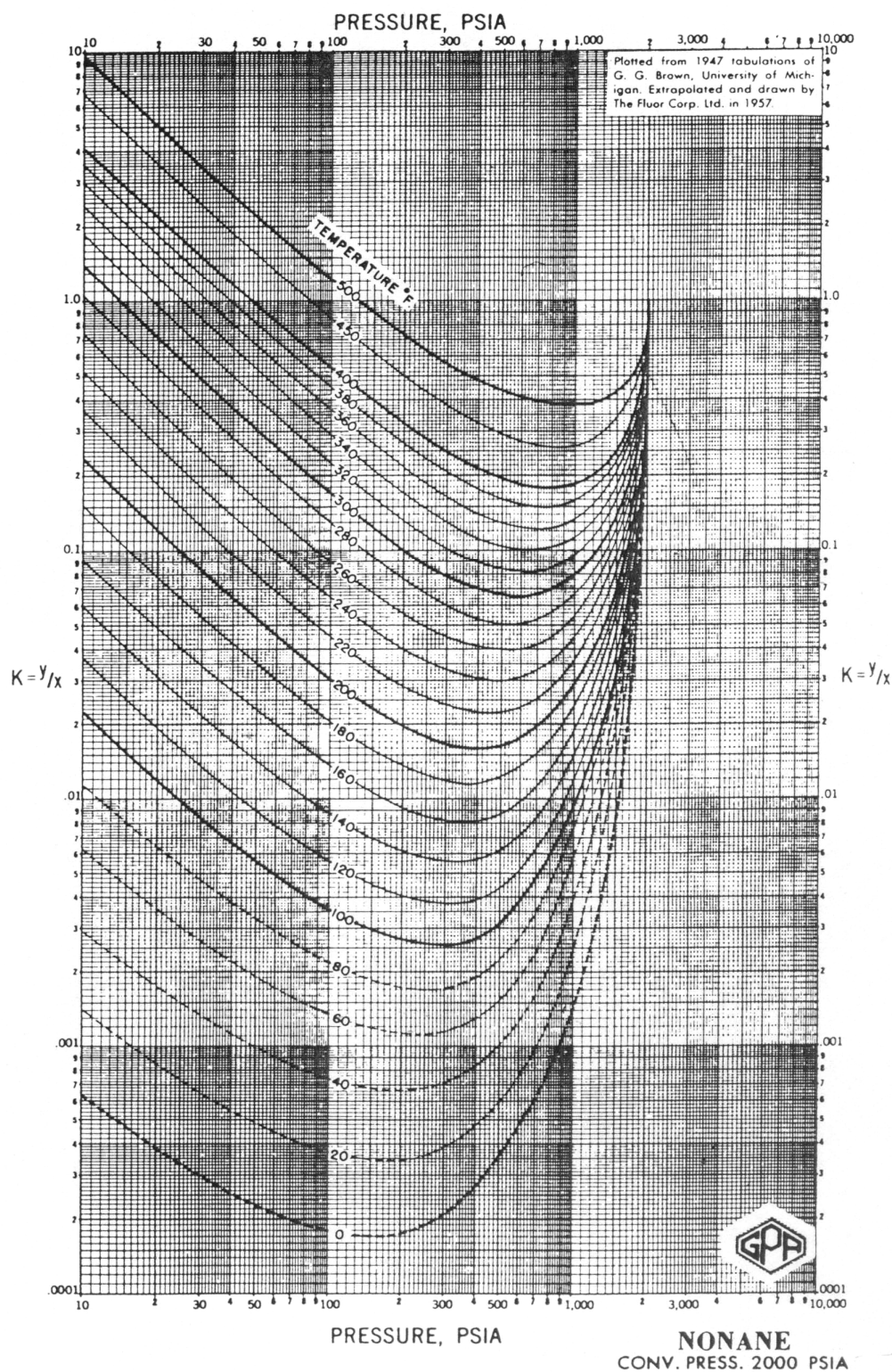


Figure A.9-12 “K” Values for Nonane

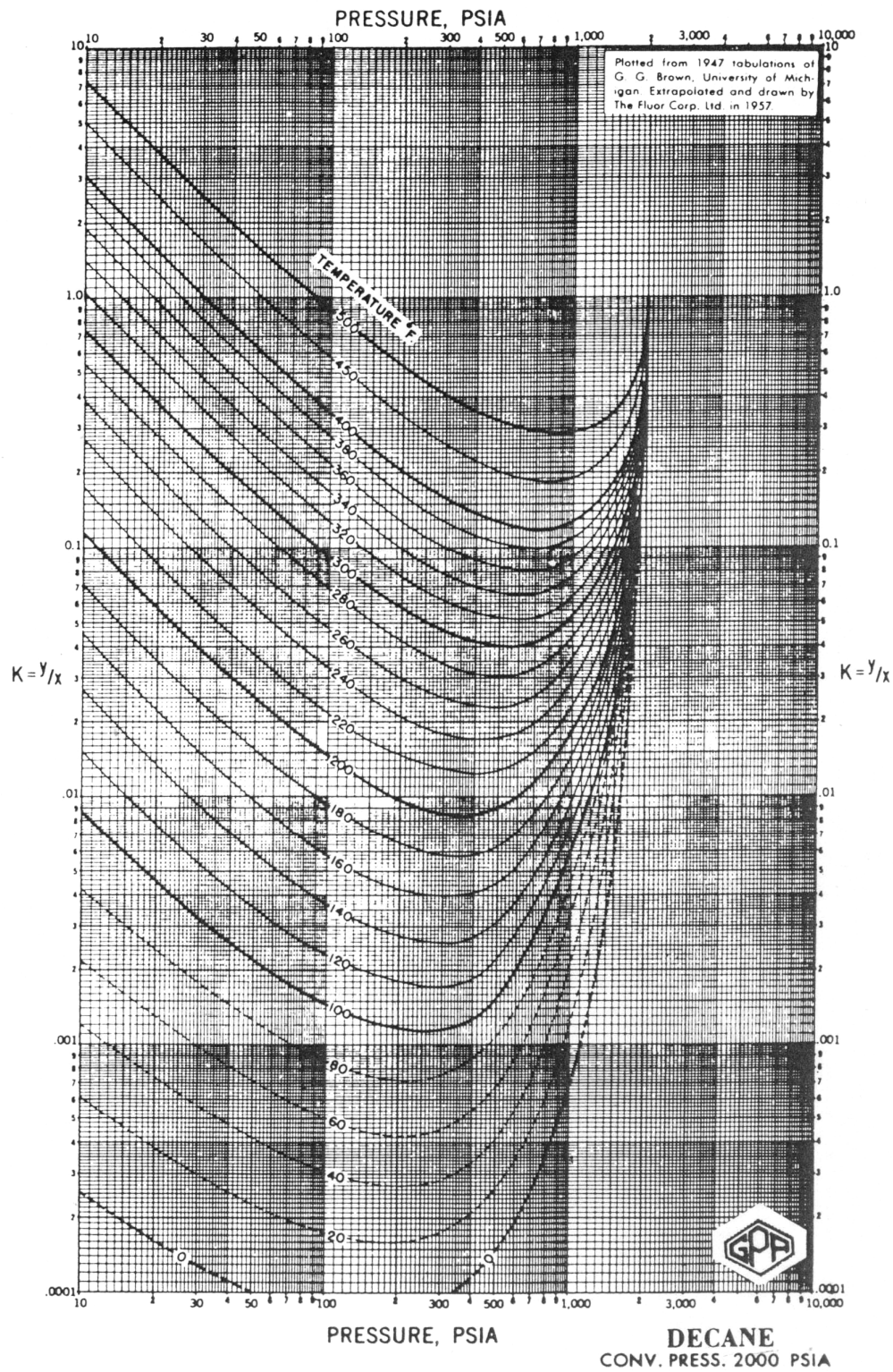
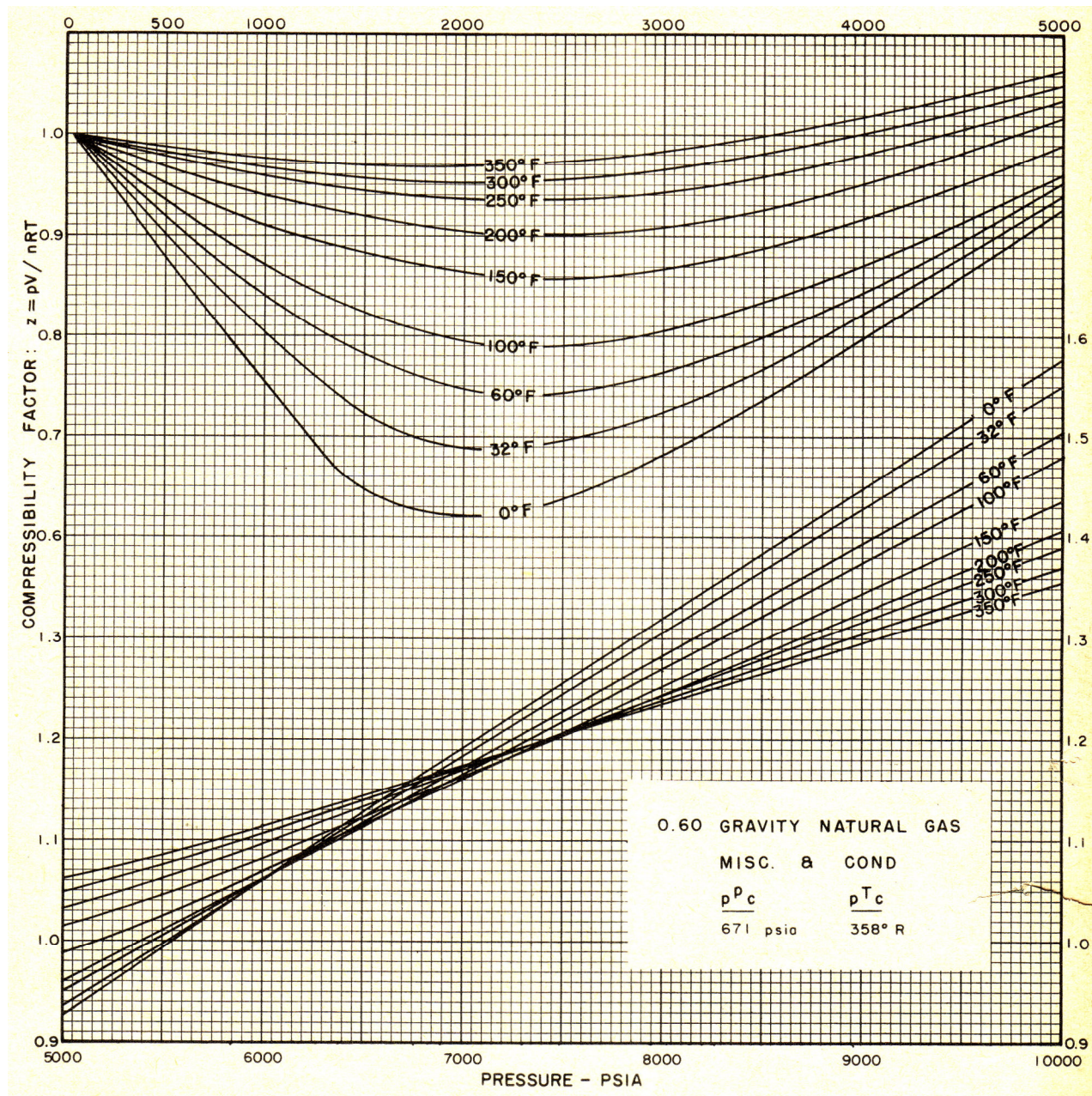


Figure A.9-13 "K" Values for Decane



# Appendix 10 Simplified Compressibility Factor Chart for Natural Gas Calculations

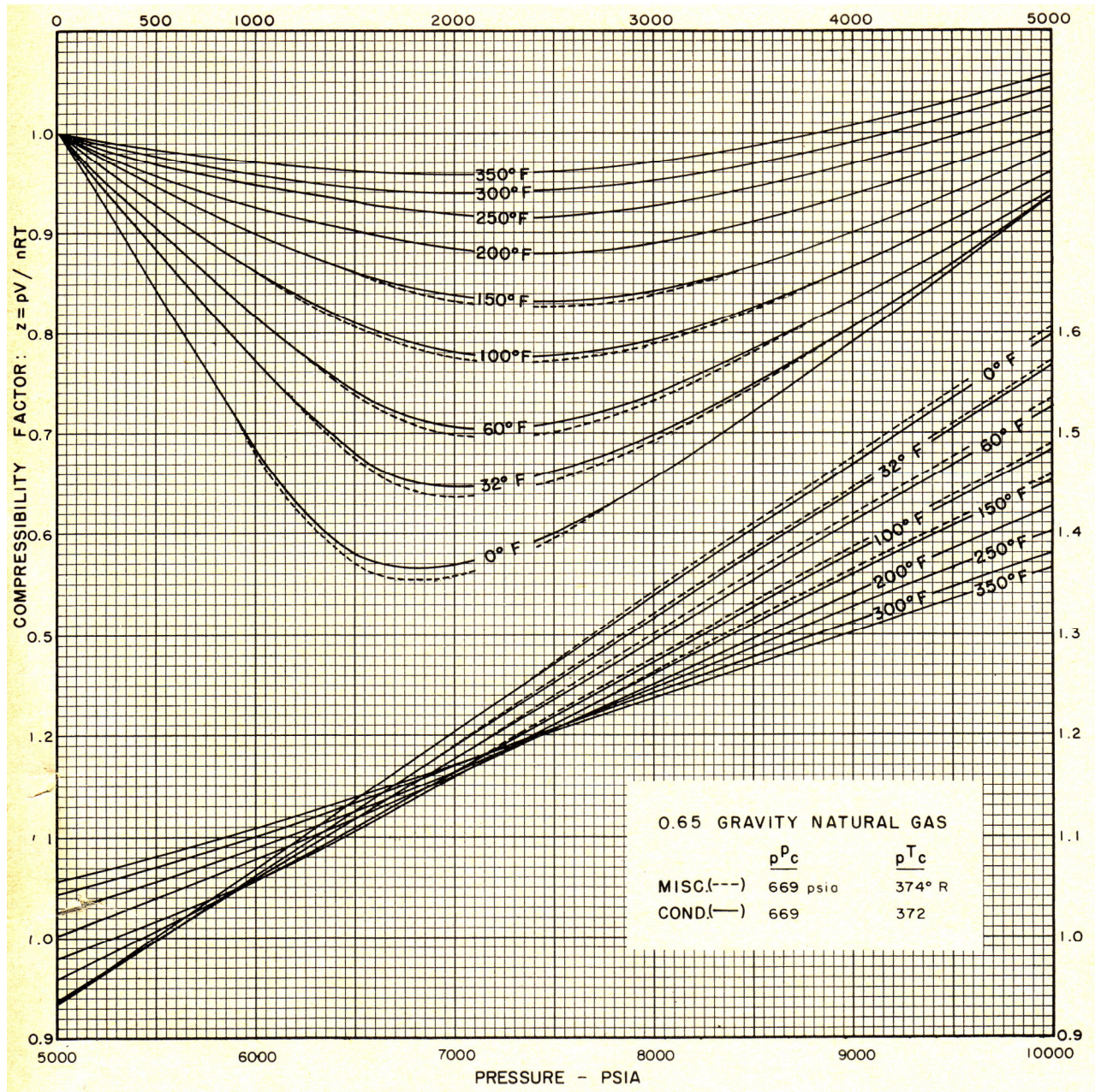
Chart A.10-1





# Appendix 10 Simplified Compressibility Factor Chart for Natural Gas Calculations

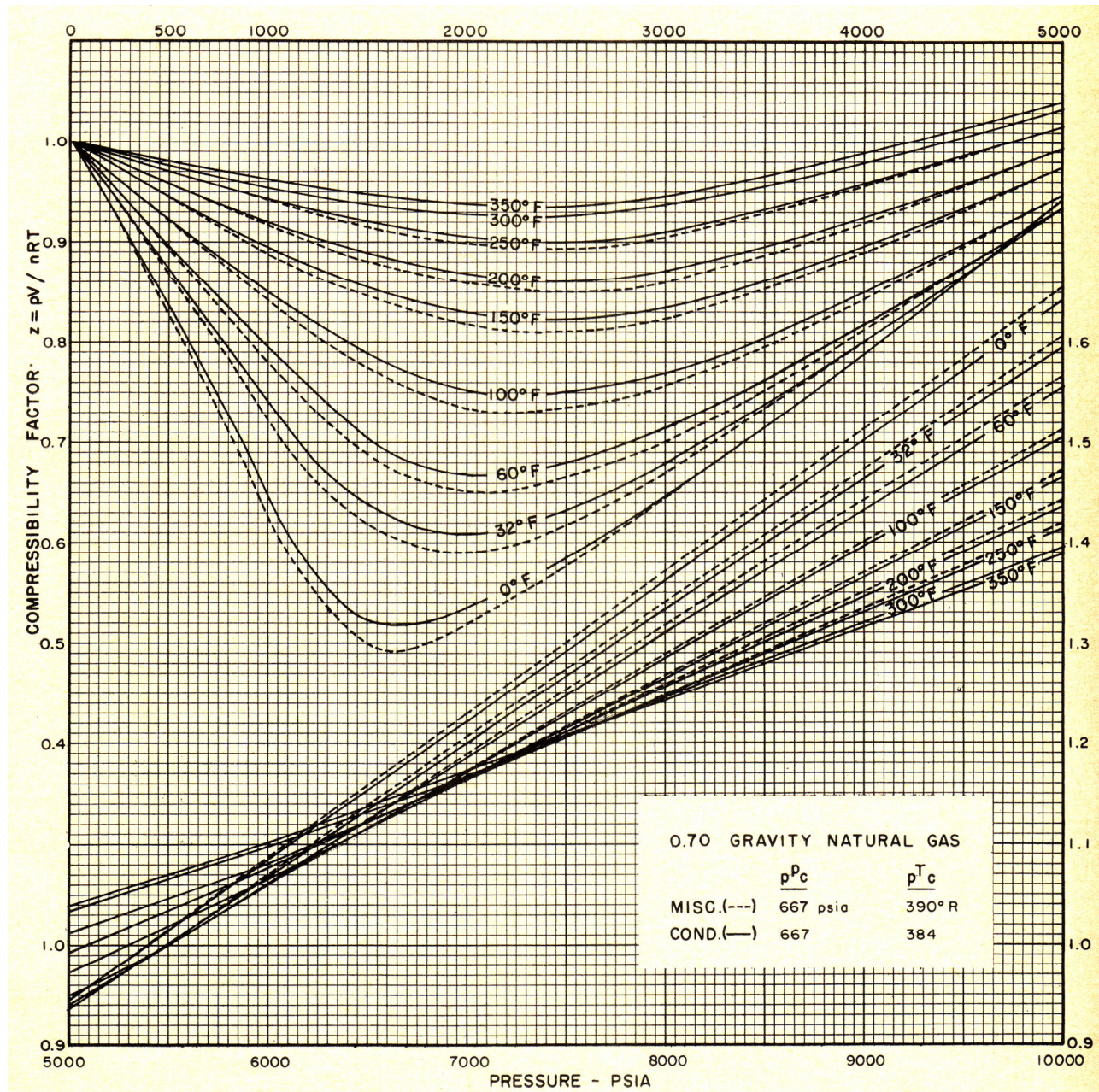
Chart A.10-2





# Appendix 10 Simplified Compressibility Factor Chart for Natural Gas Calculations

Chart A.10-3



# Chapter 1

# BASICS OF PROCESSING

## **Chapter 1 Contents**

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- 1.1.2 Chemical Compounds and Molecules
- 1.1.3 Physical Compounds
- 1.1.4 Relative Atomic Mass (Weight)
- 1.1.5 Relative Molecular Mass (Weight)
- 1.1.6 The Mole
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- 1.2.2 Paraffin Series
- 1.2.3 Olefin or Ethylene Series
- 1.2.4 Aromatic (Benzene) Series
- 1.2.5 Naphthene Series

### **1.3 PARAFFIN HYDROCARBON COMPOUNDS**

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## Chapter 1

# Basic of Processing

### 1.1 BASIC TERMINOLOGY

Throughout this course we will be using some basic chemistry and physics terminology. This is reviewed briefly.

#### 1.1.1 Elements and Atoms

All matter in the universe is composed of **elements** which cannot be broken down or subdivided into smaller entities by ordinary means. Over 100 materials have been found (or created) which are classed as elements. These include carbon, hydrogen, sulfur, oxygen, nitrogen and helium - all materials occurring in petroleum systems.

The **atom** is the basic unit of each element that can combine with it or the atoms of other elements to form a compound.

#### 1.1.2 Chemical Compounds and Molecules

A true **compound** is a substance composed of more than one atom that satisfies both of the following conditions.

1. The atoms have combined chemically.
2. The compound formed possesses properties different from the atoms of which it is composed.

Chemical compounds are formed by the union of atoms in the simplest possible numerical proportions. The **molecule** is the unit of a compound. A molecule of water is  $\text{H}_2\text{O}$ , two atoms of hydrogen combined with one atom of oxygen.

A **diatomic molecule** is formed by the combination of two atoms of the same element. Nitrogen ( $\text{N}_2$ ) and oxygen ( $\text{O}_2$ ) are the most common examples.

#### 1.1.3 Physical Compounds

A type of physical compound, called a **clathrate**, may be formed. A gas hydrate is one example of a clathrate. These compounds are relatively unstable.



### 1.1.4 Relative Atomic Mass (Weight)

In forming a compound, elements always combine according to fixed mass ratios. It is convenient to use relative atomic weight, the relative mass of the atoms of different elements, to express these ratios. The word "relative" means that the number used is a relative one. Currently, Carbon-12 is used as the standard, being assigned the relative atomic weight of 12. On this basis, the relative atomic weights of common oil and gas components are shown below (to the nearest whole number).

Atom	Symbol	Relative Atomic Weight
Hydrogen	H	1
Carbon	C	12
Nitrogen	N	14
Oxygen	O	16
Sulfur	S	32

A relative atomic weight of one element contains about the same number of atoms as a relative atomic weight of any other element. One gram of hydrogen and 12 grams of carbon each contain about  $6 \times 10^{23}$  atoms. Since relative weights represent a fixed number of atoms, they may be substituted for atoms in calculations.

### 1.1.5 Relative Molecular Mass (Weight)

The relative molecular weight of a molecule is the sum of the relative atomic weights of the atoms combining to produce the molecule. Water has a relative molecular weight of 18 ( $\text{H}_2\text{O}=2+16=18$ ). A diatomic molecule like oxygen ( $\text{O}_2$ ) has a molecular weight of 32.

### 1.1.6 The Mol

The term "***mol***" is the historical abbreviation of the words "gram molecule." The current definition of the mol is: "**The mol is the *amount of substance* of a system which contains as many *elementary entities* as there are atoms in 0.012 kilogram of Carbon-12.**" These elementary entities must be specified but include atoms, molecules, ions, electrons, etc.

The quantity 0.012 kg is 12 g, the relative atomic weight of carbon. Thus, the mol can be defined for engineering usage as that mass in grams equal numerically to the sum of the relative atomic weights of the atoms in the molecule of that substance.

By virtue of the definition, whenever the mol is used as a mass quantity without a prefix, a mass in grams is implied. If a relative molecular or atomic weight is expressed in pounds mass or kilogram, we will use the terms lb-mol and kmol, respectively, to denote this is not a standard mol. A *kilomol* (kmol) is simply 1000 mol.

$$1 \text{ kmol} = 1000 \text{ mol} = 2.205 \text{ lb-mol}$$

$$1 \text{ lb-mol} = 454 \text{ mol}$$

Throughout this course the *mol* will be used in many cases as a mass term in those processes where no chemical changes occur. It is particularly useful for gas calculations. At a given pressure and temperature equal volumes of different gas contain the same number of molecules. At 0°C [32°F] and 101.325 kPa [14.7 psia] a mol of any gas contains about  $6 \times 10^{23}$  molecules and occupies a volume of 22.4 liters.

The mol is thus a useful conversion factor from volume to mass, for the number of mols per unit volume is independent of gas composition.

### 1.1.7 Valence

Valence is a measure of the ability of atoms to form molecules by filling the electron shells of the atoms involved. The valence number is plus or minus, denoting the number of excess or shortage of electrons needed to fill its outer shell.

The question of atomic bonding is a complex subject involving many factors, as discussed in standard chemistry references. The concept is mentioned only to point out that the number of **bonds** or **linkages** used in the structural formulas that follow in the next section reflect the valence of the atoms in these compounds.

### 1.1.8 Mixture

A mixture is a combination of elements and compounds which may be separated by physical means. The properties of the mixture are a reflection of the properties of the constituents.

Natural gas and crude oil are mixtures. They are analyzed by separating the mixture into its component parts and identifying each by its properties.

## 1.2 BASIC HYDROCARBON NOMENCLATURE

Petroleum is composed of two elements, hydrogen and carbon, joined together in compound called hydrocarbons. Two simple ways of looking at these hydrocarbons is by ratio and by weight.

The average ratio of hydrogen to carbon in petroleum hydrocarbons is 2 to 1. This means that although specific compounds may vary, crude have about two atoms of hydrogen for every atom of carbon.

A single carbon atom weights 12 times as much as a hydrogen atom. Thus, despite the 2 to 1 ratio of hydrogen to carbon in 100 pounds (45 Kilograms) of crude oil, roughly 84 pounds (38 kilograms) will be carbon and 14 (6 Kilograms) will be hydrogen. The remaining 2 pounds (1 kilogram) are various impurities and must be greatly reduced because they are harmful to the environment and corrosive to both refining equipment and the machinery in which products must ultimately be used. These impurities include sulfur (0-3 lb.), Nitrogen (0-1 lb.), oxygen (0-0.5 lb.), and Chlorine. Nickel, vanadium, iron, copper, and other metals in traces so small they are measured in parts per million or parts per billion.

### 1.2.1 Classification of Hydrocarbons

There are so many different hydrocarbon compounds in crude oil that scientists can only guess at the exact number. Estimates range from 20,000 to 5,000,000 somewhere between 50,000 and 1,000,000 is a reasonable guess, with so many compounds, it's necessary to have systematic ways to classify them into manageable groupings. The two basic systems used are by carbon number and by molecular structure.

#### **Carbon Numbers**

The simplest classification is by carbon number. This is based on the number of carbon atoms found in a given hydrocarbon molecule. For example, methane ( $\text{CH}_4$ ) has one carbon atom per molecule and is  $\text{C}_1$ . Ethane ( $\text{C}_2\text{H}_6$ ) and Ethylene ( $\text{C}_2\text{H}_4$ ), through different compounds with different properties, are both classified  $\text{C}_2$ 's.

The carbon number is important because it indicates the physical state of the compound. Basically, the higher the carbon number (i.e., the more carbon atoms per molecule), the higher the boiling point, the greater the viscosity (the rate at which it will flow through a small opening) and the higher the density (weight per volume).

Compounds from  $C_1$  to  $C_4$  are gases at room temperature. Those from  $C_5$  to  $C_{17}$  are liquids, through some  $C_{17}$ 's may be solid. And those from  $C_{17}$  to  $C_{40}$  are solids. These solids are not like steel or concrete, but more like wax. They can be penetrated with a sharp instrument, but they won't pour or flow unless heated.

**$C_1$  (methane)** is used as a fuel in the refinery in addition it can sold and transported by liquefying it by lowering its temperature to  $-255^{\circ}\text{F}$  ( $-159^{\circ}\text{C}$ ). This reduces its volume by a factor of 1000 and there by simplifies transportation.

**$C_2$  (Ethane)** is used as a refinery fuel;  $C_2$  Ethylene is used in making polyethylene and other plastics.

**$C_3$ 's (propane and propylene)** are used in plastics manufacture; propane can also be liquefied for sale as LPG (Liquefied Petroleum Gas).

**$C_4$ 's (Butane and Butylenes)**, the largest gas molecule at room temperatures, can be combined to form  $C_8$ 's (liquids) for use in gasoline.  $C_4$ 's can also be added directly to gasoline to increase vapor pressure for better starts on cold mornings.

**Materials from  $C_5$  to  $C_{12}$**  are used directly in gasoline manufacture

**Materials from  $C_{13}$  to  $C_{17}$**  are used as fuels and lubricants.

**Materials from  $C_{17}$  to  $C_{40}$**  are used for heavy fuels and asphalts. They are also used as charge stocks for refinery processes that break them down into smaller compounds with lower carbon numbers (the  $C_5$  to  $C_{12}$  liquids) for use in Gasoline.

### **Molecular Structure**

A second, more complicated way to classify hydrocarbon compounds is by their molecular structure, the actual arrangement of the carbon and hydrogen atoms.

These atoms can combine in a number of ways to satisfy valence requirements. For convenience, these are separated into "families" or homologous series, each of which is given a name.



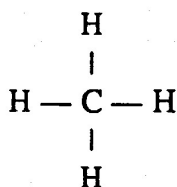
Every atom has the capacity to combine with a given number of other atoms; this is its valence number. The valence of hydrogen, for instance, is 1. One way of looking at that is to say it has a "hand" that can join with a "hand" from another atom to form a valence bond. Carbon has valence of 4 which means that each carbon atom can combine with four other atoms.

The carbon atoms can link together to form "chains" or "rings." Crude oil and natural gas mixtures consist primarily of "straight chain" hydrocarbon molecules, the bulk of which are paraffins.

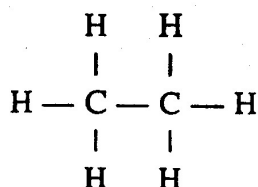
### 1.2.2 Paraffin Series Formula: $C_nH_{2n+2}$

Paraffins, also called **alkanes**, were named when early chemists thought these compounds were relatively inactive (see Appendix A.8-1).

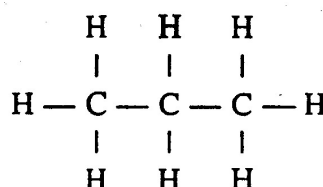
Hydrocarbons in this series are **saturated** compounds - all four carbon bonds are connected either to another carbon atom or a hydrogen atom, with one such atom for each bond.



Methane



Ethane



Propane

Notice that, all names end in **-ane**, the ending used for the paraffin series. In each case, the number of hydrogen atoms is two times the number of carbon atoms plus two more for the ends of the chain.

The paraffin hydrocarbons are the most stable of the lot because all valence bonds are fully satisfied as indicated by the single line linkage. Most reactions involve the replacement of hydrogen atoms with other atoms; the carbon linkage remains stable.

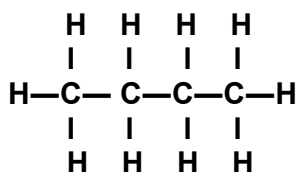
Each successive molecule in the paraffin series is created by adding a carbon and two hydrogens to the previous molecule. The incremental change in relative molecular weight is thus fourteen. Long chains containing scores of carbon atoms in series may be formed. However, the only ones normally identified by name contain ten or less carbons.

Name	Form- ula	Mol. Wt.	Name	Formula	Mol. Wt.
Methane	CH <sub>4</sub>	16	Hexane	C <sub>6</sub> H <sub>14</sub>	86
Ethane	C <sub>2</sub> H <sub>6</sub>	30	Heptane	C <sub>7</sub> H <sub>16</sub>	100
Propane	C <sub>3</sub> H <sub>8</sub>	44	Octane	C <sub>8</sub> H <sub>18</sub>	114
Butane	C <sub>4</sub> H <sub>10</sub>	58	Nonane	C <sub>9</sub> H <sub>20</sub>	128
Pentane	C <sub>5</sub> H <sub>12</sub>	72	Decane	C <sub>10</sub> H <sub>22</sub>	142

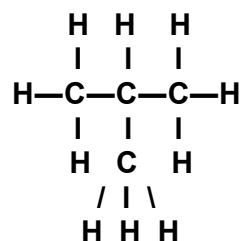
In referring to a given paraffin hydrocarbon, the abbreviation C<sub>3</sub> for propane, C<sub>4</sub> for butane, etc. may be used. Statements like "propanes plus fraction (C<sub>3</sub><sup>+</sup>)" refer to a mixture composed of propane and larger atoms.

**Paraffin isomers:** When the paraffin series molecule contains four or more carbon atoms there are different ways these can be connected without affecting the formula. Compounds which have the same chemical formula but a different atomic structure are called isomers. They possess different physical and chemical properties.

There are only two isomers of butane. In the structural diagram shown below for i-butane we could draw the carbon atom below instead of above the carbon chain. But, this would be just a "mirror image" of the molecule as drawn. It is the same molecule with the same properties. The adjective "normal" is used to designate a molecule wherein all of the carbon atoms are in a straight line. An "isomer" has the same formula but a different arrangement of the carbon atoms. In an analysis, these are often abbreviated as "n" and "i" respectively.



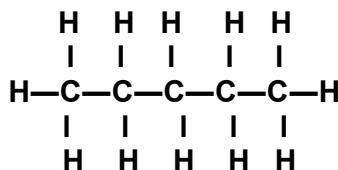
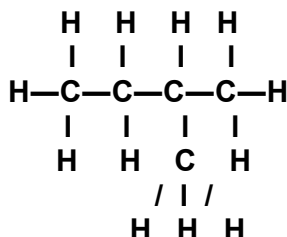
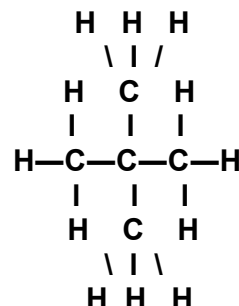
**Normal-butane**  
(n- C<sub>4</sub>H<sub>10</sub>)



**Iso-butane**  
(i- C<sub>4</sub>H<sub>10</sub>)

Even though these two compounds consist of the same number of carbon and hydrogen atoms they differ chemically and have different boiling points, densities, and refractive indices. Most important from our point of view is that the simple, straight chain paraffin has a much lower octane than the more compact, branched isoparaffins.

As the carbon number increases, the number of possible permutations (isoparaffins) increases astronomically. There are three combinations for pentanes ( $C_5H_{12}$ ), (normal pentane) and two isopentane (called, by convention, isopentane and neopentane).

**Normal-pentane****Iso-pentane****Neo-pentane**

Similarly, there are 9 possible combinations for the  $C_7$  paraffin, heptanes, 355 for  $C_{12}$  and 62, 491, 178, 805, 132 combinations for  $C_{40}$ .

An important thing to remember is that no matter how complicated or how simple, all Paraffins have the same ratio of two hydrogen atoms for every carbon atom, plus two more hydrogen, one at each end of the chain to fill the remaining valences.

Chemists express this as  $C_nH_{2n+2}$ , the formula for all Paraffins shown at the beginning of this section. If we have a two carbon atom paraffin, then  $n=2$ , thus there will be  $2 \times 2 + 2 = 6$  atoms of hydrogen.  $C_2H_6$  is, of course, ethane. You might try going back and checking one or two of the other Paraffins diagrammed above against the formula.

A final point to remember is that the valence bonds of Paraffins are saturated with hydrogen. That is, every carbon atom is holding as much hydrogen as it can; every valence not needed to link it to another carbon atom is linked to a hydrogen atom.

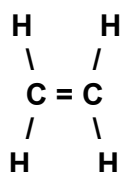
### 1.2.3 Olefin or Ethylene Series (Alkenes) Formula: $C_nH_{2n}$

Olefins (see Appendix A.8-3) are the second type of hydrocarbon important to us. Olefins are not found naturally in crude oil, but are the product of the refining process.

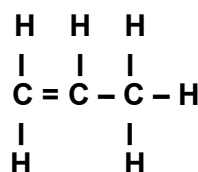
The olefin group of compounds is a simple straight chain series in which all the names end in **-ene**. Ethylene (ethene)  $C_2H_4$  is the simplest molecule in the series.

Hydrocarbons in this series combine easily with other atoms like chlorine and bromine, without the replacement of a hydrogen atom. Since they are so reactive, they are called **unsaturated hydrocarbons**.

What distinguishes olefins from Paraffins is that olefins are unsaturated.  $C_2$  paraffin, ethane, was saturated because it contained six hydrogen atoms. If we remove two of the hydrogen's and bend the two vacated carbon valence bonds around to join with each other, we create a double bond or unsaturated bond. The resulting compound is ethylene, the  $C_2$  olefin.

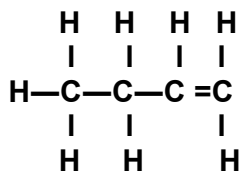


**Ethylene (Ethene)**

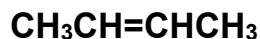
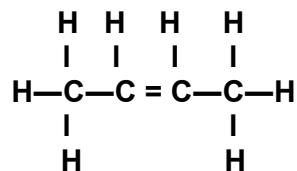


**Propylene (Propene)**

With four or more carbon atoms, isomers also may result from the position of the double bond as well as the arrangement of the carbon atoms.



**1-Butene**



**2-Butene**



These molecules possess many different properties. They may furthermore react at the double bond or be split into two molecules at the double bond to form compounds with different characteristics.

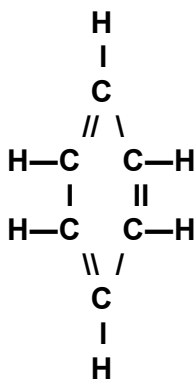
Because of the double bond, all olefins contain exactly twice as many hydrogen atoms as carbon atoms. So the chemical formula for all olefins is  $C_nH_{2n}$ . Propylene and butylenes are the  $C_3$  and  $C_4$  olefins respectively.

This double bond is also a kind of liability, because it makes olefins less stable than Paraffins. Valence bonds are normally 120 degrees apart in three dimensional space. By “bending” the valences around to make them into a double bond, we’ve created a certain amount of “springiness” in the bond. As a result, when olefins are exposed to sunlight or oxidizing agents, these bonds are prone to springing back and combining readily with other compounds, causing the olefin to lose their double bond.

#### 1.2.4 Aromatic (Benzene) Series Formula: $C_nH_{2n-6}$

Aromatics (see Appendix A.8-6) get their name from the fact that the earliest known members of this class had very strong smells.

Aromatic is the word used to describe an unsaturated hydrocarbon molecule where the carbon atoms form a ring, a cyclic compound. **Benzene**, the parent compound of this series, has the structural formula of  $C_6H_6$ .



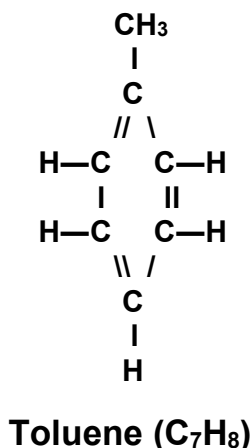
**Benzene ( $C_6H_6$ )**

Like the naphthenes, benzene has a cyclic structure called a benzene ring. But unlike the naphthenes, the benzene ring has double bonds.

Since the aromatics are **unsaturated**, they react readily. They may be oxidized to form organic acids. They also promote foaming and other operational problems in the production and handling of crude oil and natural gas.

Most petroleum contains only a trace of aromatics. Some contain significant amounts. Any analysis of crude oil and natural gas should include aromatics. Even small amounts can influence physical behavior and affect design.

All the aromatics are formed by adding carbons and their associated hydrogen to the benzene ring creating extra branches and even, additional rings. By adding a carbon and two hydrogens, for instance, we get toluene, the only  $C_7$  aromatic.



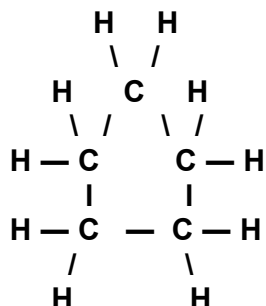
### 1.2.5 Naphthene Series Formula: $C_nH_{2n}$

Naphthenes, (see Appendix A.8-2) the third type of hydrocarbon, have the same ratio of two hydrogen atoms per carbon atom as do olefins. But they are more like Paraffins because they are saturated compounds.

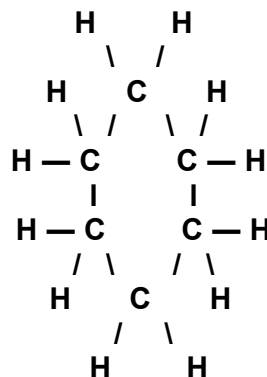
The naphthene series has a ring structure but is saturated. Naphthenes may be found in most crude oils but are seldom shown in routine analyses. Being saturated molecules, they are not very reactive. Cyclohexane is a common member of this series. Its structural formula is  $C_6H_{12}$ .

Cyclohexane is similar to benzene except that it is saturated. On chromatographic analysis it occurs between n-hexane and n-heptane. Cyclopentane ( $C_5H_{10}$ ) also occurs. On chromatographic analysis it occurs between n-pentane and n-hexane.

It's as though we took a straight  $C_5$  to  $C_6$  paraffin chain, removed the hydrogen atom from each end, and then bent it around to join the valence of the first carbon atom with the last.



**Cyclopentane ( $C_5H_{10}$ )**



**Cyclohexane ( $C_6H_{12}$ )**

This distinctive ring shape is why naphthenes are also called cycloparaffins. The two naphthenes above, cyclopentane and cyclohexane, are the basic of all naphthenes, all naphthenes are formed by adding to either a cyclopentane or cyclohexane ring.

## 1.3 PARAFFIN HYDROCARBON COMPOUNDS

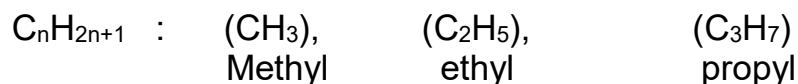
In the production, gathering, conditioning, and processing of natural gas and its associated liquids, the primary concern is the behavior of the paraffin series hydrocarbons with 10 or less carbon atoms ( $C_1$ – $C_{10}$ ). This concern includes nitrogen and water and contaminants in the gas, such as sulfur compounds.

Paraffin hydrocarbons are less reactive with other materials than many hydrocarbons, but it must be remembered that they have been in contact with the chemicals present in the reservoir rock for many millions of years. They are also conditioned by use of alcohols, glycols, and amines in which they are soluble and with which they react to some degree.

### 1.3.1 Radicals

A radical represents a group of atoms that act as a single unit in the formation of many common compounds.

**Alkyl Radical:** At least the simpler paraffins often react by replacing one hydrogen with some other radical or element. This alkyl radical has the formula:



The parenthesis indicates the radical group. The alkyl radical normally has a valence of +1.

In many cases the alkyl radical is indicated by the symbol "R." The formula for methanol is  $CH_3 OH$ ; for ethanol it is  $C_2H_5OH$ . Both may be written as  $ROH$ . When "R" is used, one cannot identify the specific alkyl radical. It is used only to show general reaction characteristics.

**Hydroxyl Radical, (OH).** This combination occurs in many common compounds. It combines with hydrogen to form water -  $H (OH)$  or  $H_2O$ ; with metallic salts like sodium, calcium and magnesium to form hydroxides (bases, caustics); and with alkyl radicals to form alcohols, such as methanol, ethanol, etc.

**( $SO_4$ ), ( $CO_3$ ).** If radicals like these combine with hydrogen, an acid is formed. When combined with metallic salts like sodium, calcium, and magnesium, a salt is formed (which occurs commonly in water systems). The scale formed in water systems is caused by precipitation of salts like these. The common names for some common radicals of this type are:



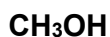
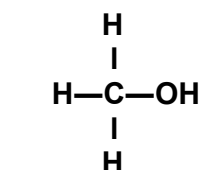
Each of the radicals has a valence found from the valence of its elements. The hydroxyl radical (OH) has a valence of minus one and is sometimes written as  $(OH)^{-1}$ .

It therefore combines in proportions fixed by this valence:  $H (OH)$ ,  $NaOH$ ,  $Mg (OH)_2$  - so that the sum of plus and minus valences equals zero.

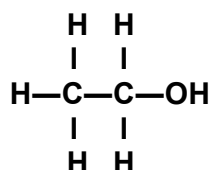
### 1.3.2 Alcohols

The common alcohols are formed from the addition of a single hydroxyl radical to an alkyl radical. The name of the alcohol ends in "ol," or the name of the alkyl radical is followed by the word "alcohol."





**Methanol**  
(methyl alcohol)



**Ethanol**  
(ethyl alcohol)

Both  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CH}_3\text{OH}$  could be written as  $\text{ROH}$  in denoting the general reaction of an alcohol.

### 1.3.3 Mercaptans

Compounds with the general formula  $\text{RSH}$  are known as mercaptans. They may be regarded as sulfur alcohols since the formula is the same if you replace the oxygen atom in the  $(\text{OH})$  radical by a sulfur atom.

Formulas for typical mercaptans are:

$\text{CH}_3\text{SH}$  - methyl mercaptan

$\text{C}_2\text{H}_5\text{SH}$  - ethyl mercaptan

### 1.3.4 Other Carbon-Sulfur Compounds

There are several other carbon-sulfur compounds present in sour petroleum fluids. Some are:

Carbonyl sulfide -  $\text{COS}$

Carbon disulfide -  $\text{CS}_2$

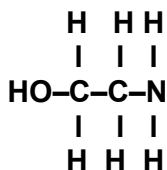
Thiophene - an unsaturated compound having the formula:



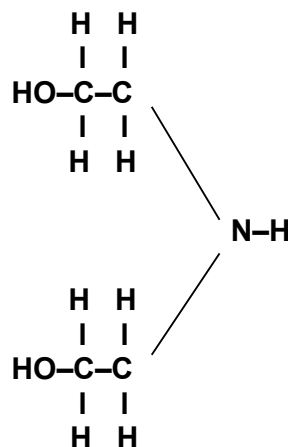
Sulfur is a very reactive element that combines chemically with many other elements and compounds. Its compounds react with carbon steel to form sulfides and oxides of iron. Many compounds polymerize and form the "sludge" so common in sour petroleum systems. This sludge is often very corrosive and should be removed by filtration.

### 1.3.5 Organic Nitrogen Compounds - Amines

There are a number of common organic compounds formed by the reaction of organic materials with ammonia (NH<sub>3</sub>). In this basic reaction one or more hydrogen atoms are replaced by an organic radical. The word "amine" is used commonly to denote this type of compound. There are a large number of amines used in the chemical industry.



HOCH2CH2NH2  
**Monoethanolamine**



(HOCH2CH2)2NH  
**Diethanolamine (DEA)**

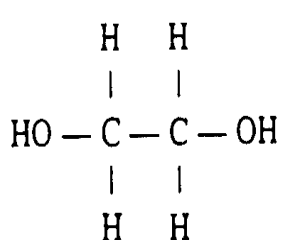
The alkanolamines are commonly used for treating sour gases and liquids, particularly monoethanolamine and diethanolamine. As the names indicate, the alkanolamines may be considered a combination of an alcohol and ammonia.

Notice that the only difference in the above compounds is how many hydrogen atoms of ammonia are replaced by the radical (C<sub>2</sub>H<sub>4</sub>OH), ethanol minus one hydrogen atom.

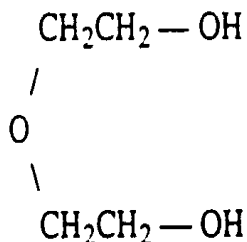
### 1.3.6 Glycols

The glycols are a family of chemicals, sometimes called diols. They may be regarded as complex alcohols since they contain alkyl and hydroxyl radicals. The glycols used for dehydration are based on the ethyl radical.

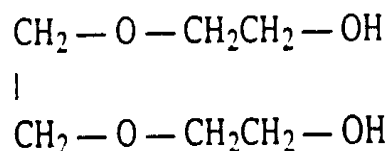
As with most compounds containing hydroxyl groups, the glycols react readily with other compounds and elements. In DEG and TEG the oxygen atom also is very reactive.



**Ethylene Glycol  
(EG)**



**Diethylene Glycol  
(DEG)**



**Triethylene Glycol  
(TEG)**

## 1.4 Analysis of Mixtures

A routine analysis of a hydrocarbon mixture is shown in Table 1.1. Notice that only paraffin hydrocarbons are shown. This is not entirely correct, although the paraffins may be the predominant series present. Notice also that all molecules heptane and larger are lumped together as a heptanes plus fraction.

The hydrocarbon portion of an analysis like this usually is obtained from a chromatograph. The printed output from this technique is a series of "peaks" rising from a base line. The area under the peak for any component is proportional to the amount present. The instrument is calibrated using standard samples of known analysis so that peak area can be converted to the amount present.

Figure 1.1 is an example of a chromatogram (chart) from a chromatographic analysis. When the ordinary peak height is so low it is difficult to measure, it is attenuated (multiplied). The attenuation factor is used to convert the peak height shown to analysis.

Component	Mol %
Nitrogen	0.34
Carbon Dioxide	0.91
Sulfur (as H <sub>2</sub> S)	0.50
Methane (C <sub>1</sub> )	21.36
Ethane (C <sub>2</sub> )	36.78
Propane (C <sub>3</sub> )	10.21
i-Butane (iC <sub>4</sub> )	6.38
n-Butane (nC <sub>4</sub> )	9.84
i-Pentane (iC <sub>5</sub> )	2.63
n-Pentane (nC <sub>5</sub> )	4.01
Hexanes (C <sub>6</sub> )	3.90
Heptanes Plus (C <sub>7</sub> +)	3.14
Total	100.00
Mol wt. C <sub>7</sub> + = 118	
Rel. Density C <sub>7</sub> + = 0.71	

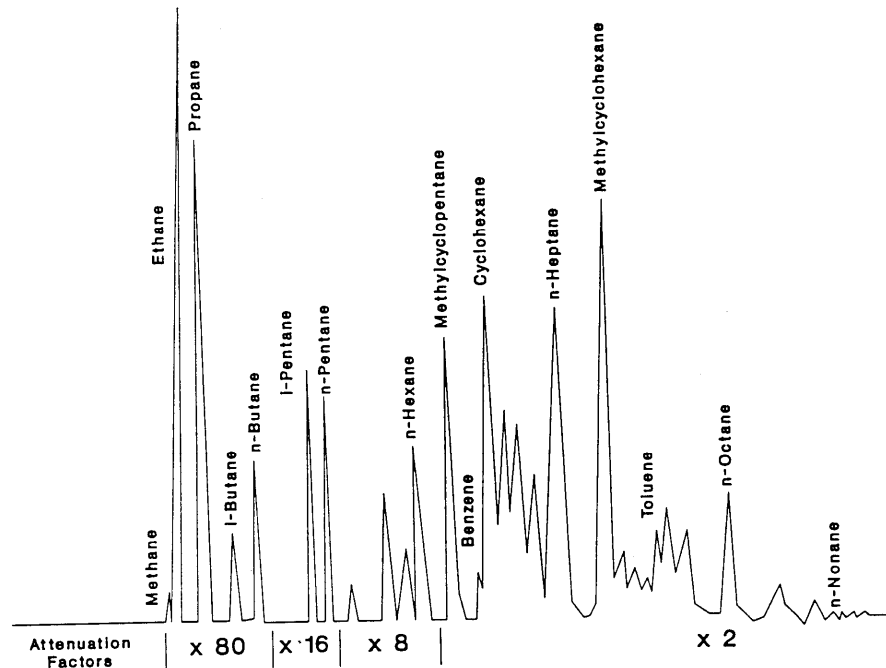
**Table 1.1 Fluid Analysis**

The chromatograph used to obtain Figure 1.1 was capable of showing hydrocarbons other than paraffins. Notice that all of these occur in the hexane-heptane range of molecules. Many chromatographs, particularly those used for routine gas analyses, are unable to detect all of these components. The nonparaffins combine with a single peak which is reported (erroneously) as being a paraffin material.

Many system operating problems are the direct or indirect result of inadequate analysis. This may result from failure to:

1. Analyze for CO<sub>2</sub> and sulfur compounds
2. Identify the presence of aromatics and other nonparaffin hydrocarbons
3. Adequately characterize the heaviest fraction





**Figure 1.1 Chromatogram of Condensed Liquid**

There are, however, some general guidelines.

1. Always analyze for  $\text{CO}_2$  and  $\text{H}_2\text{S}$ . Sulfur contents as low as 3-10 parts per million may prove troublesome. If the sulfur content (reported as  $\text{H}_2\text{S}$ ) is higher than this, a special analysis for carbonyl sulfide ( $\text{COS}$ ), carbon disulfide ( $\text{CS}_2$ ) and mercaptans is intelligent.
2. Some crude oil may contain up to 10-12% aromatics. Failure to be aware of this affects mechanical design problems and reduces validity of equilibrium calculations.
3. If the gas is from a separator, characterizing the heaviest fraction through  $\text{C}_7^+$  may be adequate; if it is wellbore gas it may not be adequate. Crude oil may need to be characterized through  $\text{C}_{20}^+$  to achieve reliable equilibrium predictions.

The prompt and proper analysis of representative samples is a critical factor. Any calculation is an exercise in futility unless the analyses used are reliable. Inadequate sampling and analysis is a major cause of problem systems.

A sampling program should be planned carefully.

## Chapter 2

# THEORETICAL PRINCIPLES OF FRACTIONATION

## **Chapter 2 Contents**

### **2.1 INTRODUCTION**

### **2.2 VAPOR PRESSURE**

### **2.3 PARTIAL PRESSURE**

### **2.4 FUNDAMENTALS**

2.4.1 Laws governing the volatility characteristics of liquid

2.4.2 Basic Gas Laws

2.4.3 Volatility Effect on Tower Design

### **2.5 EQUILIBRIUM CONSTANT ("K" values)**

### **2.6 BOILING POINT CALCULATION**

### **2.7 DEW POINT CALCULATION**

### **2.8 FLASH CALCULATION**

## Chapter 2

# Theoretical Principles of Fractionation

## 2.1 INTRODUCTION

A detailed discussion of the entire theory of fractional distillation and all the problems connected herewith is not possible within the scope of this Course and has not been attempted. The most important features of this vast subject have been dealt with and a number of references are given which should enable the reader to tackle any specific problem requiring a deeper knowledge of the various methods used in fractionation calculations. Since the majority of the Group's technologists are engaged in other fields than design work, complete discussion of tray-to-tray calculations has been omitted. However, it is felt that the technologist should be familiar with simple column evaluations, boiling point, dew point and flash calculations and be able to interpret intelligently design work should the necessity arise.

## 2.2 VAPOR PRESSURE

A gas or vapor consists of molecules in random and chaotic motion. Millions of small particles moving in all directions in the air in the room, they collide with each other repeatedly.

There are many collisions between molecules in a gas. The molecules of a vapor in a container repeatedly have collisions with the walls of the container. When many gas molecules collide repeatedly with the walls of a container, these collisions add up to a pressure exerted on the walls. If the temperature of a gas is increased, the molecules in the gas move faster. As the molecules move faster (at higher temperatures) and the collisions become more violent, molecules in a closed container strike the walls with more force. The pressure, therefore, increases.

The pressure of a gas in an open container cannot be increased, since some of the gas would escape to equalize the pressure with the surroundings. The pressure of a gas in an open container cannot be increased by increasing the temperature.



Like the molecules of gases, the molecules of a liquid are constantly in motion. Unlike the molecules of gases, the molecules of a liquid are held close together by natural attraction between the molecules. In a liquid, the attraction between molecules tends to keep each molecule confined to a small space. Within this space a molecule is usually in violent motion. The violent motion of the molecules at the surface of a liquid causes many of these molecules to escape from the liquid. If the temperature of a liquid is increased, the motion of the molecules becomes more violent.

If an empty container is partially filled with liquid, molecules escape from the surface of the liquid, forming a vapor in the space above the surface. Gas molecules which strike the surface of a liquid tend to stick to the liquid. Thus, molecules may be escaping the liquid and returning to the liquid from the gas at the same time. When a vessel contains both a liquid and a vapor, molecules are continually going from the liquid to the vapor or gas and from the vapor to the liquid. When the number of molecules leaving the liquid equals the number entering the liquid, the gas and the liquid are said to be in **equilibrium** with each other. So at equilibrium, equal numbers of molecules pass between the liquid and the vapor, or gas.

When more molecules are escaping the liquid than returning, the liquid is said to be evaporating. The process in which a greater number of molecules leave the liquid than enters it is called evaporation. When more molecules are entering the liquid from the vapor than are escaping the liquid, the vapor is condensing. The process in which a greater number of molecules enter the liquid than leave it is called condensation.

When the temperature of a liquid is increased, the pressure of the vapor in equilibrium with it increases and maintains equilibrium. When a liquid and a vapor are at equilibrium, the pressure of the vapor is called the vapor pressure of the liquid.

The pressure of a gas or vapor above the surface of a liquid in a closed container is not necessarily the same as the vapor pressure of the liquid. In order for the pressure of the gas to be equal to the vapor pressure of the liquid, the gas and the liquid must be in equilibrium with each other.

When liquid in an open container is heated until the vapor pressure equals the pressure of the atmosphere, evaporation becomes very rapid, and the liquid boils.

If the pressure over a boiling liquid is increased, the boiling temperature is increased and if the pressure over a boiling liquid is decreased, the boiling temperature is decreased. Since the pressure of the atmosphere on the top of a mountain is lower than at sea level, liquids boil at lower temperatures on top of a mountain.

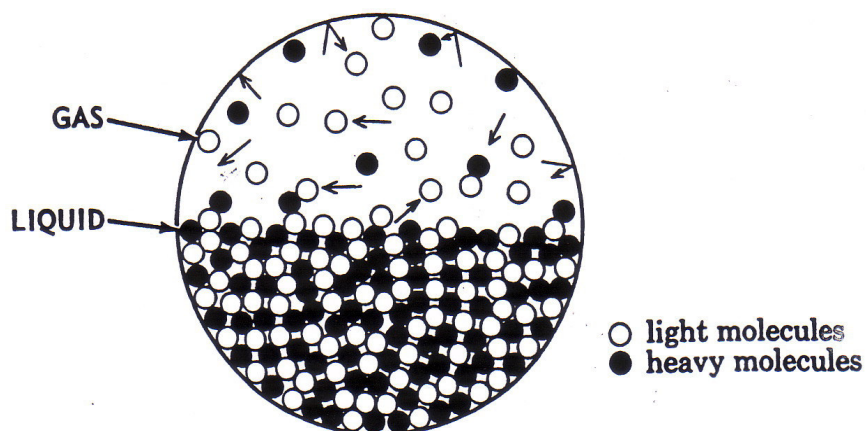
The vapor pressures for different liquids at the same temperature are not the same.

## **2.3 PARTIAL PRESSURE**

The pressure that a gas exerts on the walls of a container depends on the number of collisions between the molecules and the container wall. If more molecules are present, there are more collisions and a greater pressure. If two containers of the same volume are filled with gas to the same pressure and temperature, each contains the same number of gas molecules. For the same volume and temperature, the greater the number of molecules in a gas, the greater the pressure of the gas must be.

When two or more gases are mixed, each gas exerts a pressure on the walls of the container. Although these separate pressures cannot be measured, the total pressure can be measured. The total pressure of a gas mixture is equal to the sum of the pressures of the different gases in the mixture; the separate pressures of the gases are called partial pressures.

If a closed container is partially filled with a mixture of two liquids, molecules of both liquids escape to the gas from the liquid and return to the liquid from the gas. When the number of molecules escaping equals the number returning- for both components, the gas and the liquid are said to be at equilibrium with each other. At equilibrium, the number of molecules escaping from the liquid is equal to the number returning to the liquid for each component. The drawing shows a tank containing a mixture of two components, one heavy and one light. An example of such a system would be butane-hexane, where butane would be the light molecules and hexane the heavy molecules.



At equilibrium the number of light molecules escaping from the liquid is equal to the number returning to the liquid. Also, at equilibrium the number of heavy molecules escaping from the liquid is equal to the number of heavy molecules returning to the liquid. However, at equilibrium the number of light molecules escaping and returning to the liquid is not equal to the number of heavy molecules escaping and returning to the liquid. Light molecules are able to escape the liquid more rapidly than the heavy ones. Therefore, at equilibrium, there are more light molecules escaping and returning to the liquid. Because the light molecules are able to escape the liquid faster than the heavy ones, the light molecules tend to concentrate or to be enriched in the vapor. For example, if the liquid contains half light and half heavy molecules at equilibrium, the gas contains more light molecules than heavy molecules.

## 2.4 FUNDAMENTALS

### 2.4.1 Laws Governing the Volatility Characteristics of Liquid

Fractional distillation is an operation which is based on the differences in volatility or different “escaping tendencies” of the products which have to be separated. It is obvious that for solving the numerous problems in technical fractionation a thorough knowledge of the fundamental laws and rules governing the volatility characteristics of systems consisting of two or more components is a prerequisite.

#### Henry's Law

This law states that at a given temperature the partial vapour pressure of a relatively volatile substance above its solution (in a relatively non-volatile solvent) is proportional to its concentration in the solution.

This can be expressed by:

$$p_i = C_i x_i \dots\dots\dots (1)$$

Where:

$x_i$  = mole fraction of a certain component in the liquid,  
 $p_i$  = partial vapour pressure of this component,  
 $C_i$  = proportionality factor.

In general, this law holds only for low concentrations of component “i”. In certain cases, however, it is applicable throughout the entire range of concentrations. Such solutions are said to behave ideally and on extrapolating Henry's law in such cases to the pure compound (i.e. increasing the concentration of the dissolved substance) we see that, since when  $x_i$  becomes 1,  $C_i$  equals  $p_i$ , this factor is then equal to the vapour pressure ( $P_i$ ) of the pure substance and to the system pressure.

Thus the mathematical expression becomes:

$$p_i = P_i x_i \dots\dots\dots (2)$$

In this form and restricted to ideal solutions Henry's law is known as Raoult's law.



Many hydrocarbon systems closely approach the hypothetical ideal solution and Raoult's law can therefore be applied in these cases without introducing too serious an error. Mixtures of paraffins and Naphthenes are, in general, very nearly ideal, while mixtures of aromatics with Naphthenes or paraffins are further away from ideal solutions.

It must be realized, however, that ideal behaviour only occurs with substances as closely related as hydrocarbons, and is most uncommon for other instances.

A particularly simple case where Raoult's law is not valid is the case of two or more components completely immiscible in the liquid phase. In this case the total pressure is independent of the relative amounts in which these components are present and is simply equal to the sum  $P = \sum P_i$  of the vapour pressures of the pure components at the given temperature. The total pressure is therefore higher than the vapour pressure of any component. Such a system is called a pseudo-azeotrope.

### **Dalton's Law**

The second important law underlying the theory of fractional distillation is Dalton's law regarding partial pressures and their additivity. Mathematically, Dalton's law is expressed as follows:

$$p_i = P y_i \quad \text{and} \quad \sum p_i = P \dots\dots\dots (3)$$

Where:

$p_i$  = partial pressure of component "i",

$P$  = total pressure of system,

$y_i$  = mole fraction of component "i" in the vapour phase.

It follows from (2) and (3) that

$$P x_i = P y_i \dots\dots\dots (4)$$

$$\frac{y_i}{x_i} = \frac{P_i}{P}$$

$$y_i = x_i P_i / P \dots\dots\dots (5)$$

From equation (4) (known as Raoult-Dalton's law) it follows that the concentration of any component in a vapour which is in equilibrium with a liquid mixture can be calculated by multiplying the concentration of that component in the liquid phase by the ratio of the vapour pressure of the pure component to the total pressure of the system. All concentrations are to be expressed as mole fractions.

### **2.4.2 Basic Gas Laws**

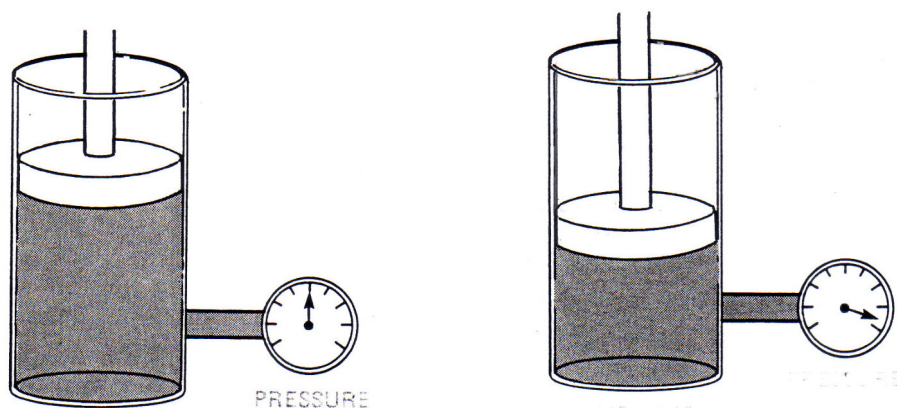
The particular relationships between gas temperature, pressure, and volume have been formulated into three laws;

- Boyle's Law,
- Charles' Law, and
- General Gas Law.

These laws describe how temperature, pressure, and volume of a gas are related to each other. If a change occurs in one of these properties, the change will affect one or both of the other two.

#### **Boyle's Law**

Boyle's Law deals with the relationship of pressure to a volume of gas. The illustration in Figure 2.2 shows a piston in a cylinder filled with gas. The pressure in the cylinder is related to the number of collisions between the molecules of the gas and the molecules of the cylinder walls. As the molecules collide, a force is applied over the area of the wall. When the piston is moved into the cylinder the volume of the cylinder decreases. With less volume, the space between the molecules is reduced, resulting in more collisions between the gas molecules, as well as more collisions between the gas molecules and the container walls. One other effect should also be noted. With a decreased volume, the inner surface area of the container is smaller. The overall result of increased collisions and reduced area is an increase in pressure. If the piston is retracted, the volume of the cylinder increases the number of collisions decreases, and pressure decreases.



**Figure 2.2 Boyle's Law Example**

Boyle's Law states that at a given temperature, the pressure of a gas varies inversely with its volume. This means that if volume increases, pressure decreases, and if volume decreases, pressure increases. Boyle's Law can be represented mathematically, as follows:

$$P_1 V_1 = P_2 V_2 \quad (\text{Temperature constant}) \dots\dots\dots (6)$$

One example of where the principle of Boyle's Law applies is in the operation of a gas or air compressors.

### **Charles' Law**

Charles' Law deals with the relationship between temperature and volume. Charles' Law states that at a given pressure, the temperature of a gas varies directly with its volume. This means that if temperature increases, volume increases, and if temperature decreases, volume decreases. Charles' Law can be represented mathematically, as follows:

$$V_1 / T_1 = V_2 / T_2 \quad (\text{Pressure constant}) \dots\dots\dots (7)$$

Figure 2.3 illustrates what happens if a balloon is heated. The heat increases the temperature of the gas molecules in the balloon, which, in turn, increases the motion of the molecules. The increased motion causes the molecules to try to move apart. The molecules push on the walls of the balloon, causing the balloon to expand, and thus increasing the volume of the gas.

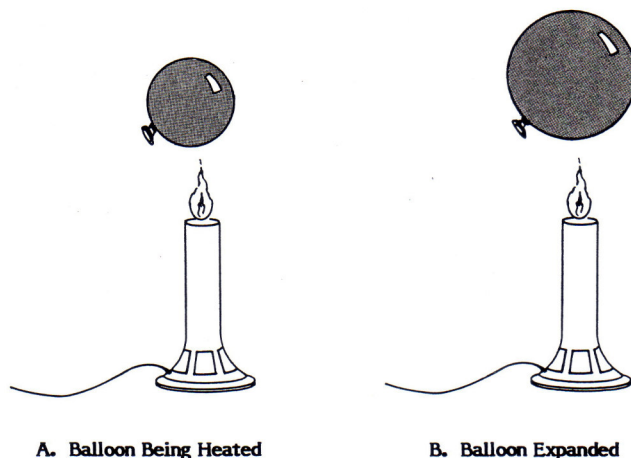


Figure 2.3 Charles' Law Example

### **The General Gas Law**

The General Gas Law expresses the interrelationship between temperature, pressure, and volume. This law can be stated as follows: pressure times volume, divided by temperature is constant ( $PV/T = \text{Constant}$ ) for a certain amount of gas. It should be noted that the General Gas Law only applies when temperatures and pressures are expressed in **absolute units**.

According to the General Gas Law, if a certain amount of gas is confined in a given volume, and the volume is decreased, both pressure and temperature will increase. This is a result of an increase in the molecular activity of the gas. This is the principle that is at work in an air compressor: as the volume of air is decreased, the pressure and temperature increase.

The temperatures of compressed air can become high enough to cause operating problems such as the breakdown of lubricating oil's ability to lubricate. As noted earlier, high temperatures reduce oil's viscosity. In extreme cases, the temperatures can be high enough to cause combustion of the oil.

The General Gas Law is sometimes referred to as the "ideal" gas law, because it is a highly theoretical concept. However, the concept is extremely useful in analyzing real gases, because real gases react in much the same way as ideal gases.



The General Gas Law relates the properties of temperature, pressure, and volume of a gas. It can be stated in terms of the following formula:

$$PV/T = \text{Constant} \dots \dots \dots (8)$$

This formula is often represented in the following way:

$$P_1V_1/T_1 = P_2V_2/T_2 \dots \dots \dots (9)$$

With this formula, changes in a set of conditions from one state (1) to another (2) can be related mathematically.

The perfect gas law is written for a single set of conditions as

$$P \times V = n \times R \times T \dots \dots \dots (10)$$

Where:

**P** = Absolute pressure (psia)

**V** = Volume (cubic feet)

**T** = Absolute temperature (°R)

**n** = Number of molecules

**R** = Gas constant (10.72 for units shown)

**1** = Condition 1

**2** = Condition 2

Actual gas mixtures vary in performance from the relationships defined by the perfect gas law due to the molecular interaction of different molecules. This deviation is called the compressibility factor and is a number that expresses the deviation of a particular gas mixture from the relationships expressed by the perfect gas laws. The symbol for the compressibility factor is *z* (can be calculated from Appendix 10). Using this factor, the real gas law becomes.

$$P \times V = z \times n \times R \times T \dots \dots \dots (11)$$

## 2.4.3 Volatility Effect on Tower Design

Briefly, here are some of the factors that dictate the design of a column.

As you might guess, two important factors are

1. The throughput, or flow rate of material, and
2. The ease of separation.

One way to quantify the relative ease of separation is to compare the volatilities of the components to be separated.

Because the boiling points change with pressure, it is more convenient to look at curves as shown in Figure 2.4 from these curves we can find the boiling point of a compound at any pressure, or conversely, the vapor pressure of a compound at any pressure.

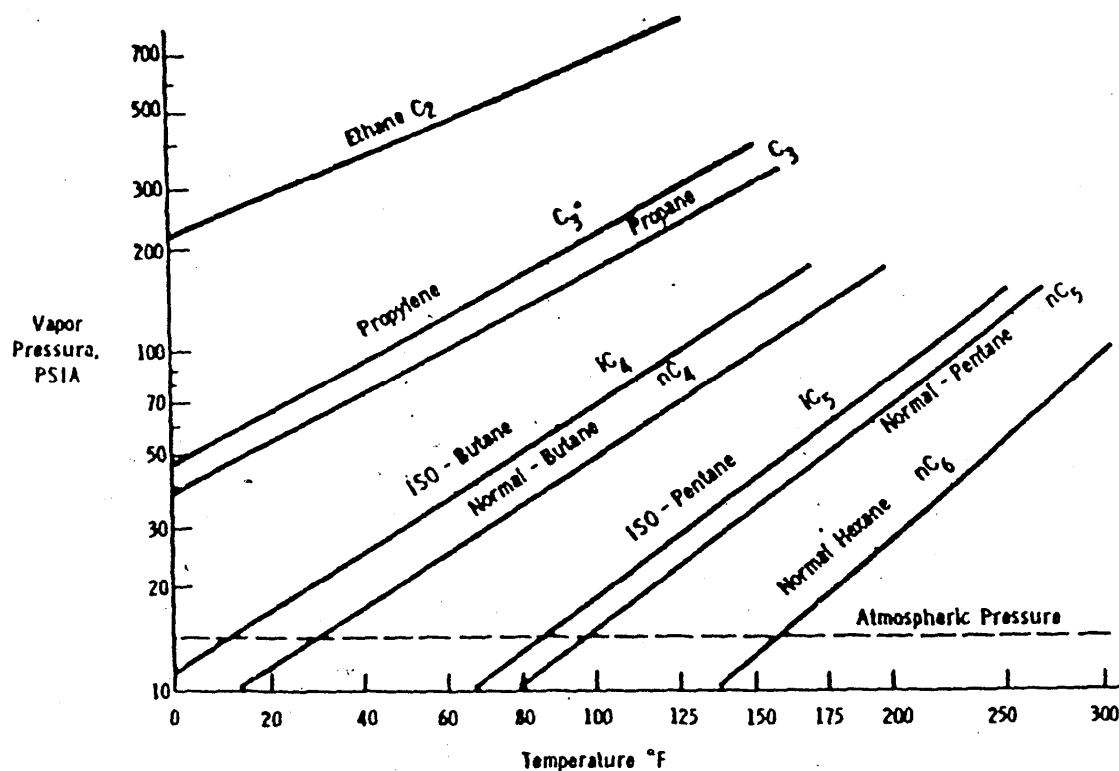


Figure 2.4 Vapor Pressure Light Hydrocarbons

For example, we see the vapor pressure of propane at 100°F is 190 psia; and the vapor pressure of propylene is 226 psia at 100°F. The ratio of these two vapor pressures is an expression of their relative volatilities.  $226/190 = 1.2$ . This ratio is defined as ( $\alpha$ ). The nearer  $\alpha$  is to 1, the greater the difficulty of separation. The more difficult separations require more trays in a column and more reflux. All this requires more energy. The separation of normal butane and i.pentane is much easier.  $\alpha$  at 100°F equals  $52/20$  or 2.6. This separation would require fewer trays and less energy.

$\alpha$  is somewhat higher at lower temperatures. Therefore, other things being equal, it is desirable to operate at lower temperatures and, thereby, lower pressures. However, "other things are not equal" and there is a limit as to how low a pressure we can operate. That limit is usually the temperature of the cooling water for the overhead condenser. Because we must condense the overhead product, we must have a coolant whose temperature is below the boiling range of the overhead. Usually it is not economically practical to refrigerate the coolant, so water or air is normally used. The available coolant temperature is usually the factor that establishes the tower design pressure.

To see how  $\alpha$  affects tower design, let's look at two separations. First, a depropanizer - a distillation column designed to separate propane from i.butane and heavier components.  $\alpha$  is  $190/72$  or 2.6. Although there are heavier components in the bottom and lighter components in the overhead, we need only consider what we call the key components, namely the heaviest major component in the overhead and lightest major component in the bottoms. For this separation, propane from butane, the tower typically requires 30 trays, 5 to one reflux, and is about 50 ft. in height. The diameter is largely dependent on the throughput.

In contrast, let's look at a tower to separate ethyl benzene and xylene.  $\alpha$  is approximately 1.08. A tower for this separation has about 350 trays and uses 100 to 1 reflux. A large depropanizer tower might cost about \$500,000, while an ethyl benzene-xylene tower might cost about \$5 million. Of course, there is a considerable difference in the cost of utilities to operate these two columns.

An additional factor that determines tower size is purity of product. As we say earlier, each equilibrium stage has less of the impurity than the adjacent stage. It follows then that we must specify the desired purity. That is, the mole fraction of an impurity that we will accept in the product. For our depropanizer we might accept, say, 1 to 2 % butane in the overhead propane product and we much tolerate a loss of 2 % propane in the bottoms.

Obviously, to achieve a lower concentration of butane in the overhead, and still maintain the low loss of propane in the bottom, would require more trays, more reflux, and consequently, a taller and larger diameter tower with its attendant increase in investment and utility costs. **To summarize**, the height of a tower and number of trays is largely dependent on the relative volatility of the key components and the permissible mole fraction of these key components in the products.

## 2.5 EQUILIBRIUM CONSTANT ("K" Values)

The fact that components in a non-ideal mixture do influence the volatility of the other components results in deviations from Raoult – Dalton's law which are of the same order of magnitude as the ones which can be corrected for by the introduction of fugacities. As the theoretical treatment of this subject is very complicated, a solution of the problem is found by introducing the concept of "k values".

For a number of pure hydrocarbons and a few other compounds the  $\frac{y_i}{x_i}$  ratios for mixtures have been determined experimentally over a wide range of temperatures and pressures, and the values thus obtained, the so-called k values, have been plotted versus P and T in "k value charts" (see Appendix 9).

It should be mentioned that some of the k charts are based on experimental data and some of the graphs are calculated from fugacities.

Using k values, equation (4) becomes:

$$\frac{y_i}{x_i} = k_i \quad \text{or} \quad y_i = k_i x_i \dots\dots\dots (12)$$

### Applications

It is possible to calculate boiling points, dew points, vapour pressures and dew pressures of mixtures.

## 2.6 BOILING POINT CALCULATION

The boiling point of a mixture (at a given pressure) is defined as the temperature at which, when the temperature of the liquid mixture is raised, the first infinitesimal amount of vapour escapes as a bubble. This temperature is also known as the "bubble point". The vapour will contain a certain amount of each component, depending on the volatility of that component, and it is clear that if the concentration in the vapour phase ( $y_i$ ) is expressed in mole fraction,  $\sum y_i$  must equal 1.

Starting with a liquid of known composition the problem has to be solved by trial and error, since at a given pressure the temperature has to be found, at which the corresponding  $k_i$  values, when multiplied by  $x_i$ , result in  $y_i$  values adding up to 1.

The following example illustrates the procedure:

**System pressure: 150 psia**

Composition metric tons	M.wt.	Ton- moles	Mole fr. ( $x_i$ )	$k$ at 150°F	$y_i$	$k$ at 200°F	$y_i$	
C <sub>3</sub>	88	44	2	0.0161	1.95	0.0314	2.85	0.0459
iC <sub>4</sub>	1160	58	20	0.1613	0.98	0.1581	1.60	0.2581
nC <sub>4</sub>	5916	58	102	0.8226	0.74	0.6087	1.25	1.0282
	7164		124	1.0000		0.7982		1.3322
					too low			too high

By graphical interpolation we find a boiling point of 169°F under 150 psia. With this temperature a check calculation should be made and, if necessary, the procedure should be repeated within narrower limits until the correct value is found. In those cases, where no  $k$  values of the components are available, the vapour pressure will have to be used.

Vapour pressures should not, however, be used in combination with  $k$  values.



**Example:** Determine the bubblepoint of the mixture shown at 4.0 580 psia assuming that the C7<sup>+</sup> fraction has the properties of C<sub>8</sub>. This is a trial-and-error solution. One must guess a temperature, find  $K_i$  and calculate  $\sum K_i x_i$ . The right temperature has been assumed when  $\sum K_i x_i = 1.0$  (or 100).

Comp.	$x_i$	$K_i$	$K_i x_i = y_i$
CO <sub>2</sub>	1.25	1.50	1.88
H <sub>2</sub> S	0.50	0.41	0.21
C <sub>1</sub>	21.36	3.48	74.33
C <sub>2</sub>	36.78	0.58	21.33
C <sub>3</sub>	10.21	0.16	1.63
iC <sub>4</sub>	6.38	0.063	0.40
nC <sub>4</sub>	9.84	0.043	0.42
iC <sub>5</sub>	2.63	0.017	0.04
nC <sub>5</sub>	4.01	0.012	0.048
C <sub>6</sub>	3.90	0.0036	0.014
C <sub>7+</sub>	3.14	0.00033	0.001
			100.30

This solution is the final try at  $T = -14^\circ\text{C}$  ( $7^\circ\text{F}$ ). Since percentages rather than mol fractions are used, the right-hand column should sum to 100.

### Vapour Pressure Calculation for Hydrocarbon Mixtures

The calculation of the vapour pressure of mixtures at a given temperature is very simply made if Raoult-Dalton's law is valid. ***The mole fraction of each component is multiplied by the vapour pressure of the component at the desired temperature and the values obtained are added together.*** The sum represents the vapour pressure of the mixture.

A more exact method would be to use  $k$  values and to determine the boiling pressure for the given temperature in essentially the same fashion as has been shown in the preceding section for the determination of the bubble point at a given pressure.

## 2.7 DEW POINT CALCULATION

The dew point of a mixture is the temperature at which, when the temperature of the vapour is lowered, the first infinitesimal droplet of condensate is formed. This temperature is of practical importance for establishing the top temperature of a fractionating column. In the case of a dew point calculation the vapour composition is known and by dividing the  $Y_i$  values by the corresponding  $k_i$  values one arrives at  $x_i$  values which should add up to 1. At trial and error calculation similar to that carried out for the bubble point leads to the dew point. The same remarks regarding the use of  $k$  values and vapour pressures as made under "Boiling Point Calculation" also apply to the dew point calculation.

### Calculation of Dew Pressure

The dew pressure at a given temperature is the pressure at which condensation starts to take place and is, therefore, an important value in connection with partial condensation for making reflux. According to Raoult-Dalton's law:

$$x_i = \frac{y_i P}{P_i}$$

and since

$$\sum x_i = P \sum \frac{y_i}{P_i} = 1$$

$$P = \frac{1}{\sum \frac{y_i}{P_i}}$$

For the calculation of  $P$  (the dew pressure) the molal concentration of each component is divided by its vapour pressure and the values obtained are added together. The reciprocal of the sum is the dew pressure.

Also in this case a more exact solution can be obtained by using  $k$  values and determining dew pressures at the given temperature by trial and error.

**Example:** Determine the dewpoint of the mixture shown at 4.0 580 psia, assuming the C7<sup>+</sup> fraction has the properties of C<sub>8</sub>.

Comp.	$y_i$	$K_i$	$y_i/K_i = x_i$
CO <sub>2</sub>	1.25	4.83	0.26
H <sub>2</sub> S	0.50	2.38	0.21
C <sub>1</sub>	21.36	6.36	3.36
C <sub>2</sub>	36.78	2.84	12.95
C <sub>3</sub>	10.21	1.57	6.50
iC <sub>4</sub>	6.38	1.02	6.25
nC <sub>4</sub>	9.84	0.86	11.44
iC <sub>5</sub>	2.63	0.55	4.78
nC <sub>5</sub>	4.01	0.49	8.18
C <sub>6</sub>	3.90	0.28	13.93
C <sub>7+</sub>	3.14	0.097	32.37
			100.23

These results are for an assumed temperature of 153°C. It is obtained after a series of trials.

## 2.8 FLASH CALCULATION

So far we have only considered vaporization and condensation of infinitesimal amounts of material at the boiling and dew points. In many cases it is desired to know the amount and composition of the vapour in equilibrium with liquid at temperature and pressure conditions in between the bubble point and the dew point. For instance, the degree of vaporization of a crude oil or some other feedstock after leaving the furnace is an important item in design calculations. Often it is desired to know the amount vaporized at a series of temperatures and pressures for a given material. When such a series of values is plotted against temperature with pressure as a parameter, the resulting graph is called a "flash curve". A flash calculation is based on a combination of a material balance and vapour liquid equilibrium relations.

Assume a feed of 'n' components and take F moles of total feed as a basis.

Let  $V$  = total moles of feed-vapour

$L$  = total moles of feed-liquid

$$\text{So } V + L = F$$

$x_i$  = mole fraction of component i in the liquid phase

$Y_i$  = mole fraction of component i in the vapour phase

$Z_i$  = mole fraction of component i in the total feed

$k_i$  = k value for component i at flash conditions.

The following material balance for a component holds true:

$$\begin{aligned} & Lx_i + VY_i = Fz_i \\ \text{Or } & Lx_i + V k_i x_i = Fz_i \\ \therefore & Lx_i \left(1 + \frac{V k_i}{L}\right) = Fz_i \end{aligned}$$

$$\text{Hence } Lx_i = \frac{Fz_i}{1 + k_i \frac{V}{L}}$$

This is the most convenient form of the so-called flash equation. When temperature and pressure are set, a value of  $\frac{V}{L}$  is assumed and  $Lx_i$  for all components is calculated.

Now as  $\sum Lx_i = L \sum x_i = L$ , and as  $V = F - L$ , the assumed value of  $\frac{V}{L}$  can be checked against the calculated one. The flash calculation has to be repeated until the calculated  $\frac{V}{L}$  value is equal (within the limits of k value accuracy) to the assumed value of  $\frac{V}{L}$ .

When the above-mentioned procedure has been finished the vapour-liquid composition of the feed at the given temperature and pressure can be calculated from:

$$\begin{aligned} x_i &= \frac{Lx_i}{L} = \frac{Lx_i}{\sum Lx_i} \\ \text{and } y_i &= k_i x_i \quad \text{or } y_i = \frac{Fz_i - Lx_i}{V} \end{aligned}$$

By keeping the pressure constant and changing the temperature, a series of values of  $V$  (all in mole fractions) at different temperatures can be obtained and a flash curve for the pressure under consideration can be plotted.

Table 2-1

## Sample Flash Calculation at 400°F and 50 psia (Kuwait Crude)

Com- ponent	Boiling point °F	% by wt.	Mol. wt. (1)	Moles	Mole % = 100 $z_i$	Vapour pressure at 400°F psia (2) $P_i$	$P_i$ 50 = $k$	Take V/L = 25/75		Take V/L = 30/70	
								$k \frac{V}{L} + 1$	$Lx_i$	$k \frac{V}{L} + 1$	$Lx_i$
C <sub>2</sub>		0.05	30	0.0017	0.36	5900	118	40.3	0.009	51.6	0.007
C <sub>3</sub>		0.50	44	0.0114	2.44	2400	48	17.0	0.143	21.6	0.113
C <sub>4</sub>		1.45	58	0.0250	5.36	1200	24	9.0	0.60	11.3	0.47
C <sub>5</sub>		1.50	72	0.0208	4.46	550	11	4.67	0.96	5.71	0.78
A	100	1.22	81	0.0151	3.24	520	10.4	4.47	0.72	5.46	0.59
B	149	1.51	90	0.0168	3.60	300	6	3.00	1.20	3.57	1.01
C	190	3.03	96	0.0316	6.77	190	3.8	2.27	2.98	2.63	2.57
D	233	3.03	108	0.0281	6.02	115	2.3	1.77	3.40	1.99	3.03
E	272	3.29	120	0.0274	5.87	75	1.5	1.50	3.91	1.64	3.58
F	311	3.14	133	0.0236	5.06	45	0.9	1.30	3.89	1.386	3.65
G	350	3.73	146	0.0255	5.47	27	0.54	1.18	4.64	1.231	4.44
H	388	3.17	163	0.0194	4.16	17	0.34	1.11	3.75	1.146	3.63
I	431	3.29	180	0.0183	3.92	10	0.20	1.07	3.66	1.086	3.61
J	471	3.52	200	0.0176	3.77	6	0.12	1.04	3.63	1.051	3.59
K	512	3.47	214	0.0162	3.47	3.4	0.068	1.023	3.39	1.029	3.37
L	547	3.48	235	0.0148	3.17	2.1	0.042	1.014	3.13	1.018	3.11
M	581	2.73	255	0.0107	2.29				2.29		2.29
N	608	3.10	271	0.0114	2.44				2.44		2.44
O	644	3.39	285	0.0119	2.55				2.55		2.55
P	680	3.98	307	0.0130	2.79				2.79		2.79
Q	717	3.34	328	0.0102	2.19				2.19		2.19
R	740	2.86	342	0.0084	1.80				1.80		1.80
S	900	41.22	470	0.0877	18.80				18.80		18.80
		100.00		0.4666	100.00			$L = \sum Lx_i = 72.87$		70.41	

Lower than 75      slightly  
higher  
than 70

Graphical, interpolation gives:

V = 29.2 mole %

L = 70.8 mole %

- (1) Determined experimentally.
- (2) From Shell Data Char.
- (3) Graphical interpolation is only permitted if a well-defined point of intersection is obtained. Extrapolation is never permitted. Figures thus obtained must be verified by a subsequent check calculation.



# **Chapter 3**

# **FUNDAMENTALS OF SEPARATION IN TOWERS**

## **Chapter 3 Contents**

### **3.1 Distillation (Fractionation)**

- 3.1.1 Principles of Distillation
- 3.1.2 Reflux
- 3.1.3 Reboiling
- 3.1.4 Types of Heat Exchangers

### **3.2 Tower Hardware**

- 3.2.1 Trays
- 3.2.2 Bottom Strainer
- 3.2.3 Reflux distributor
- 3.2.4 Top Tower Demister

## Chapter 3

# Fundamentals of Separation in Towers

### 3.1 DISTILLATION (FRACTIONATION)

Distillation is a separation process requires differences to be recognized and utilized. We separate many things by detecting a difference in a physical property, color, size, weight, shapes for example it also requires acting according to such information. Separation by distillation implies a difference in boiling points of two or more materials.

The components or compounds making up crude oil are numbered in thousands. Many of these components have similar physical properties including boiling points that may differ by only a few degrees. Therefore, it is difficult to separate some pure compounds from the complex mixture of components in crude oil by distillation alone. There are other methods of separation used in a refinery for example, extraction with a solvent, crystallization, and absorption. However distillation is the most common method. Fortunately, rarely need pure compounds and it is often enough to separate groups of compounds from each other by boiling range.

If crude oil were a final product, it would have just been a low-grade fuel struggling to establish itself against coal. If we separate the many compounds in crude oil into groups we find that these groups have characteristics that make them considerably more valuable than the whole crude oil.

Some of these groups are products some may be feedstock to other processing units where they are chemically changed into more valuable products. These products, in turn, are usually separated or purified by distillation.

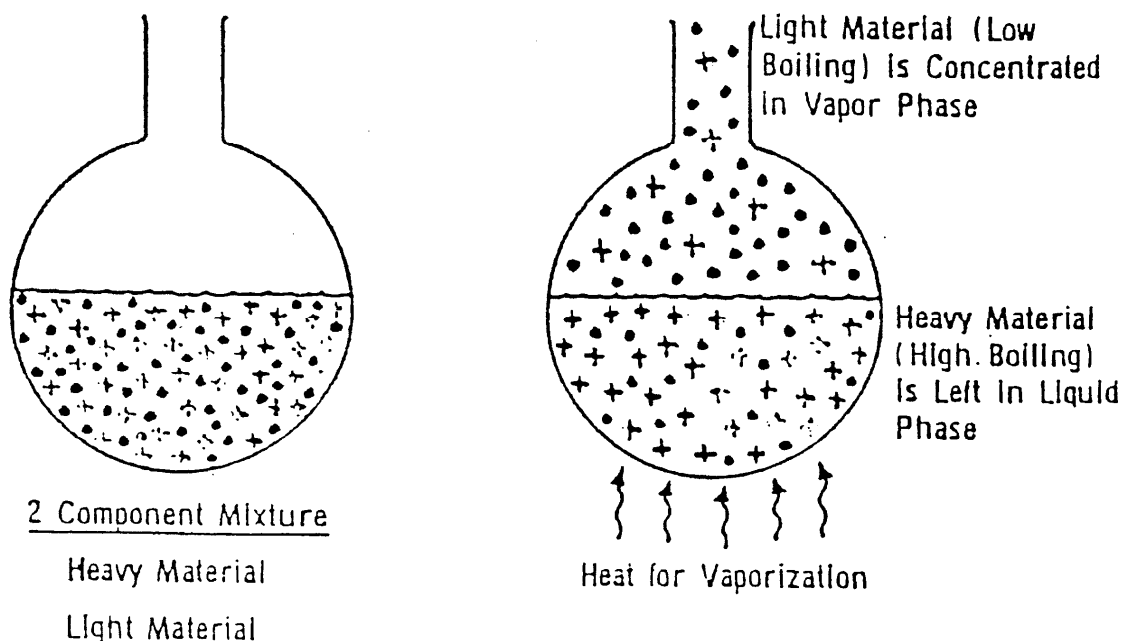
#### 3.1.1 Principles of Distillation

The basic principle of distillation is simple when a solution of tow or more components is boiled, the lighter component the one most volatile or the one with the greatest tendency to vaporize (vaporizes preferentially).

This results in the vapor above the liquid being relatively rich in the lighter, more volatile material. And the liquid is left with proportionately more of the less volatile or heavier liquid. Thus a separation, to some degree, has taken place. This process is shown in Figure 3.1.

A two component mixture, comprising crosses and dots, is contained in a vessel. We Heat is add until the more volatile material, in this case the dots, start to vaporize. Now the vapor contains a higher proportion of dots than does the original liquid.

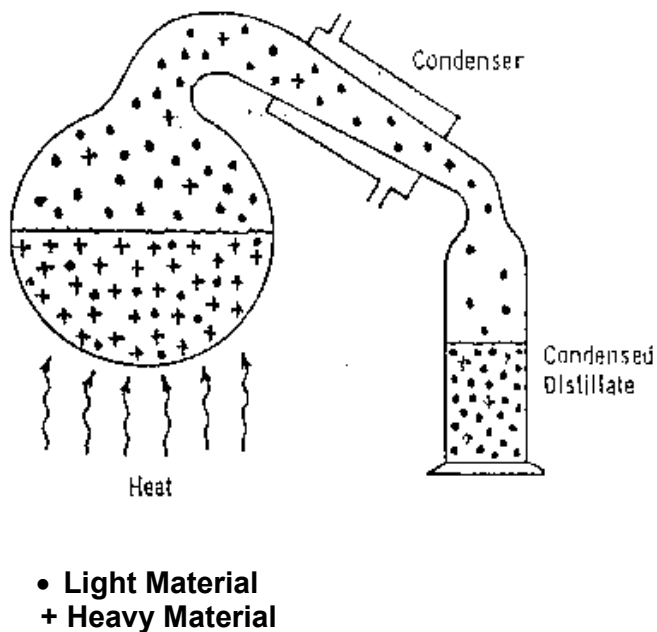
It is important to note that equilibrium will be established. That is, at a given temperature and pressure there is an equilibrium in composition reached. By equilibrium we mean there is a given concentration as "dots" in the vapor and in the liquid depending upon the original concentration of each component in the liquid and their respective properties in relation to each other.



**Figure 3.1**

Now, let's develop this simple distillation concept into a practical operation as it is used in the refinery. First, let's separate and remove the product see Figure 3.2.

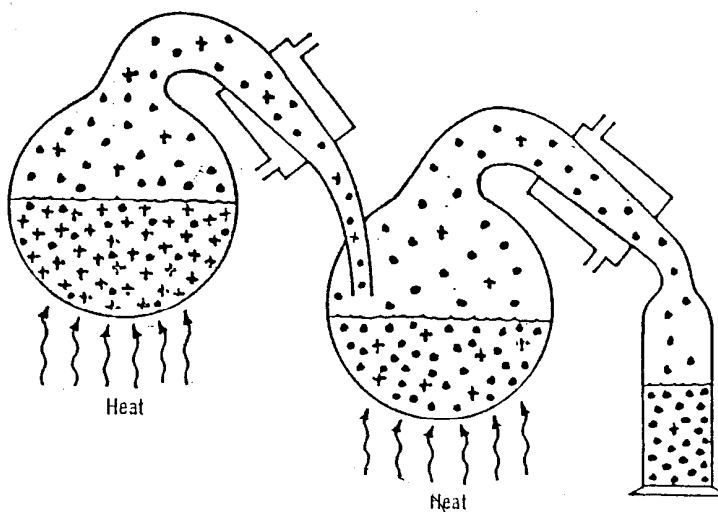
By cooling the overhead vapor, we condense and remove it from the original mixture. Thus to have made a partial separation, partial because you will note that there are a few "crosses" in the distillate product. This has occurred because at the temperature and pressure we are conducting the distillation; the heavier component still vaporizes to some extent. This is because the components of interest in a given distillation usually have fairly close boiling points



**Figure 3.2 Simple Distillation**

Therefore, to purify the distillate product, we may have to conduct a second distillation as shown in Figure 3.3. Obviously, we can continue to cascade these simple distillations until we achieve the desired purity of product.

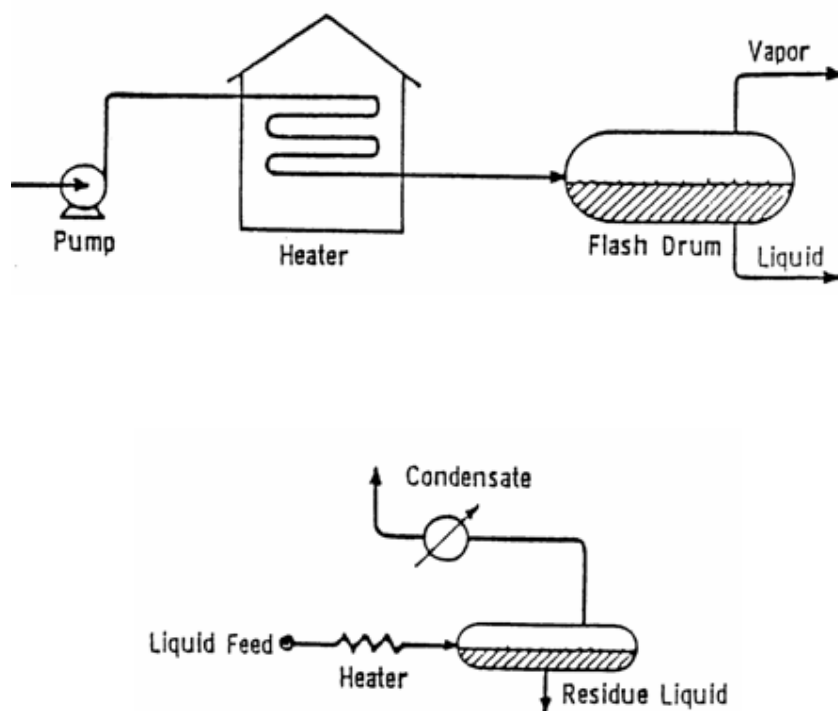
The distillations depicted so far are those we call batch, and normally practical in the refinery, although it is done frequently in the laboratory. Let us make our distillation equipment look more like refinery pieces of equipment and let us make continuous instead of batch operation.



**Figure 3.3 Stage Distillation**



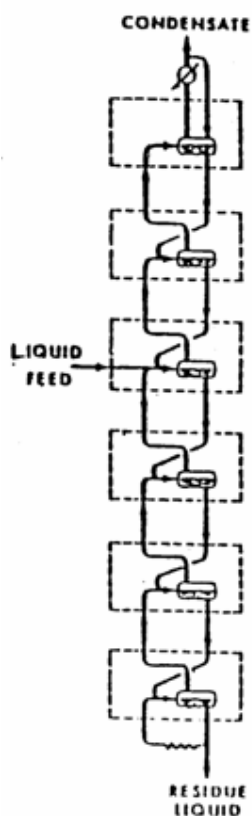
This is called Flash Vaporization. As shown in Figure 3.4. The liquid is pumped continuously through a heater and into a drum where the pressure is lower. The lighter material flashes instantly, vapor and liquid flow from the drum continuously. The same system is shown diagrammatically in the in the lower section of Figure. 3.3 Suppose we have 50% of the charge taken overhead. That is, we set the temperature and the pressure of the system in such a way that half the charge is boiled off. And further, suppose the resulting overhead product does not contain the desired concentration of the lighter product. As we have seen before, we can increase the purity by adding a stage of distillation.



**Figure 3.4 Flash Vaporization**

Suppose we add two more stages of distillation as shown in Figure 3.5. Although this is accomplishing our goal of increasing the purity of the light fraction, we are also making large amounts of the intermediate product, each of which contains the same light fraction.

If we compare feeds to and products from two continuous stages, we note that the liquid from the upper stage and the feed to the lower stage are similar in that both are leaner in the lighter component than is the feed to the upper stage. Therefore, we could combine each intermediate product with the feed to the next lower stage. This would improve the yield of the light fraction and all the original feed would be recovered eventually in the overhead and bottom products.

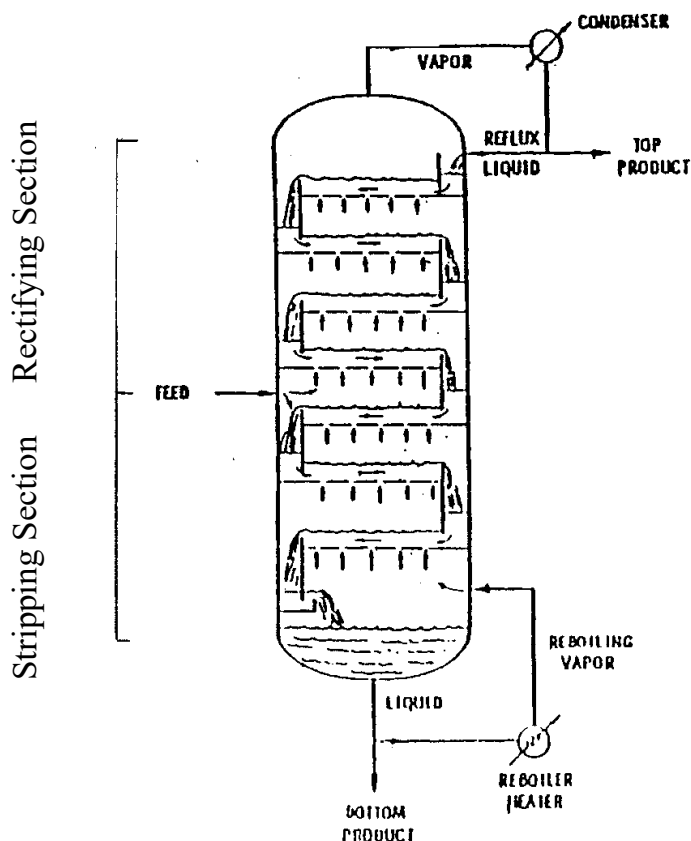


**Figure 3.5 Schematic Illustration of a Typical Distillation Operation**

An obvious simplification in equipment can be made if we allow the hot vapor from the stage above the next higher (the intermediate product). This eliminates the need for the intermediate condensers and heaters. Now we have the continuous, multi-stage distillation.

### **Tower Sections**

We have described staging for the purpose of concentrating the lighter component in the overhead. The same principles apply to concentrating the heavier component in the bottom product. The upper two stages are called **rectifying stages**. These below the feed are called **stripping stages**.



**Figure 3.6 Distillation Tower With Cross – Flow Trays**

The upper rectifying section increases the purity of the overhead product while the stripping section increases recovery of the overhead product. In many cases, the bottom product is the one of primary interest. For the bottom, or heavy, product the rectifying section improves purity.

### **Equilibrium Stage**

We now have the concept of stages. Let us define the term "stage" and see how it is actually designed mechanically.



### 3.1.2 Reflux

The word reflux is defined as "flowing back". Applying it to distillation tower, reflux is the liquid flowing back down the tower from each successive stage.

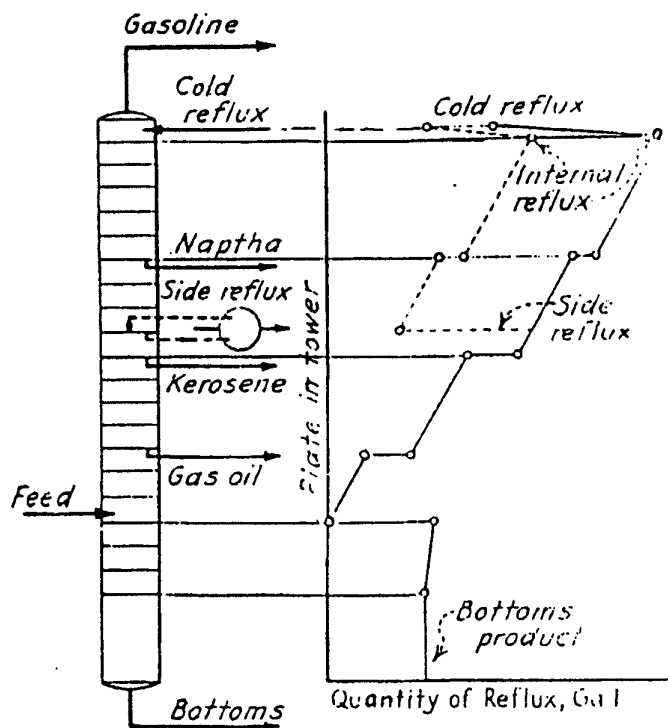
#### Kinds of Reflux (Figure 3.9)

##### **Cold Reflux**

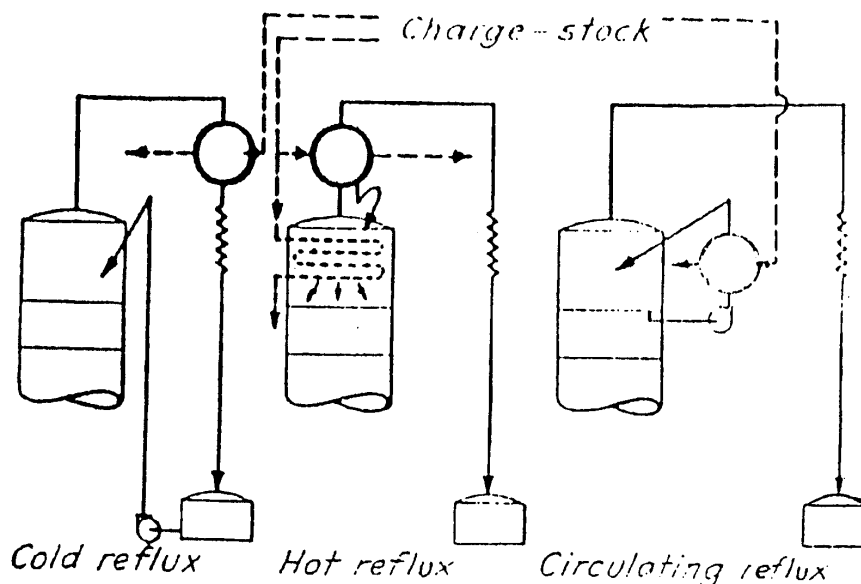
Cold reflux is defined as reflux that is supplied at temperature a little below that at the top of the tower. Each pound of this reflux removes a quantity of heat equal to the sum of its latent and sensible heat required to raise its temperature from reflux drum temperature to the temperature at the top of the tower. A constant quantity of reflux is recirculates from the reflux drum into the top of the tower. It is vaporized and condensed and then returns in like quantity to the reflux drum.

##### **Hot Reflux**

It is the reflux that is admitted to the tower at the same temperature as that maintained at the top of the tower. It is capable of removing the latent heat because no difference in temperature is involved.



**Figure 3.8 Relative Amount of Reflux or Overflow Liquid at Each Tray of Contact**



**Figure 3.9 Methods of Removing Reflux Heat**

### Internal Reflux

It is the reflux or the overflow from one plate to another in the tower, and may be called hot reflux because it is always substantially at its boiling point. It is also capable of removing the latent heat only because no difference in temperature is involved.

### Circulating Reflux

It is also able to remove only the sensible heat which is represented by its change in temperature as it circulates. The reflux is withdrawn and is returned to the tower after having been cooled.

### Side Reflux

This type of reflux (circulating reflux) may conveniently be used to remove heat at points below the top of the tower. If used in this manner, it tends to decrease the volume of vapor the tower handles.

### Reflux Ratio

It is defined as the amount of internal reflux divided by the amount of top product. Since internal hot reflux can be determined only by computation. Plant operators usually obtain the reflux ratio by dividing actual reflux by the top product. It is denoted by  $R$  which equals  $L/D$ .



**The Importance of Reflux Ratio**

In general, increasing the reflux improves overhead purity and increases recovery of the bottom product. The number of stages required for a given separation will be dependent upon the reflux ratio used.

**Two points to consider**

1. A minimum number of plates (stages) required at total reflux.
2. There is a minimum reflux ratio below which it is impossible to obtain the desired enrichment however many plates are used.

**Total Reflux**

Total reflux is the conclusion when all the condensate is returned to the tower as reflux, no product is taken off and there is no feed.

At total reflux, the number of stages required for a given separation is the minimum at which it is theoretically possible to achieve the separation and total reflux is carried out at:

1. Towers start-up
2. The testing of the tower

**Minimum Reflux**

At minimum reflux, the separation can only be achieved with an infinite number of stages. This sets the minimum possible reflux ratio for the specified separation.

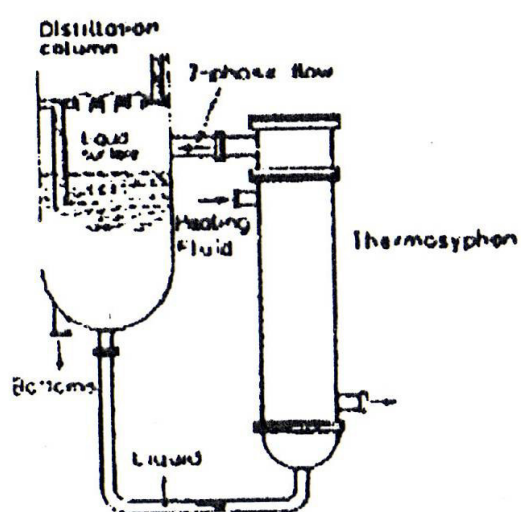
**Optimum Reflux Ration**

Practical reflux ratio will lie between the minimum for the specified separation and total reflux. The optimum value will be the one at which the specified separation is achieved at the lowest annual cost (steam or vapor). For many systems, the optimum value of reflux ratio will lie between 1: 2 to 1: 5 times minimum reflux ratio.

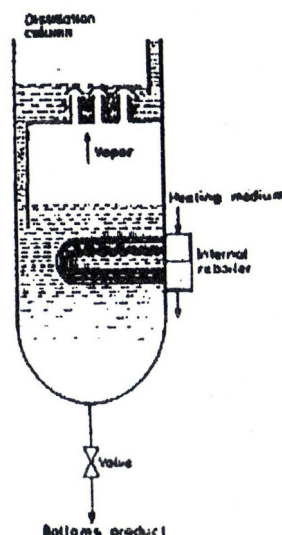
### 3.1.3 Reboiling

In all our distillations discussed so far. We have added heat. Heat can be added in two ways. As we have seen, we add heat by means of the feed. We can also add heat by means of a reboiler.

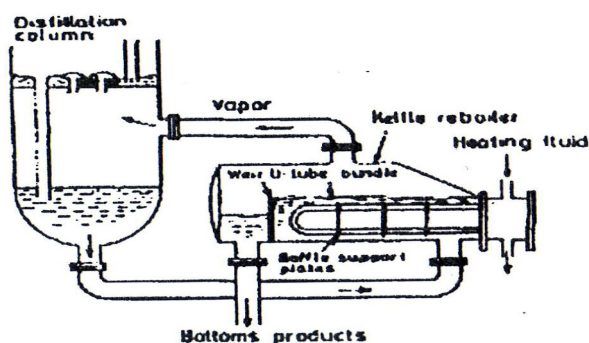
The reboiler is a heat exchanger through which the bottom liquids circulate. Heat is transferred to the bottom materials which cause vaporization of the lighter components. This vapor travels up the column to provide the stripping action and the additional heat necessary to vaporize the down coming reflux. Figure 3.10 shows different types of reboilers.



(A) Thermosyphon Reboiler



(B) Internal Reboiler



(C) Kettle reboiler

Figure 3.10 Types of Reboilers

### 3.1.4 Types of Heat Exchangers

#### 3.1.4.1 Shell & Tube H.E

##### Inter- and After-Cooling:

When gas is compressed it is heated and must be cooled prior to further compression to avoid excessive temperatures or to reduce horsepower. Hot gas must be cooled also before injection into a pipeline to avoid higher pressure drop and thus higher compression cost.

Cooling is accomplished by three media: cooling air, cooling-tower water, or tempered cooling water. Air cooling is accomplished by fin-tubed heat exchangers, discussed below. Cooling towers are beyond the present scope; cooling towers cool recirculated water by evaporating a portion of it. Tempered cooling water is usually an ethylene glycol solution in water. This, in turn is cooled using seawater.

##### Condensing:

Conventional distillation columns require overhead product condensation to provide the necessary reflux and to supply the distillate product in convenient liquid form. A coolant (air, water) or refrigerant is used for this purpose.

##### Gas-to-Gas Exchange:

This important service is often found in NGL recovery. Here the goal is to allow the cold residue gas to approach as closely as possible the temperature of the inlet gas, thus either maximizing the savings in refrigeration or allowing a lower processing temperature.

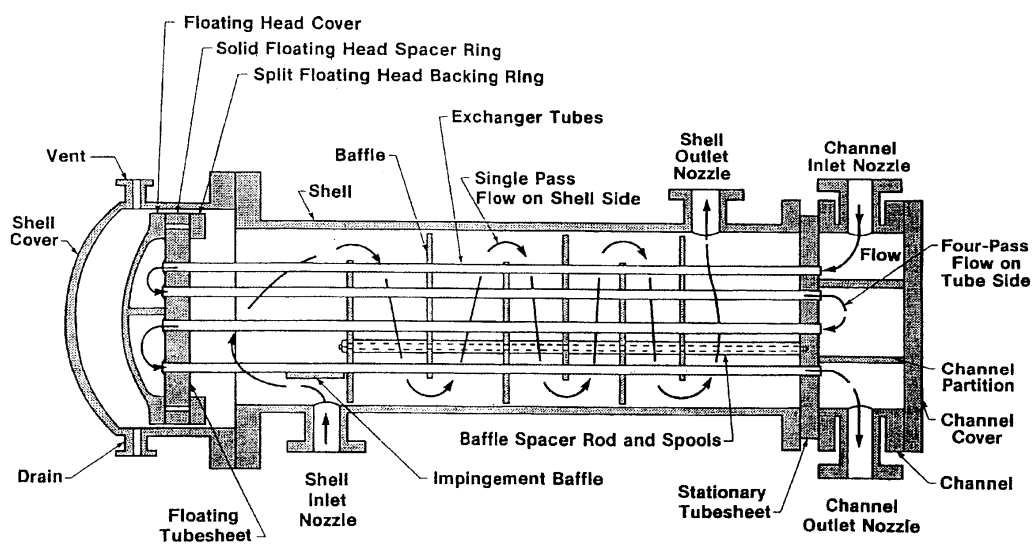


Figure 3.11 Shell & Tube H.E.

### 3.1.4.2 Kettle Type H.E

#### Reboiling:

This service is very similar to chilling, except that the vaporizing fluid is now the process stream and the energy source is the heating medium, which can be hot gas, hot water, steam, hot oil or hot combustion gases.

Reboiling is required in such services as condensate stabilizers or fractionators and amine and glycol solution regenerators. Boiling also occurs in the refrigerant side of a chiller.

#### Chilling:

Recovery of NGL from natural gas can be increased by cooling the gas in an exchanger with a refrigerant stream, such as liquid propane. The cold propane removes heat from the gas, vaporizing in the process.

- |   |  |
|---|--|
| 1. Stationary Head—Channel                  | 20. Slip-on Backing Flange               |
| 2. Stationary Head—Bonnet                   | 21. Floating Head Cover—External         |
| 3. Stationary Head Flange—Channel or Bonnet | 22. Floating Tubesheet Skirt             |
| 4. Channel Cover                            | 23. Packing Box                          |
| 5. Stationary Head Nozzle                   | 24. Packing                              |
| 6. Stationary Tubesheet                     | 25. Packing Gland                        |
| 7. Tubes                                    | 26. Lantern Ring                         |
| 8. Shell                                    | 27. Tierods and Spacers                  |
| 9. Shell Cover                              | 28. Transverse Baffles or Support Plates |
| 10. Shell Flange—Stationary Head End        | 29. Impingement Plate                    |
| 11. Shell Flange—Rear Head End              | 30. Longitudinal Baffle                  |
| 12. Shell Nozzle                            | 31. Pass Partition                       |
| 13. Shell Cover Flange                      | 32. Vent Connection                      |
| 14. Expansion Joint                         | 33. Drain Connection                     |
| 15. Floating Tubesheet                      | 34. Instrument Connection                |
| 16. Floating Head Cover                     | 35. Support Saddle                       |
| 17. Floating Head Flange                    | 36. Lifting Lug                          |
| 18. Floating Head Backing Device            | 37. Support Bracket                      |
| 19. Split Shear Ring                        | 38. Weir                                 |
|   | 39. Liquid Level Connection              |

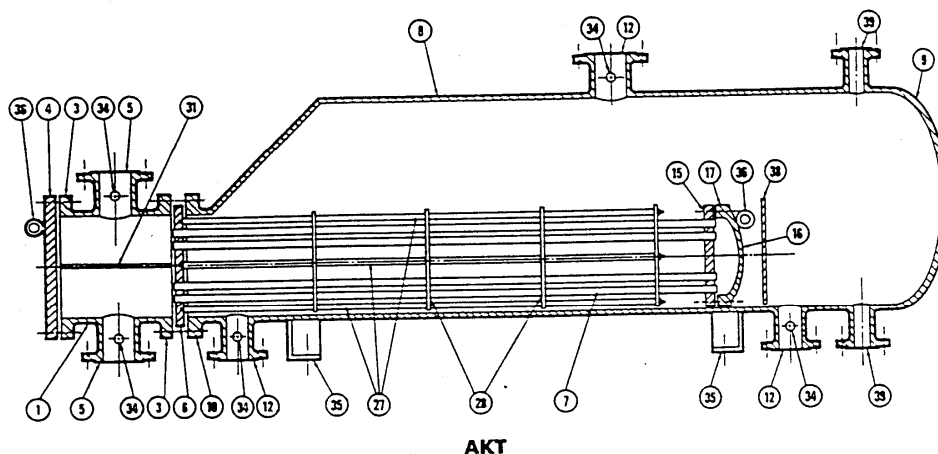
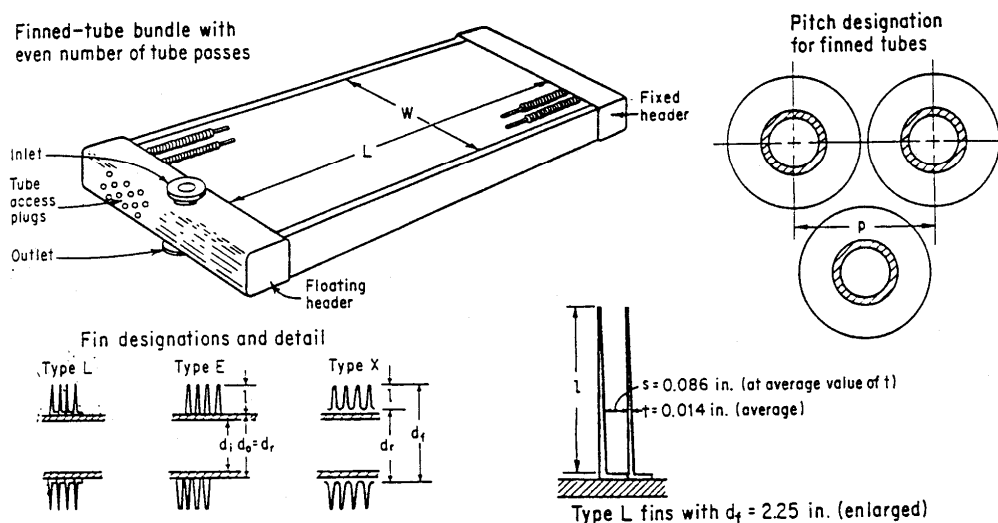


Figure 3.12 Kettle type H.E.

### 3.1.4.3 Air-Cooled Heat Exchangers

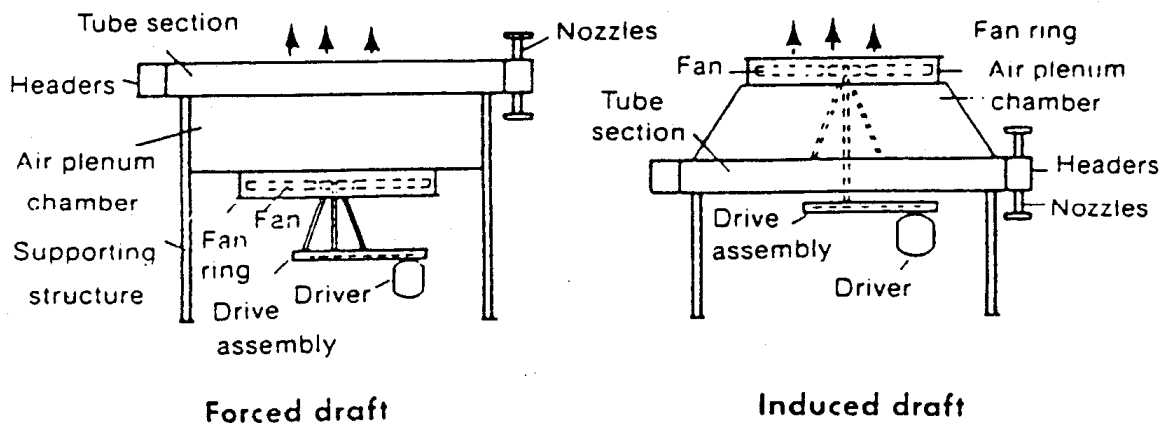
Air-cooled exchangers have the process fluid inside the tubes and ambient air on the outside, either moving by natural convection or blown by a fan. Because of the low heat-transfer coefficient for atmospheric air, fins are used on the outside of the pipes (Figure 3.13).

Both **induced** and **forced draft** fans are used (Figure 3.14). The latter are specified in most applications. When recirculation of cooling air is a problem, induced draft fans are used to provide positive outflow of the air.



**Figure 3.13 Details of Finned Tubes and Exchanger Bundle**

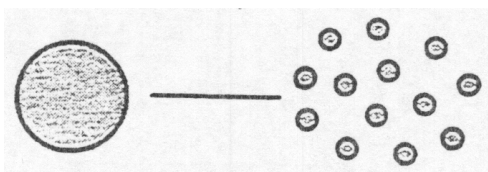
Special precautions are needed for cold climates. Wind skirts or housing may be necessary, as well as air recirculation



**Figure 3.14 Typical side elevations of air coolers**

## 3.2 TOWER HARDWARE

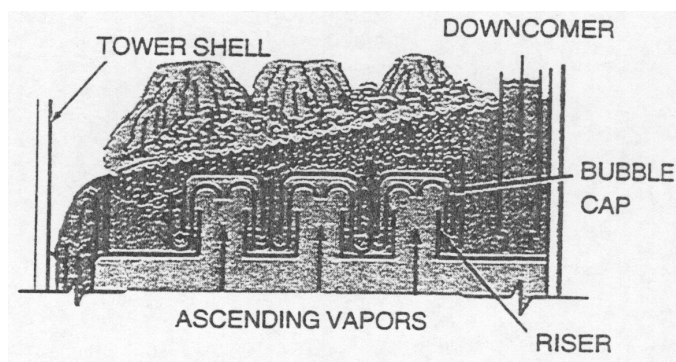
In order for good separation (or fractionation) to occur in a distillation column, the vapors must have good contact with the liquid on each tray. Look at the following drawing. When the large bubble is broken into several smaller bubbles, the smaller bubbles expose more surface area for vapor liquid contact.



### 3.2.1 Trays

#### Bubble Cap Tray

Figure 3.15 shows what happens when vapors pass through a bubble cap tray.

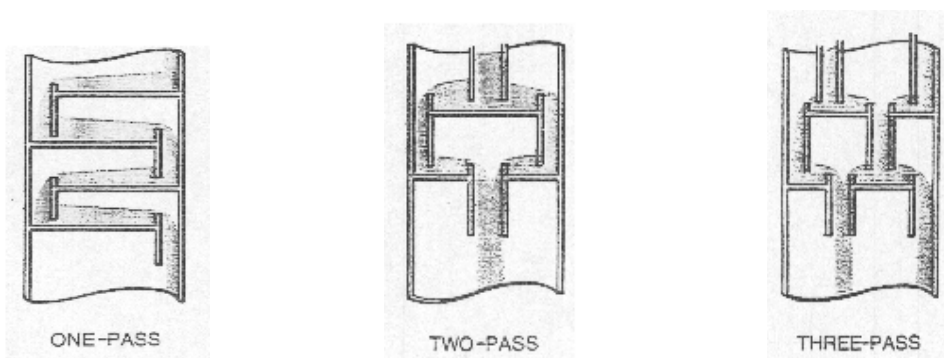


**Figure 3.15 Bubble Cap Tray**

The vapor is broken into small bubbles which increases the surface area for vapor-liquid contact. The bubble cap sits on top of a riser. The riser channels vapors into the bubble cap. Reflux flows down from one tray to the next through downcomers (Figure 3.16).

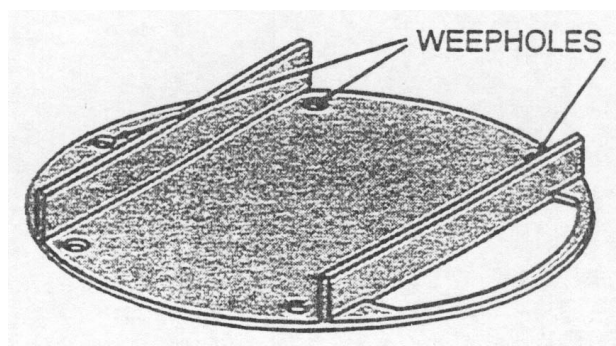
Downcomers must be large enough to allow for drainage from one tray to the next or flooding might occur on some of the trays. Downcomers can be designed in several different ways to provide smooth flow from tray to tray. In a one-pass system, liquid flows completely across each tray. In the two- and three-pass systems, liquid flows across the trays in different direction (s).





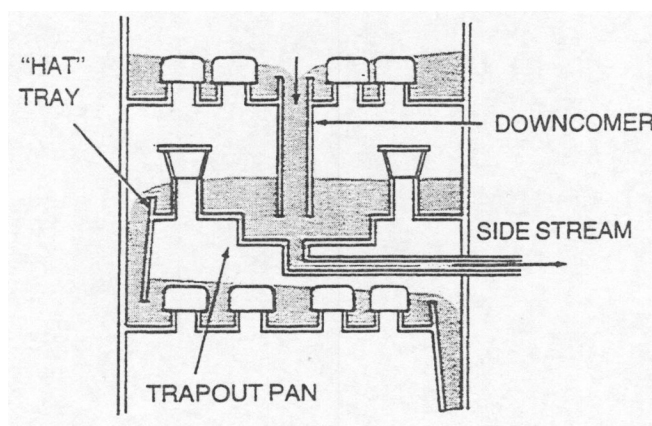
**Figure 3.16 Flow Pass System**

Trays have small holes drilled through them that allow for complete drainage when a tower is shut down. These holes are called weep holes (Figure 3.17).



**Figure 3.17 Weep holes**

Most trays in the tower are level, but trays where a side stream is being drawn off have a low place at the middle of the tray. These low areas on trays are called trapout pans. (Figure 3.18)



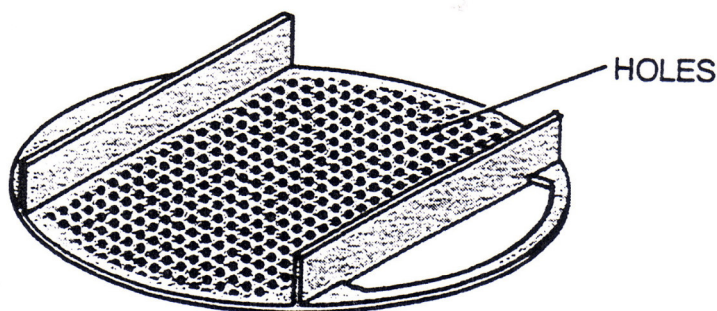
**Figure 3.18 Draw off Tray (Trapout Pans)**

Liquid flows down into the trapout pan through a downcomer in the middle of the tower. The risers on a tray where a side stream is being drawn off are much taller than normal to prevent vapor-liquid contact on this tray. Because the tall risers and caps look something like a "top hat", this type of tray is often called a hat tray.

The purpose of most trays in a distillation column is to provide maximum contact between vapor and liquid phases. Different types of trays can be used to provide this contact. The most common tray, a bubble cap tray, insures good vapor-liquid contact by forcing the vapors to flow through small slots, or teeth, or holes in the body of the bubble cap.

### **Sieve Deck Tray**

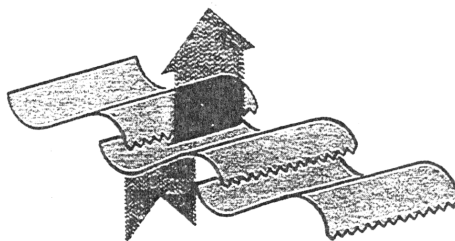
This tray (Figure 3.19) is a sheet of light metal with a large number of holes drilled through it. Vapor rising through the holes keeps the liquid on the tray and bubbles up through it. The overflow weir keeps a constant depth of liquid on the tray. The sieve deck is equipped with downcomers and weirs like the bubble cap tray. A sieve deck tray is inexpensive and easy to clean. It maintains good liquid and vapor contact as long as it is operated at its design load. Because the sieve deck tray has fixed openings and does not have covers over the holes, it does not perform well if tower loads are constantly changing.



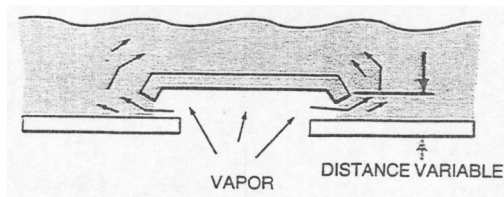
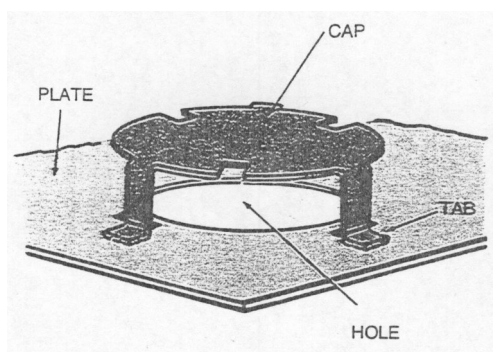
**Figure 3.19 Sieve Deck Tray**

**S-section tray**

The S-section tray (Figure 3.20) is also inexpensive to construct. It is made of overlapping S-shaped sections which form long, continuous bubble caps and troughs for the liquid and the vapor. Each long cap has slots cut in its lower edge which act like bubble cap teeth, forcing vapor to bubble, or flow through the liquid on the troughs. The S-section tray must be put together exactly in order to work well. Small differences in the position or leveling of the S-sections affect the efficiency of vapor-liquid contact.

**Figure 3.20 S-section tray****Valve Tray**

A valve tray (Figures 3.21 & 22) has a variable opening for vapors to flow through. Look at detailed drawing of a valve cap.

**Figure 3.21 Valve Tray (Schematic)****Figure 3.22 Valve Tray (Detailed Drawing)**

The hole has a cover that consists of a cap held in place by guides which go down through the plate, or tray and hook underneath it. When there is no vapor flow, the caps sit over the hole and close it. Under low pressure the caps start to rise. As the flow of vapors increases, the caps rise until it is stopped by the guide tabs. The valve tray is similar to the bubble cap tray. Both are more adaptable to variations in tower loads than a sieve deck tray. The valve trays and bubble cap trays are designed to perform well with variable tower loads.

### **Selection of Tray Type**

The principal factors to consider when comparing the performance of bubble-cap, sieve and valve trays are: cost, capacity, operating range, efficiency and pressure drop.

#### **Cost:**

Bubble-cap trays are appreciably more expensive than sieve or valve trays. The relative cost will depend on the material of construction used; for mild steel the ratios, bubble-cap: valve: sieve, are approximately 3.0:1.5:1.0. However, comparative quotations over the last few years show the relative costs in dollars per square foot of tray area to be: bubble-cap tray, 20; flexitray, 14; Uniflux, 10; sieve, 10; and turbo grid, 10. These are costs before installation.

#### **Capacity:**

There is little difference in the capacity rating for the three types (the diameter of the column required for a given flow-rate); the ranking is sieve, valve, and bubble-cap.

#### **Operating range:**

This is the most significant factor. By operating range is meant the range of vapour and liquid rates over which the plate will operate satisfactorily (the stable operating range). Some flexibility will always be required in an operating plant to allow for changes in production rate, and to cover start-up and shut-down conditions. The ratio of the highest to the lowest flow rates is often referred to as the "turn-down" ratio. Bubble-cap trays have a positive liquid seal and can therefore operate efficiently at very low vapour rates.

Sieve trays rely on the flow of vapour through the holes to hold the liquid on the tray and cannot operate at very low vapour rates, but, with good design, sieve trays can be designed to give a satisfactory operating range; typically, from 50 per cent to 120 per cent of design capacity.

Valve trays are intended to give greater flexibility than sieve trays at a lower cost than bubble-caps.

**Efficiency:**

The Murphree efficiency of the three types of trays will be virtually the same when operating over their design flow range and no real distinction can be made between them.

**Pressure Drop:**

The pressure drop over the trays can be an important design consideration, particularly for vacuum columns. The trays pressure drop will depend on the detailed design of the tray but, in general, sieve plates give the lowest pressure drop, followed by valves, with bubble-caps giving the highest.

**Summary**

Sieve trays are the cheapest and are satisfactory for most applications. Valve trays should be considered if the specified turn-down cannot be met with sieve trays. Bubble-caps should only be used where very low vapour (gas) rates have to be handled and a positive liquid seal is essential at all flow-rates.

**Tray Stability**

A tray is stable when it can operate with acceptable efficiencies under conditions which fluctuate, pulse, or surge, developing unsteady conditions. This type of operation is difficult to anticipate in design, and most trays will not operate long without showing loss in efficiency.

**Flooding**, occurs when the **pressure drop across a tray is so high** that the liquid cannot flow down the tower as fast as required. The pressure drop across the tray increases to very high values, and the tray efficiency drops markedly. When the froth and foam in the down comer back up to the tray above and begin accumulating on this tray. The down comer then contains a mixture of lower density than the clear liquid, its capacity becomes limited, disengagement is reduced, and the level rises in the down comer. The level extends onto the tray above, and will progress to the point of filling the tower, if not detected and if the liquid and vapor loads are not reduced.

**Pulsing** occurs when the **vapor rate is low and unsteady**, when the **slots and holes opening are low**, and when **the liquid dynamic seal is low**. With irregular vapor flow enters the caps or holes, the liquid pulses or surge, even to the point of dumping. The best cure is a steady vapor rate and good slot or hole opening to allow for reasonable upsets.

**Dumping liquid** occurs at **high liquid rates and low vapor loads**. Some of slots or holes will dump liquid instead of passing vapor, resulting in poor tray efficiency. For towers with conventional down comers, dumping usually occurs at the upstream raw of caps or holes, where the liquid has the largest head and kinetic energy.

**Blowing**, occurs when **the vapor rate is extremely high, regardless of the liquid rates**, causing large vapor streams or continuous bubbles to be blown through the liquid. Blowing is usually accompanied by accessing entrainment of large droplets and slugs of liquid up to the tray above. The pressure drop across the tray can be quite high and increase very rapidly with any increase in vapor rate. The efficiency and contact is low and entrainment is usually high.

**Coning** occurs at **low liquid rate or seals**. The vapor pushes the liquid back from the slots or holes and passes upward with poor liquid contact. This causes poor tray efficiency.

**Entrainment** occurs when **mist and liquid particles carry up in the vapor from the liquid on one tray through the riser or holes to tray above**. Sufficient tray spacing must be available to prevent the quantity of material from significantly affecting the efficiency of the tower.

**Puking** usually occurs **at a high liquid rate and low gas rate**. At high liquid rate the liquid level on each tray will rise. As the level rises, the flow of gas up the tower is restricted. The gas pressure in the bottom of the tower will begin to rise. It will reach the point that a surge of a gas will suddenly move up the tower with enough velocity to carry the liquid with it.

Reducing the liquid flow rate will usually eliminate puking. Puking should not be confused with "carryover". Puking occurs almost instantaneously. Furthermore, if the liquid rate is not reduced, the tower will puke again when the liquid stacks up. Carryover is usually caused by a high vapor flow rate. It happens continuously, whereas puking is an intermittent thing.

### **Operating Range**

Satisfactory operation will only be achieved over a limited range of vapour and liquid flow rates. A typical performance diagram for a sieve plate is shown in Figure 3.23.



The upper limit to vapour flow is set by the condition of flooding. At flooding there is a sharp drop in plate efficiency and increase in pressure drop. Flooding is caused by either the excessive carry over of liquid to the next plate by entrainment, or by liquid backing-up in the down comers.

The lower limit of the vapour flow is set by condition of weeping. Weeping occurs when the vapour flow is insufficient to maintain a level of liquid on the plate. "Coning" occurs at low liquid rates, and is the term given to the condition where the vapour pushes the liquid back from the holes and jets upward, with poor liquid contact.

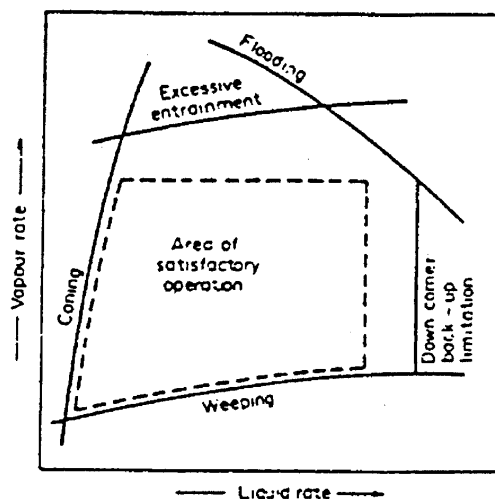


Figure 3.23 Tray Performance Diagram

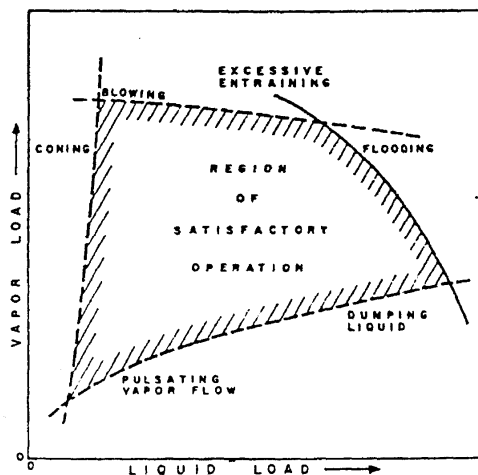


Figure 3.24 Qualitative Region of Satisfactory Operation

### 3.2.2 Bottom Strainer

During the operation of a tower the bubble caps, bolts, and other foreign objects may be dislodged and carried along with bottom stream. To prevent these objects leaving the tower and damaging pumps, a strainer is installed in the bottom outlet line (Figure 3.25). Strainers must have openings small enough to catch small objects, but large enough not to hinder the flow of liquid, or product, or oil out of the tower. The holes in the strainers must be kept open so that the flow of liquid out of the tower will not be stopped, or hindered.

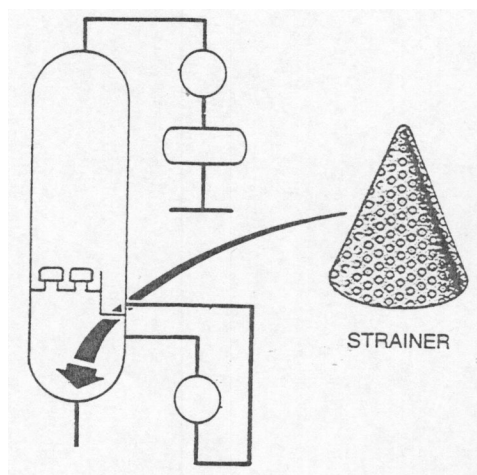


Figure 3.25 Tower Bottom Strainer

### 3.2.3 Reflux distributor

Reflux entering the top of the tower should be spread evenly across the top tray to avoid dead spots. One way to disperse reflux is to place a reflux distributor (Figure 3.26) in front of the inlet line. A reflux distributor is simply a plate or baffle that prevents liquid from spraying across the tray. Reflux entering the tower is forced to flow under the baffle so that the liquid is distributed evenly across the tray.

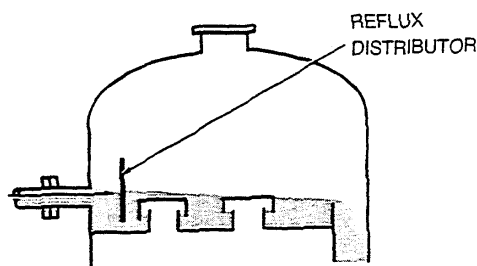
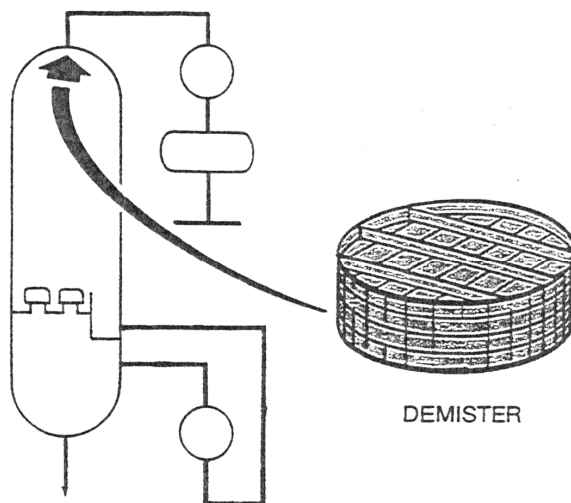


Figure 3.26 Reflux distributor

### 3.2.4 Top Tower Demister

Sometimes small drops of liquid suspended in vapor are carried up from one tray to the next or into the overhead vapor line. This is called **entrainment**. Entrainment between trays can usually be prevented by controlling vapor velocity. When the overhead product must be a dry vapor or gas, entrainment is a more serious problem.



**Figure 3.27 Top Tower Demister**

Entrainment at the top of a tower can be cut down by placing a demister on the vapor outlet line. Demisters (Figure 3.27) are constructed of fine-gauge wire knitted into mesh. Vapors can pass easily through the mesh, but drops of liquid cannot. Demisters must be kept clean of dirt and foreign matter, or the flow of vapor will be restricted, or stopped.

**CHAPTER 4**

**FRACTIONATORS CONTROL,  
OPERATION &  
TROUBLESHOOTING**

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## CHAPTER 4

# Fractionators Control, Operation & Troubleshooting

### 4.1 FRACTIONATOR CONTROL

The fractionator operates by using a controlled temperature gradient from top to bottom. The composition of the top product is fixed by its bubble point or dew point. The bottom product is controlled by its bubble point.

The fractionator always must operate so that the material and energy balances around it are satisfied on a steady-state basis. Any momentary upsets will be reflected by internal unstable operation which causes intolerable "upsets." Furthermore, it is a "sluggish" device. Liquid "hold-up time" is fairly large since flow rates are relatively low compared to its capacity. Therefore, an inherent time lag occurs when controlling at the tower extremities.

The fractionator must process that feed inlet rate, condition and composition that comes to it. Attempts will be made to control these but the success for this will vary. The fractionator control system must, therefore, be fairly flexible.

A demethanizer and/or deethanizer normally are used to remove noncondensibles that are prohibited in the saleable products. The problem is to keep these noncondensibles from passing out the bottom (fairly easy) with only minimum loss of saleable products out the top (more difficult). Therefore, the overhead product is the more critical of the two, although both are important.

Usually, a depropanizer and/or debutanizer are producing a commercial overhead product that must meet certain specifications. At this point (hopefully) no noncondensibles are in the system. In the usual situation the propane, butane or LPG mix are less valuable per unit volume than the heaviest product (natural gasoline, condensate, etc.). This latter product should contain all of the propane and butane that the sales specifications allow. Still, the most sensitive control problem is to keep the methane and ethane levels low (from previous fractionation) to meet vapour pressure specs and maintain the heavier ends at a concentration to satisfy weathering tests.



There are several rules that should be followed in fractionator control:

1. The lesser of the two streams should be manipulated (controlwise) to obtain the greatest sensitivity in product quality.
2. Separation should be manipulated to control the purity of the purest product; the material balance should be manipulated to control the quality of the less pure product.

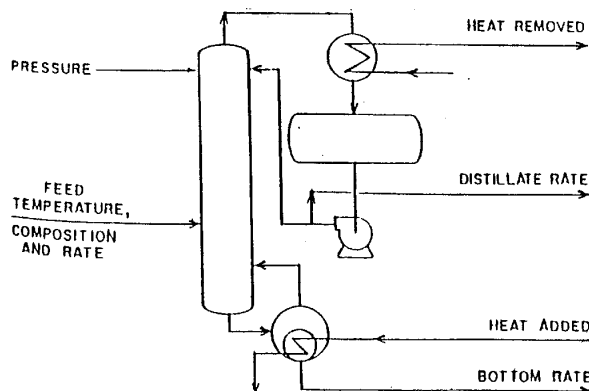
Older control systems attempt to accomplish these functions by the use of pressure, temperature, level and flow controls on each stream independently. The next plateau was to recognize that these streams were not really independent and to address the interaction between them by means of control loops. The next level of sophistication is to add a chromatograph to sense directly those composition changes that are critical and transmit the proper signal to the controls. A simple analog system may be used to accomplish this. The final plateau is reached by "marrying" all of these to a computer which has been properly programmed. All streams being sensed feed their information into this computer or programmable logic controller which runs through a dynamic simulation and then tells the controls what to do.

A computer does not solve the control problem; it can only react within the limits imposed on it by its creator. It also represents an expensive control system.

As a guide in this endeavour, a series of control systems will be shown. These systems should be viewed as examples to illustrate the principles involved.

Some of the variables that can be manipulated when controlling a tower are as follows:

- Tower pressure
- Feed flow rate
- Feed composition
- Feed temperature
- Heat added (boil-up)
- Bottom product flow rate
- Heat removed reflux
- Distillate product flow rate.



### 4.1.1 Feed Section Control

#### Feed Composition

It has a great influence upon operation of a distillation unit. Unfortunately, though, feed composition is seldom subject to adjustment. For this reason, it is necessary to make change elsewhere to the operation of the column in order to compensate for variations in feed composition.

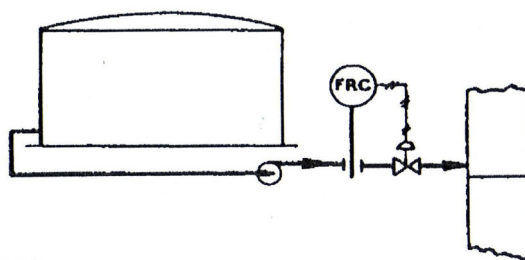
#### Feed Rate Control

Regardless of the process used to recover liquid, both flow rate and composition will vary to the first fractionator. A combination surge drum and vessel to flash-off a portion of the methane and ethane might be used ahead of this fractionator. The level must fluctuate in this vessel. One simple approach is to use a liquid level control with a long displacement type float. By setting it on 100-200 % proportional control, large level fluctuations will dampen out rate changes.

Figure 4.1 (A) to (D) show several possible arrangements.

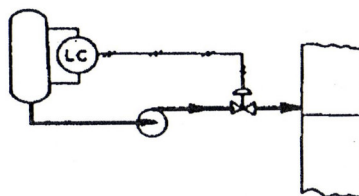
The pump would be eliminated in the first three if the tank is at a high enough pressure. If the tank is large, **(A)** could be used.

Figure 4.1 (A)



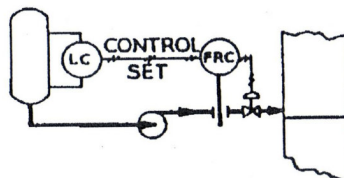
A level indicator with level alarms would be required on the tank to guard against low and high levels. Method shown **(B)** would use the wide band (and maybe long float) with or without the pump.

Figure 4.1 (B)



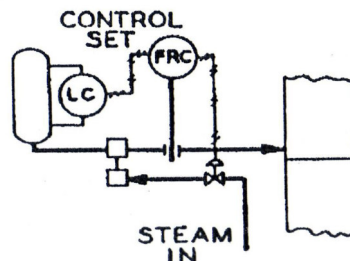
Method shown in Figure 4.1(C) is a further addition that might be necessary when the pressure on the accumulator is not constant. The LC resets the flow recording controller (FRC).

In each of these systems, any pump used would have to be of the centrifugal type subject to back pressure control.



**Figure 4.1 (C)**

Figure 4.1 (D) shows a steam pump layout. The level controller sets the control point for flow. The flow controller actuates the valve on the steam line. Few steam pumps are now used, but this diagram illustrates a simple interlock system.

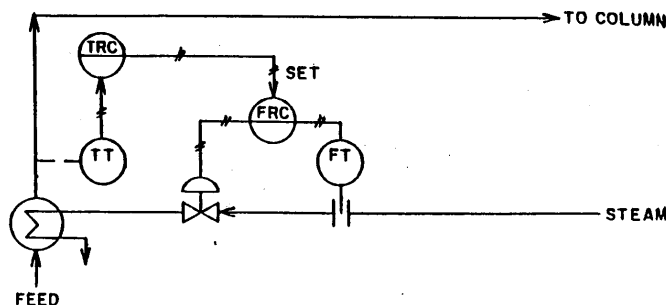


**Figure 4.1 (D)**

### **Feed Temperature (Thermal Condition)**

For efficient separation; it is usually desirable to have the feed at its bubble point when it enters the tower, unless the feed comes directly from some preceding distillation step, an outside source of heat is required.

Steam may be used to heat the feed, any change in feed temperature, a corrective adjustment to the supply of steam into the exchanger. To maintain feed temperature; usually a three mode controller is used. The use of a cascade loop (Figure 4.2) can provide superior temperature control.



**Figure 4.2 Improved Column Feed Temperature Control**

Constant temperature feed does not necessarily mean constant feed composition (quality). If the feed composition varies, its bubble point varies. It is common practice to set the temperature control at a point which is equivalent to the bubble point of the heaviest feed.

### **Feed Temperature Changing**

Now let's consider how changing the temperature of the feed affects separation changes in the fractionator. Suppose we raise the temperature of the feed and hold the reflux rate and other tower variables constant. As the feed enters the column more of the feed is vaporized because of the higher temperature. Some of the heavy material that previously fell to the bottom of the tower is contained in these vapors. So the products formed above the feed tray become heavier. The increase in temperature causes the lightest materials in the liquid at the bottom of the tower to boil out, so the bottom product becomes heavier. Since more vapor goes overhead when the temperature of the feed is increased, the amount of top product formed increases. Because less liquid falls to the bottom of the column when the feed temperature increases, the amount of bottom product formed decreases. So heavier overhead, bottom and side draw products are produced by increasing the feed temperature.

If we reduce the temperature of the feed, the separation changes will again reverse. Less heavy material is vaporized when the feed enters the column, so the top and side draw products become lighter. The material that no longer vaporizes is actually lighter than the liquid at the bottom of the column. When this material falls to the bottom of the column, the bottom product gets lighter. Lighter overhead, bottom, and side draw products are produced by decreasing the temperature of the feed. When the feed temperature is reduced, the amount of top product produced decreases and the amount of bottom product formed increases.

### 4.1.2 Top Section Control

#### **Column Pressure Control**

Most distillation control systems are based upon maintaining the column pressure at some constant value. Any variation of the pressure will upset the control system by changing the equilibrium conditions of the material in the column.

The set point for pressure is a compromise between two extremes. The pressure must be high enough to cause condensation of the overhead vapor by heat exchange with the cooling medium (usually cooling water). On the other hand, the pressure must be low enough to permit vaporization of the bottom liquid by heat exchange with the heating medium (usually steam or hot oil).

Column pressure can be controlled by manipulating the material balance (rate of distillate product) or by manipulating the condensing temperature (bubble/dewpoint pressure of distillate).

The optimum pressure is determined by the cost. It is usually more economical to select the lowest pressure which will allow satisfactory condensation of the distillate product at cooling water temperature. The type of pressure control to be used depends on whether the overhead product is vapor, liquid or liquid and vapor.

#### **Vapour Distillate Product**

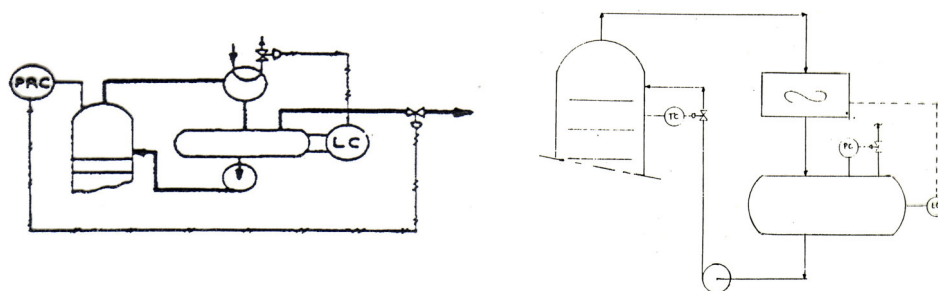
A tower producing vapor overhead product should always be pressure-controlled by regulating the flow of vapor from the reflux drum. The system pressure will quickly respond to changes in the flow.

The liquid from the reflux drum is returned to the tower top tray on flow or temperature control. The condenser should condense exactly as much vapor as is required for reflux.

The level controller must therefore regulate the condensing capacity of the condenser. When the condenser is an air cooler, this can be done by adjustment of the fan blade angle. In case of a water-cooled condenser, the cooling water flow can be controlled.

Figure 4.3 (A) shows a simple back pressure control on the vapour from the partial condenser. In this case, only enough liquid is condensed to provide reflux. The pressure tap could be on the tower, or on the reflux accumulator.

A proportional response plus reset might be used, although a narrow band proportional control alone could be adequate since pressure offsets are often not critical.

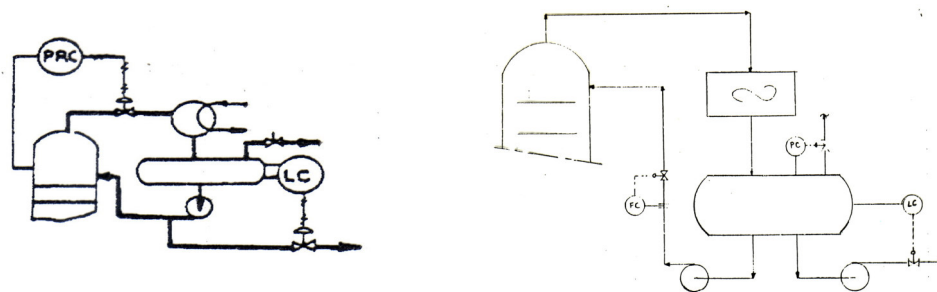


**Figure 4.3 (A) Partial Condenser**

### Liquid and Vapor Distillate Products

In this case the level controller regulates the flow of liquid product. The reflux is on flow or on temperature control (Figure 4.3). Condenser over capacity does not present a problem in this case.

Figure 4.3 (B) shows a system for a total condenser that has proven suitable for a narrow boiling range product. The disadvantage is that a large control valve must be placed in the overhead line.



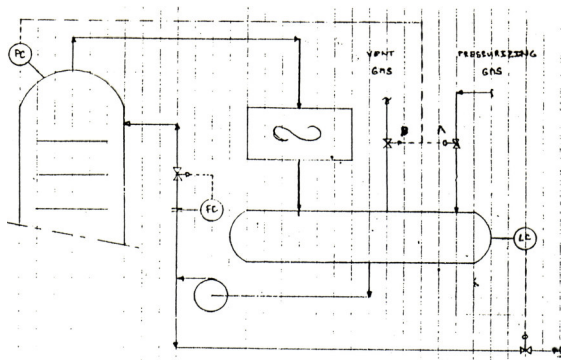
**Figure 4.3 (B) Total Condensers**

When it is desired to operate the tower at a pressure higher than the liquid vapor pressure, gas of sufficiently high pressure should be admitted to the reflux Drum on pressure control (Figure 4.3 C). The controller should be a split range type.

When fuel gas is used as pressurizing gas, it must be realized that the heavier components of the gas (propane, butane and pentane) will dissolve in the liquid. If this not convenient, an inert gas (e.g.  $N_2$ ) should be used.



Figure 4.3 (C)



### Liquid Distillate Product

When the overhead vapour is totally condensed in the condenser, the pressure in the reflux drums is equal to the liquid vapour pressure. The pressure is then a function of the condenser outlet temperature. The best way of pressure control for tower operating at a pressure equal or close to the vapour pressure is to bypass vapour around the condenser directly to the reflux Drum.

Figure 4.3 (D) is an example of one type of hot vapour bypass to control tower pressure. The condenser is partially flooded. The vapour bypass changes the surface temperature of the liquid in the accumulator, hence controlling tower pressure.

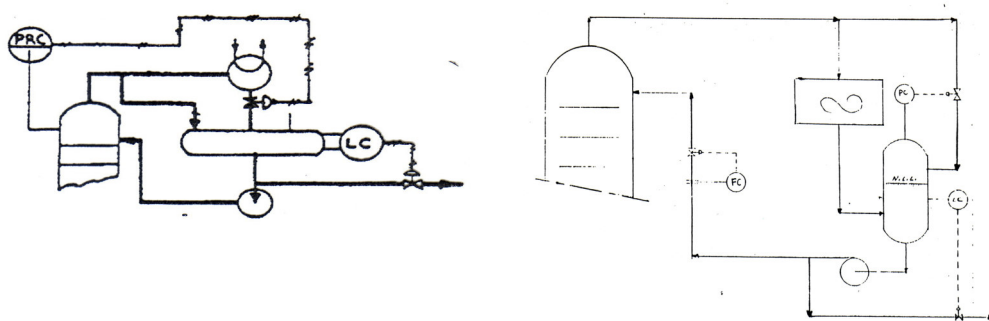


Figure 4.3 (D) Partially Condenser

The temperature of the condensed product in the accumulator can also be controlled by controlling the cooling medium. This is shown schematically in Figure 4.3 (E) this method is not recommended if the cooling medium is cooling water as it induces fouling and scaling in the condenser. If the cooling medium is air, louvers or variable pitch for blades can be used to control air flow. Induced draft coolers are preferred because the tube bundle is not exposed to precipitation.

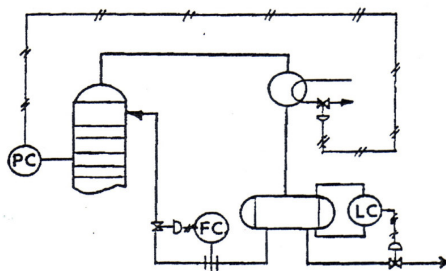
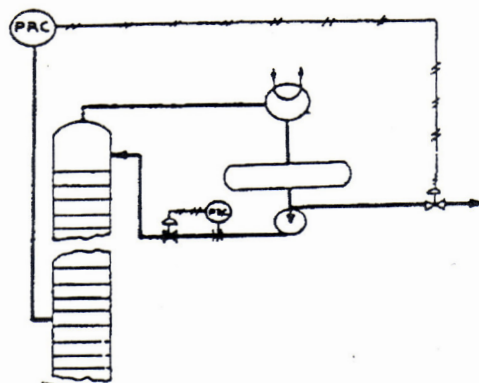
**Figure 4.3 (E)**

Figure 4.3 (F) shows a flooded condenser system for a total condenser. In this system the accumulator runs completely full of liquid and pressure is controlled by manipulating the heat transfer area in the condenser. This method is commonly used in NGL fractionators.

**Figure 4.3 (F)  
Flooded Condenser**

Most pressure control systems are based on manipulating the cooling rate at the condenser. If the condenser is allowed to operate without restriction, the column pressure will be as low as possible given the cooling medium and operating conditions. This is called "floating pressure control" and has the benefit of reducing the difficulty of separation, as relative volatilities tend to increase with decreasing pressure for most hydrocarbon separations.

### **Reflux Controls**

Since distillation achieves separation of materials by counter currently contacting vapor and liquid, reflux furnishes the continuous supply of liquid to the top of the tower, just as the reboiler furnishes the continuous supply of vapor to the bottom of the tower.

The rate of reflux would be controlled by a flow control set manually or representing a ratio to distillate stream.

## Reflux Rate Changing

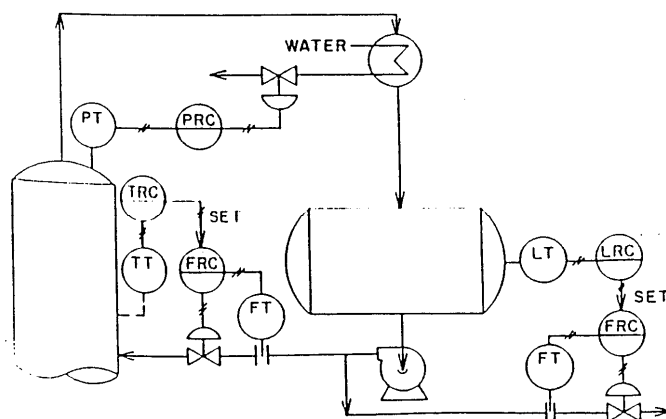
Vapors at the top of the tower are cooled and condensed to liquid. Part of this liquid is returned to the tower as cooling reflux. Let's consider the effect of making separation changes in a fractionator by varying the reflux rate. Reflux as a "coolant" that removes heavy fractions by condensing them.

Suppose the reflux rate is increased from 1,000 to 1,200 barrels per hour, and the other tower operating conditions are held constant. This extra reflux flowing down the tower causes the temperature on each tray to decrease. Some of the heavier hydrocarbons in the upward flowing vapors will now condense and fall back down the tower. The heaviest components are condensed out of the vapors on each tray in the column. As a result, the fraction formed on each tray will be lighter. The extra reflux flowing down the tower reduces the temperature of the liquid at the bottom of the column. When the bottom temperature decreases, the amount of light material vaporized out of the liquid at the bottom of the tower is decreased. So the liquid at the bottom of the column becomes lighter. Since the amount of product drawn to the stripper columns remains constant, increasing the reflux rate causes more bottom product to be formed. Because fewer vapors are now going overhead, the amount of top product formed is decreased, or less. Lighter overhead, bottom, and side draw products are produced by increasing the reflux rate.

If we decrease the reflux rate from 1,000 barrels to 800 barrels, the separation changes are reversed. The temperature on each of the trays increases, and a higher tower temperature mean heavier products. So overhead, bottom, and side draw products become heavier. The amount of overhead product produced increases and the amount of bottom product formed decreases.

When composition of the distillate product is the important consideration it is desirable to maintain a constant temperature in the upper section as shown in Figure 4.4.

Measuring temperature in a column usually requires that the sensing device be in the liquid on the tray. Heat transfer from a liquid medium to the sensing device is much greater than the heat transfer from a gas medium.



**Figure 4.4 Temperature Cascaded Reflux Flow for Improved Overhead Composition Control**

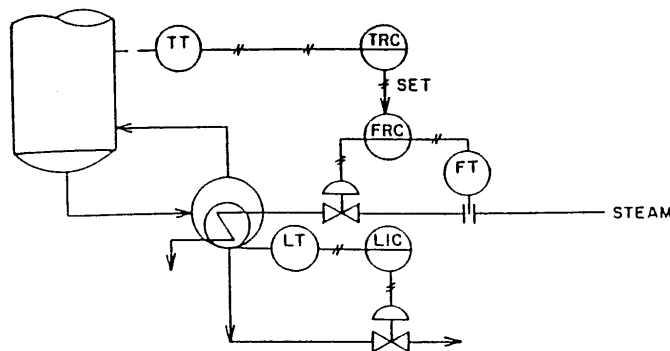
### 4.1.3 Bottom Section Control

#### Reboiler Control

Boil-up rate is controlled by setting the flow of heat to the reboiler. A flow controller is placed in the line carrying the heating medium to the reboiler.

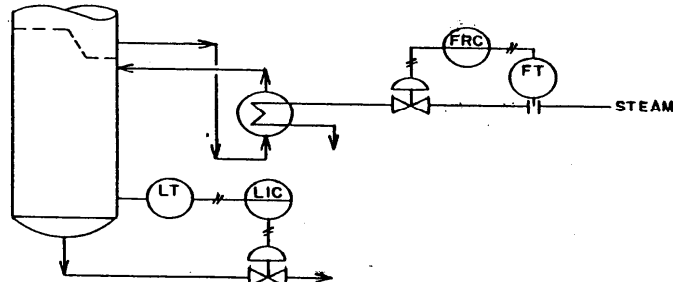
The amount of lighter boiling material in the bottom product is determined by the set point of the steam rate controller. A setting which permits a greater amount of steam into the reboiler will cause more of the lighter material to be driven back into the column as vapours.

The rate of bottom product withdrawal is controlled by the level in the reboiler, Figure 4.5 shows a kettle type reboiler.



**Figure 4.5 Kettle Reboiler Control**

Other types include thermosyphon reboilers and forced-circulation reboilers. For them, the bottom product is withdrawn from the column (Figure 4.6)



**Figure 4.6 Thermosyphon Reboiler Control**

## **4.2 STARTING-UP PROCEDURE**

This section describes the Initial unit starting up; some variation in the following procedure is possible for subsequent start-ups, depending upon how complete a shutdown has been made.

It should be remembered that H.C or flammable gas should never be charged into process lines or vessels indiscriminately. If the line or vessel has contained air, suitable purging should be done. Similarly air should not be allowed to enter lines or vessels which have contained hydrocarbons, until proper safety precautions have been taken.

Before the unit is put on stream, it is necessary to check for proper mechanical condition of equipments, availability of utilities, etc. When those things are in order, the plant can be put on stream.

The detailed instructions are divided into the following sections.

### **4.2.1 Prepare Unit for Introducing H.C**

- Check that all blinds have been removed and that all safety valves are installed.
- Check that all utilities are available where required.
- All instruments should be ready for service

### **4.2.2 Steam Drying**

If the equipments have been washed or hydrostatically pressure tested prior to the startup, they should be steam dried.

To steam-dry the columns, pressure the columns up to any safe pressure with steam. While doing this, purge the unit and drain the condensate. Then allow the equipment to approach the steam temperature. Then stop the flow of steam and open all drains and vents. By quickly, depressuring the unit to atmospheric pressure, any hot condensate left should vaporize and blow out. The hot steam vapors should then be purged out with fuel gas before the steam has an opportunity to condense.

Gas should always be put in a vessel immediately after stopping the steam purge to avoid pulling a vacuum on the vessel.

### 4.2.3 Leak Test

During the steam drying at the equipment, the leak test will be accomplished with the steam at a pressure of 4 kg/cm<sup>2</sup> g., for the equipments at the discharge of the compressors. For the equipments at the suction of the compressors the leak test will be accomplished with air at a pressure of 0.5 kg/cm<sup>2</sup> g.

### 4.2.4 Pressure Up With Nitrogen or Fuel Gas

- The compressors should be pressurized up with nitrogen.
- Pressurize the distillation section with the fuel gas of the refinery at about 0.5 kg/cm<sup>2</sup> after stopping the steam purge.
- Pressurize the compressor discharge drum.

### 4.2.5 Start the Unit (Actual VRU)

1. Ascertain that cooling water is flowing through the tubes of the feed cooler.
2. Start up the main compressor and the main fractionator off gas booster compressor
3. When the main compressor is operating, introduce the liquid feed from the Preflash tower over-head drum.
4. As the pressure on the compressor discharge drum rises, the pressure controller can be put in service with gas released to the fuel gas header.
5. After a good working level is established in the drum, startup the deethanizer feed pump.
6. As a liquid appears in the bottom of the deethanizer, start the flow of steam through the reboiler and the flow of cooling water through the condenser.
7. As the pressure on the column rises, the pressure controller on the reflux drum can be put in service with overhead gases being released to the fuel gas header.
8. When a sufficient level appears in the reflux drum, start the deethanizer reflux pump. The reflux will be maintained to hold a proper level in the reflux drum.



9. When a sufficient level has been established in the bottom of the deethanizer column, send some bottom product into the depropanizer.
10. The depropanizer pressure is raised by keeping the column on total reflux in the following manner:
  - As a liquid level appears in the bottom of the depropanizer, start up steam injection to the reboiler and cooling water injection to the condenser.
  - As the tower pressure and temperature increase, a liquid level will appear in the depropanizer reflux drum DB 104. Start up the depropanizer reflux pump and hand control the liquid level in the reflux drum by means of FV.
  - When the column pressure reaches its operating value, pressure control valve PV will open. This will allow overhead gas to be vented to the flare system.
  - When a sufficient level has been established in the depropanizer column, send depropanizer bottom to the debutanizer.
  - As a liquid level appears in the bottom of the debutanizer start up the steam injection to the reboiler and the cooling water injection to the condenser.
  - As the tower pressure and temperature increase a liquid level will appear in the debutanizer reflux drum. Start up the debutanizer reflux pump and hand control the liquid level in the reflux drum by using FV.
  - When the column pressure reaches its operating value, pressure control valve will open, and the overhead gas will be vented to the flare system.
  - When a sufficient level has been established in the depropanizer column, start the light gasoline pump, and send the bottom product to the storage. Before starting up the light gasoline pump, ascertain that cooling water is flowing through the light gasoline cooler.

#### **4.2.6 Establish Normal Operating Conditions**

- Adjust the reboiler heating and the reflux rate to obtain the desired products.
- When the columns are operating at conditions to produce on-specification products increase the depropanizer and debutanizer pressure at the normal value to produce a liquid overhead product and commission the reflux drum controller to send overhead product to storage.
- Then increase the feeds rate to the design value.

## 4.3 NORMAL OPERATION

In normal operation the plant must be controlled to achieve the production of the product streams at proper specifications.

### 4.3.1 Products Specifications and Operating Variables

#### Propane product

**Ethane content more than 4 % vol:**

- Increase bottom temperature
- Decrease top pressure
- Decrease reflux

**Butane content more than 1%vol:**

- Decrease bottom temperature
- Increase reflux
- Increase top pressure
- Change feed inlet to a lower tray.

#### Butane LPG product

**Vapor pressure more than 6.5 kg /cm<sub>2</sub>g:**

- Increase bottom temperature
- Decrease top pressure
- Decrease reflux
- Change feed inlet to upper tray.

**Pentane content more than 2 % vol or 95 % vaporization more than 2°C:**

- Decrease bottom temperature
- Increase reflux
- Increase top pressure

### **Light gasoline**

**Butane content more than 1 % mole:**

- Increase bottom temperature
- Decrease top pressure
- Decrease reflux

### **Propane recovery**

**Propane recovery less than 85.6 %:**

- Increase pressure
- Decrease bottom temperature
- Increase reflux

### **Butane recovery**

**Butane recovery less than 98.3 %:**

- Increase pressure
- Decrease bottom temperature
- Increase reflux

### **Review**

1. Quality control over distillation products is maintained by setting specifications for these products.
2. The temperature at which a petroleum product generates ignitable vapors is called the flash point.
3. You can increase the temperature in a column by increasing the feed temperature or decreasing the reflux rate.
4. You can decrease the temperature in a column by decreasing the feed temperature or increasing the reflux rate.
5. A temperature decrease means that products get lighter.
6. When the tower temperature increases, the amount of overhead product produced increases and the amount of bottom product formed decreases.
7. When the tower temperature decreases, the amount of overhead product produced decreases and the amount of bottom product formed increases.
8. The temperature on the top tray of a tower should be just high enough to completely vaporize the overhead product.
9. In order to store the overhead product in liquid form, the pressure in a condenser or accumulator must be slightly higher than the vapor pressure of the product at the temperature it is being stored.
10. The ideal temperature at the bottom of the tower is the temperature at which the vapor pressure of the bottom product is slightly below the operating pressure of the tower.

## Butane Recovery Calculation (Work Sheet)

COMP.	L.VOL%	Sp. Gr. @ 60/60°F	WEIGHT (L. vol% x Sp. Gr.)	WF%
C <sub>3</sub>	-----	0.5077	-----	-----
i-C <sub>4</sub>	-----	0.5631	-----	-----
n-C <sub>4</sub>	-----	0.5844	-----	-----
i-C <sub>5</sub>	-----	0.6247	-----	-----
n-C <sub>5</sub>	-----	0.6310	-----	-----
<b>TOTAL</b>	<b>100.00</b>		-----	<b>100.00</b>

1. LPG Production, Kg = -----
2. (i + n) C<sub>4</sub>, in LPG, wt% = ----- (From Table)
3. Butane in LPG (item 1x item 2), Kg = -----x ----- = -----
4. Feed Gas Rate , N M<sup>3</sup> = -----
5. " " " , MMSCF = -----
6. (i + n) C<sub>4</sub>, in Feed Gas, mol % = ----- (From Analysis)
7. Water content, lb / MM scf = ----- (From Chart)
8. (I+N) C<sub>4</sub>, in Feed Gas, Kg \* = -----
9. Total C<sub>4</sub>, in Feed Gas, Kg = -----
10. Butane Recovery (item 3 / item 9 x 100) = ----- %

$$* = \frac{\text{Item 6}}{100} \times \frac{\text{Item 4}}{22.414} - \frac{\text{Item 7} \times \text{Item 5}}{18 \times 2.205} \times 58.124$$

## 4.4 TROUBLESHOOTING

This part deals with common operating problems. It is not apropos to try to cover all problem situations. The following are discussed:

1. Flooding
2. Dry trays
3. Damaged trays
4. Water in a hydrocarbon column
5. Foaming
6. Condenser fogging

### 4.4.1 Flooding

#### Design

Flooding is a common operating problem. Companies naturally wish to obtain, maximum capacity out of fractionation equipment and thus often run routinely close to flooding conditions. New columns are typically designed for around 80% of flood. Clearly, the column needs some flexibility for varying operating conditions. Vendors, state that their modern methods for determining percentage of flood represent very closely the true 100% flood point. The designer, therefore, shouldn't expect to design for 100% of flood and be able to accommodate variations in operating conditions. Designers recommend a percentage of flood of not more than 77% for vacuum towers or 82% for other services, except that for columns under 36" diameter, 65-75% is recommended.

#### How to Identify Type & Location of Flooding

The tower operator can quickly determine which type of flooding will tend to be the limiting one for a particular system. If a rigorous computer run is available for the anticipated or actual operation, the operator can quickly calculate the expected limiting column section. The operator can then provide DP cell recording for the entire column and limiting section (s), a DP cell is the best measure of internal traffic and flooding tendency.

#### **1. Increase in pressure drop and a decrease in temperature difference:**

Flooding across a column section reflects itself in an increase in pressure drop and a decrease in temperature difference across the affected section. Product quality is also impaired, but it is hoped that the other indicators will allow correction of the situation before major change in product quality. When a column floods, the levels in the accumulator and bottom often change. It can occur that the accumulator fills with liquid carried over while the reboiler runs dry.

**2. Pressure fluctuation:**

Also, in a flooded column, the pressure will often tend to fluctuate. This may help to differentiate between flooding and a high column bottom level, if the bottom level indicator reading is suspect. The high bottom level will give higher than normal pressure drop but often not the magnitude of pressure fluctuations associated with flooding.

**3. Possible capacity increase:**

Here is a tip for possible capacity increase for towers with sloped downcomers. Usually, the tray vendor doesn't use the dead area next to the bottom part of the sloped downcomer as active area if the trays are multipass, since he would require a different design for alternate trays. This area could be used for additional vapor capacity in an existing column.

**4. Temperature profile:**

Another method of locating trouble spots is by the use of temperature profile data. In fractionating columns the temperature of any given plate is dependent on the pressure and composition of the material on the tray. A plot of temperature versus plates for the column is called the temperature profile. When a column is operated to yield a product consisting mainly of one component only (e.g. deisopentanizer with a top product of 95%, pure isopentane) the temperature gradient over the trays near the product outlet will be very small. When both top and bottom product are very narrow boiling range products only one steep column temperature gradient will be located near the feed inlet where all components to be separated are present in appreciable quantities.

When wide boiling range products are manufactured to flattening down of the temperature profile will occur over the trays near the product outlets.

Comparison of the known profile for normal operation with that when operation is poor may help to locate the source of the trouble. In a flooded area the composition of the liquid on all trays will be the same and hence the temperature will not change over this section.



## **Operating Difficulties Causing Flooding**

### **1. Fouling:**

Sometimes upsets in operation are caused in sections of a column due, for example, to local fouling. Differential pressure measurements are helpful in locating the sections that are causing the difficulties. Careful and repeated tests have to be made to determine the sections at which the increased pressure drop first occurs.

### **2. Operation near Critical Conditions:**

When a column is operated under conditions of temperature and pressure which are very near to the critical values of the hydrocarbons to be processed, fractionation can be poor owing to the fact that a column section contains only one phase and is consequently flooded.

### **3. High Loads in Rectifying Section:**

The highest load in the rectifying section of a column normally occurs at the top plate. Sometimes this tray is flooding and further increases in reflux are ineffective because it merely goes overhead as liquid. A heat balance around the overhead condenser shows, if much liquid is entrained, which is an indication of overloading of at least the top part of the column.

### **4. Way of Introducing Feed:**

The way of introducing the feed into the column may also be a source of trouble, as the vapour or liquid entering may upset the flows in that part of the column. Furthermore attention must be given to the velocity of the vapour and liquid feed in the inlet. Too high a vapour velocity may cause atomization of the liquid feed resulting in considerable entrainment.

### **5. Reboiler:**

The reboiler may be the cause of operating troubles in the bottom section. This is especially the case with reboilers of the thermosyphon type. Here fluid is driven through the reboiler by the static head driving force created by vaporization in the reboiler tubes. Frictional losses oppose the flow of fluid through the circuit. As a result the flow will adjust itself in such a manner that a balance is obtained between the static head driving force and the flow resistance. If the resistance increases owing to fouling in the pipes or if the lines are too small, the balancing liquid level in the column may build up and rise even as high as the bottom tray, which causes flooding.

**6. Downcomer Backup Flood:**

If the downcomer backup for valve trays exceeds 40% of tray spacing for high vapor density systems ( $3.0 \text{ lbs/ft}^3$ ), 50% for medium vapor densities, and 60% for vapor densities under  $1.0 \text{ lbs/ft}^3$ , flooding may occur prior to the rate calculated by jet flood. Another good rule of thumb is that the downcomer area should not be less than 10% of the column area, except at unusually low liquid rates. If a downcomer area of less than 10% of column area is used at low liquid rate, it should still be at least double the calculated minimum downcomer area.

Many plant nontechnical operators do not understand that high vapor rates as well as high liquid rates can cause down comer backup flooding. It is well to explain to the plant operators the mechanism of downcomer backup flooding and show them with a diagram how the head of liquid in the downcomer must balance the tray pressure drop. Then it can be explained how vapor flow is a major contributor to this pressure drop.

**4.4.2 Dry Trays**

This problem, as with flooding, also impairs product quality. No fractionation occurs in the dry section, so the temperature difference decreases. However, unlike flooding, the pressure drop decreases and stays very steady at the ultimate minimum value. This problem is usually easier to handle than flooding. The problem is caused by either insufficient liquid entering the section or too much liquid boiling away. The problem is solved by reversing the action that caused the dry trays.

Since the changes usually occur close to the source of the problem, the source can usually be quickly found with proper instrumentation. Too little reflux or too much sidestream withdrawal is two examples of insufficient liquid entering a section. Too hot a feed or too much reboiling are examples of excessive liquid boiloff.

**4.4.3 Damaged Trays****Effects and reasons**

Trays can become damaged several ways. A pressure surge can cause damage. A slug of water entering a heavy hydrocarbon fractionator will produce copious amounts of vapor. The author is aware of one example where all the trays were blown out of a distillation column. If the bottom liquid level is allowed to reach the reboiler outlet line, the wave action can damage some bottom trays.

Whatever the cause of the tray damage, however, it is often hard to prove tray damage without column shutdown and inspection, especially if damage is slight. Besides poorer fractionation, a damaged tray section will experience a decrease in temperature difference because of the poorer fractionation. An increase in pressure difference may also result since the damage is often to downcomers or other liquid handling parts. However, a decrease in pressure difference could also occur.

### **Bottom Level**

Trays are particularly vulnerable to damage during shutdown and startup operations. Several good tips to minimize the possibility of tray damage during such periods are provided.

It is important to avoid high bottoms liquid level as mentioned previously. Initial design did not provide sufficient spacing above and below the reboiler return vapor line. A distance equal to at least tray spacing above the line to the bottom tray or better tray spacing plus, say, 12" and a distance of at least tray spacing below the line to the high liquid level is absolutely necessary. Probably more tray problems occur in this area of the column than any other. In spite of good initial design, however, the bottoms liquid level needs to be watched closely during startup.

If a tower does become flooded in the bottom section, a common operator error is to try to pump the level out too quickly. This can easily damage trays by imposing a downward acting differential pressure produced by a large weight of liquid on top of the tray and a vapor space immediately below the tray. To eliminate the flooding, it is better to lower feed rate and heat to the reboiler. It is important to be patient and avoid sudden change.

### **Steam/Water Operations**

Steam/water operations during shutdown have high potential for tray damage if not handled correctly. If a high level of water is built up in the tower and then quickly drained, as by pulling off a bottom manway, extensive tray damage can result, similar to pumping out hydrocarbons too fast during operation.

Steam and water added together to a tower can be a risky operation. If the water is added first at the top, for instance, and is raining down from the trays when steam is introduced, the steam can condense and impose a downward acting differential pressure. This can result in considerable damage. If steam and water must be added together,

start the steam first. Then *slowly* add water, not to the point of condensing all the steam. When finished, the water is removed first. One vendor estimates that he sees about six instances of tray failure per year resulting from mishandled steam/water operations.

### **Depressuring**

Depressuring a tower too fast can also damage the trays by putting excessive vapor flow through them. A bottom relief valve on a pressure tower would make matters worse since the vapor flow would be forced across the trays in the wrong direction. The equivalent for a vacuum tower would be a top vent valve which would suck in inert or air and again induce flow in the wrong direction. Such a top vent should not be designed too large.

## **4.4.4 Water in Hydrocarbon Column**

Here small amounts of water are meant rather than large slugs which could damage the trays. Often the water will boil overhead and be drawn off in the overhead accumulator bootleg (water drawoff pot). However, if the column top temperature is too low, the water is prevented from coming overhead. This plus too hot a bottom temperature for water to remain a liquid will trap and accumulate water within the column. The water can often make the tower appear to be in flood.

Many columns have water removal trays designed into the column. Top or bottom temperatures may have to be changed to expel the water if the column isn't provided with water removal trays. In some instances, the water can be expelled by venting the column through the safety relief system.

It should be remembered that water present in a hydrocarbon system, being immiscible, will add its full vapor pressure to that of the hydrocarbons. The operator wondered why the pressure was so high on a certain overhead accumulator until he noticed the installed bootleg.

A small steady supply of water entering a column through solubility or entrainment can, in some cases, cause severe cycling at constant intervals during which time the water is expelled. After expulsion of water, the column lines out until enough is built up for another cycle.

## **4.4.5 Foaming**

The mechanism of foaming is little understood. During the design phase, foaming is provided for in both the tray downcomer and active areas. "System factors" are applied that derate the trays for foaming. Oil absorbers are listed as moderate foamers. Heavy oil mixed with light gases often tends

to foam. The higher the pressure, the more foaming tendency, since the heavy oil will contain more dissolved gases at higher pressures. Liquids with low surface tension foam easily. Also, suspended solids will stabilize foam. Foaming is often not a problem when a stabilizer is not present.

No laboratory test has been developed to adequately predict foaming. Oil that doesn't foam in the laboratory or at low column pressure might well foam heavily at high column pressure. In general, aside from adding antifoam, there seems to be no better solution to foaming than providing adequate tray spacing, and column downcomer area. One designer solved a downcomer foaming problem by filling the downcomer with Raschig rings to provide coalescing area.

For troubleshooting suspected foam problems, vaporize samples of feed and bottoms to look for suspended solids. Also, one can look for the Tyndall effect as described in the section on condenser fogging.

#### **4.4.6 Condenser Fogging**

Fogging occurs in a condenser when the mass transfer doesn't keep up with the heat transfer. The design must provide sufficient time for the mass transfer to occur. A higher temperature differential ( $\Delta T$ ) with noncondensibles present or a wide range of molecular weights can produce a fog. The high  $\Delta T$  gives a high driving force for heat transfer. The driving force for mass transfer, however, is limited to the concentration driving force ( $\Delta Y$ ) between the composition of the condensable component in the gas phase and the composition in equilibrium with the liquid at the tube wall temperature. The mass transfer driving force ( $\Delta Y$ ) thus has a limit. The  $\Delta T$  driving force can, under certain conditions, increase to the point where heat transfer completely outstrips mass transfer, which produces fogging.

##### **Nature of a Fog**

Fog, like smoke, is a colloid. Once a fog is formed, it is very difficult to knock down. It will go right through packed columns, mist eliminators, or other such devices. Special devices are required to overcome a fog, such as an electric precipitator with charged plates. This can overcome the zeta potential of the charged particles and make them coalesce.

A colloid fog will scatter a beam of light. This is called the "Tyndall Effect" and can be used as a troubleshooting tool.

# **CHAPTER 5**

# **RECOVERY OF LPG**

## **Chapter 5 Contents**

### **5.1 RECOVERY OF LPG FROM NATURAL GAS LIQUIDS**

- 5.1.1 Purposes of Natural Gas Plants
- 5.1.2 Gas Plant Operations and Processes

### **5.2 RECOVERY OF LPG FROM CRUDE OIL**

### **5.3 RECOVERY OF LPG FROM REFINERY CONVERSION PROCESSES**

- 5.3.1 Catalytic Reforming
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## CHAPTER 5

# Recovery of LPG

## 5.1 RECOVERY OF LPG FROM NATURAL GAS LIQUIDS

### 5.1.1 Purposes of Natural Gas Plants

Natural gas plants are expected to meet the requirements of rigid regulations of the applicable authorities and to meet quality specifications imposed by end users.

The main functions of gas plants may be summarized as follows:

1. To receive the raw natural gas withdrawn from underground geological reservoirs and remove all the impurities which are objectionable to the pipeline transmission companies.
2. To deliver the gas at a specified pressure. Since gas plant process may result in gas pressure reduction, the plants must be capable of repressuring the gas for transmission purposes. Increased gas pressures may be also required for gas cycling, pressure maintenance of reservoir or gas lift work. Pipeline gas pressure is usually around 1,100 psi.
3. Depending on the nature and constituents of the raw gas, to separate and remove certain by-products such as ethane, propane/butane mixture (LPG), condensate, Sulphur, helium and / or others.
4. To conserve hydrocarbons. This may be regarded as one of the gas plant main concerns as gas wastage must be restricted to a minimum.

### 5.1.2 Gas Plant Operations and Processes

The gas processing companies in their modern gas plants are using some of the most novel processes to produce marketable gas. These Processes may include the removal of the water vapour from the raw gas, extraction of the acid and other non-combustible gases, separation and recovery of the liquid hydrocarbons, removal of Sulphurous compounds and other operations.

Gas plant processes may be summarized as follows, using Figure 1.1 as a pictorial guide.

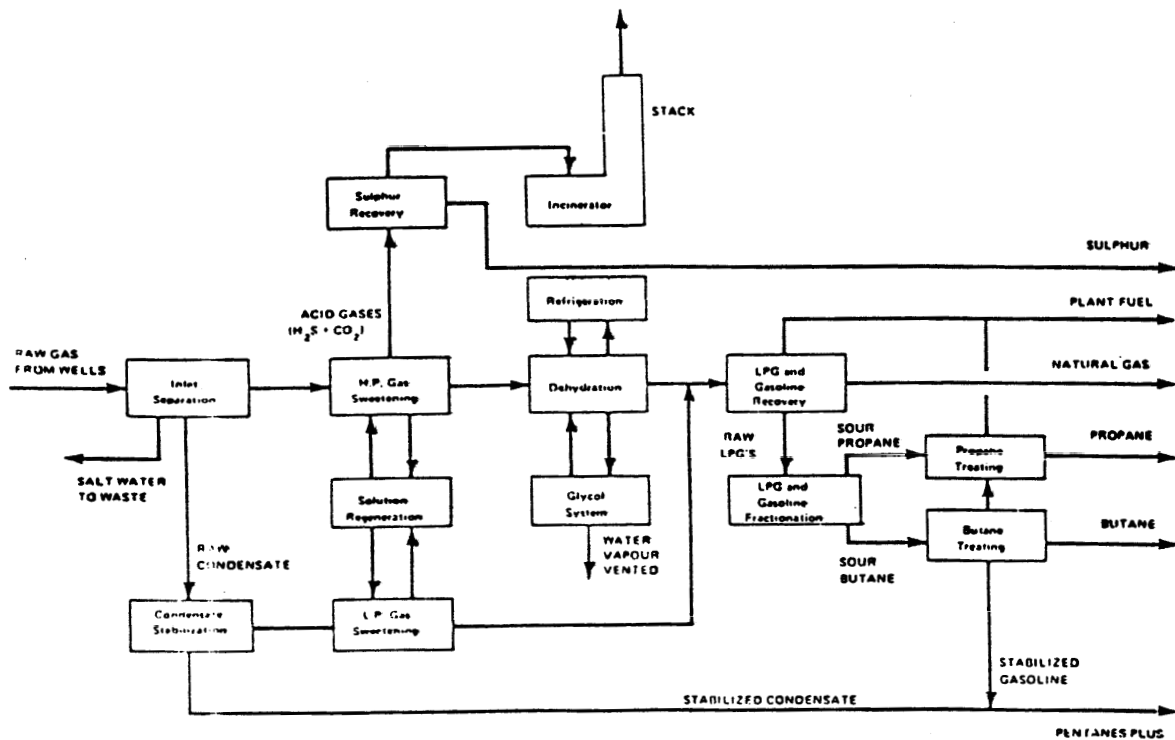


Figure 1.1 Block Diagram of Gas Processing Plant

### Inlet Separation:

The first step in processing the feed gas after entering the plant is the separation of its liquid components. Certain other impurities, such as salt water, silt, sand etc., are also removed in this section.

The equipment items, employed in this stage are separators. They may be of vertical or horizontal design and sized sufficiently to allow the free condensate and salt water to separate from the gas phase.

### Gas Sweetening:

Next, the gas is directed to the sweetening section which removes the sour and other undesirable gases from the feed gas stream. These gases may include hydrogen sulphide (H<sub>2</sub>S), carbon dioxide (CO<sub>2</sub>), and mercaptans (RSH). The extracted “acid gases”, as they are commonly called, are used as feed stock in the Sulphur plant, where most are converted to elemental Sulphur.

If the  $H_2S$  content of gas fields is high enough to warrant the installation of Sulphur facilities. However, if it is low enough and economics so not favor its conversion to Sulphur, it may be burned in specially designed incinerators or flare stacks to Sulphur dioxide and disposed to the atmosphere together with the carbon dioxide.

Various types of sweetening processes are employed today by the industry most of which involve the absorption of the acid gases from the sour gas using a circulating, scrubbing solution. A large number of solutions are available on the market, each one being adaptable to a specific type of sour gas.

The most widely used solvents are the Ethanolamine, (Monoethanolamine and Diethanolamine) and sulphinol.

After scrubbing the gas in the absorption towers the rich solution is directed to the regeneration section where the acid gases are released with the assistance of heat at low pressure. The regenerated scrubbing solution is then recirculated to the scrubbing contactor for removal of more acid gases from the sour feed gas.

#### **Dehydration:**

Dehydration of the gas follows the sweetening process to reduce the water content to the level permitted by the transmission line contract. Most of the water vapours, absorbed into the gas during its direct contact with the sweetening agents, must be removed here to eliminate a potential source of trouble in high pressure pipelines.

In some plants, and depending on the type of process used, the sales gas water content is specifically controlled in this stage. Other plants using more processing facilities downstream can reduce the water vapour content in the gas as specified.

The predominant type of dehydration processes is Glycol Process. This is used in plants where the water vapour content is high. The wet gas is contacted with a glycol solution of specified strength in the absorption towers to absorb the water content on a continuous basis. The rich glycol solution then flows to the glycol regenerator where its water content is released by heating.

Another method of gas dehydration consists of directing the wet gas through a bed of solid desiccants. The desiccants may be one or more of several varieties and have the property of absorbing the water present in the wet gas. Silica gel particles or some variation of this substance are well known for their drying ability.

Small gas plants with no other LPG and gasoline facilities may employ dry desiccants designed to extract the water from the gas stream and remove all the gasoline constituents as well.

**Refrigeration:**

In this method the gas stream is chilled by means of refrigeration to condense the water vapour and the heavier hydrocarbon vapours, such as propane, butane and pentane. To prevent the water vapour from freezing upon condensation the gas is sprayed with glycol at points ahead of the chillers. Separation equipment then removes the gasoline from the water – glycol mixture.

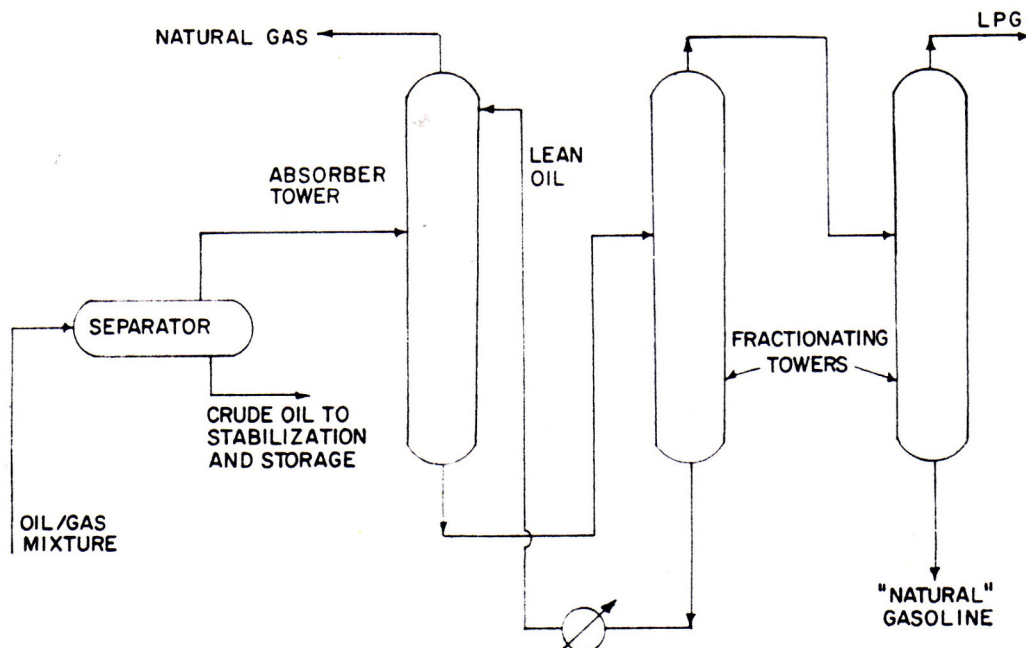
The rich glycol is sent to the glycol regeneration facilities to drive the absorbed water out by heating. The regenerated glycol is then available for removal of more water present in the gas. The gasoline constituents, removed from the refrigeration systems, are further processed downstream.

Refrigeration, generally, is favored in modern gas plants as being the best single step for preparing the gas stream for LPG recovery and removal of a large portion of gasoline constituents.

**Recovery of LPG and Gasoline:**

This is a section installed in major gas plants to scrub the chilled gas stream with low molecular weight absorption oil and remove liquefiable hydrocarbons and gasoline constituents. The basic processing scheme is to direct the pre-chilled gas to the bottom of an absorbing tower and to bring it in direct contact with pre-chilled lean absorption oil. Raw LPG products and gasoline are recovered using a re-absorber, rich oil de-etherizer and a rich oil fractionator.

The absorbed hydrocarbons are stripped from the rich oil by heating in a dry stripper called a rich oil fractionator. The warm lean oil is pumped back to the absorption towers for further scrubbing duties while the raw liquid hydrocarbons are sent to the fractionation process to become finished products.



**Figure 5.2 Recovery of LPG from Natural Gas  
(Simplified flow diagram)**

### **Condensate Stabilization:**

The condensate Stabilization process is a step designed to eliminate all possible vapour hydrocarbons and toxic gases contained in the raw condensate that was separated in the inlet separation facilities of the plant. The stabilizer operates at lower pressure than its source of feed to flush off its light vapours, (Methane and Ethane), hydrogen sulphide and other non-combustible gases and recycle them into the same gas stream for further processing. The stabilized condensate is withdrawn and pumped to the storage tanks or to sales.

Nearly all gas plants, small or large, are equipped with condensate stabilization facilities to stabilize the condensate which is always present in the wet gas.

### **LPG and Gasoline Fractionation:**

LPG and gasoline fractionation facilities are installed, in conjunction with the LPG and gasoline recovery equipment, to fractionate the hydrocarbon mixture into the respective products of Propane, Butane and Gasoline.

The fractionation process involves a De-propanizing section, which separates and removes the propane from the mixture, and a De-butanizing stage, which removes butane from the gasoline. The gasoline is withdrawn from the bottom of the De-butanizer tower and sent to storage or sales after blending it with the stabilized condensate. The separated Propane and Butane products are subjected to further treating for removal of certain undesirable components, such as hydrogen sulphide, mercaptans and water. The distillation processes in the De-propanizer towers are accomplished through temperature and pressure gradients established and maintained across the towers. Close control of the temperature and pressure conditions is required to produce finished products of definite vapour pressures.

### **LPG Product- Treating:**

Propane and Butane are subjected to further purification treatments to eliminate the residual hydrogen sulphide and other Sulphurous contaminants that have escaped from the earlier gas sweetening process and were carried through the rest of the plant. Further thermo pipeline specifications may impose certain penalties on the producer delivering off-specification LPG products.

Propane treating is usually accomplished by passing the product through a mole sieve bed. Mole sieve is a substance that has a great affinity for hydrogen sulphide, mercaptans, water and other polar compounds. These impurities are adhered to and sustained on the mole sieve surfaces until regeneration with hot fuel gas is carried out. Clean Propane is next withdrawn from the bottom of the mole sieve and pumped to storage or sales.

Mole sieve beds apply similarly to treating Butane products but Caustic wash systems may be more efficient and effective.

## 5.2 RECOVERY OF LPG FROM CRUDE OIL

The crude tower is one of the most complex distillation units in the refinery. A schematic drawing of an actual crude tower is shown in Figure 5.3. It shows the process flow of feed and products along with the design temperatures. The tower is about 150 feet (45.7 meter) high and 27 feet (8.23 meter) in diameter.

Crude is pumped (Figure 5.4) from tankage through heat exchanges and a crude heater where an oil temperature of approximately 670°F is reached. The crude enters the tower just above the bottom where a high percentage is vaporized. The vapor starts up the tower, contacting liquid (or reflux) flowing down the tower. At each tray the downcoming liquid condenses the heavier components in the rising vapor. The hot vapor provides the heat to vaporize the lighter components in the liquid. Several trays up in the tower a special tray is located which provides for the removal of a portion of the liquid from that location in the tower.

The same arrangement is made at six more locations up the tower. Four of these side draws are for the removal of products. Three are for the removal of heat. This liquid is cooled and returned to the tower. At the top of the tower, vapor is removed by means of the overhead line.

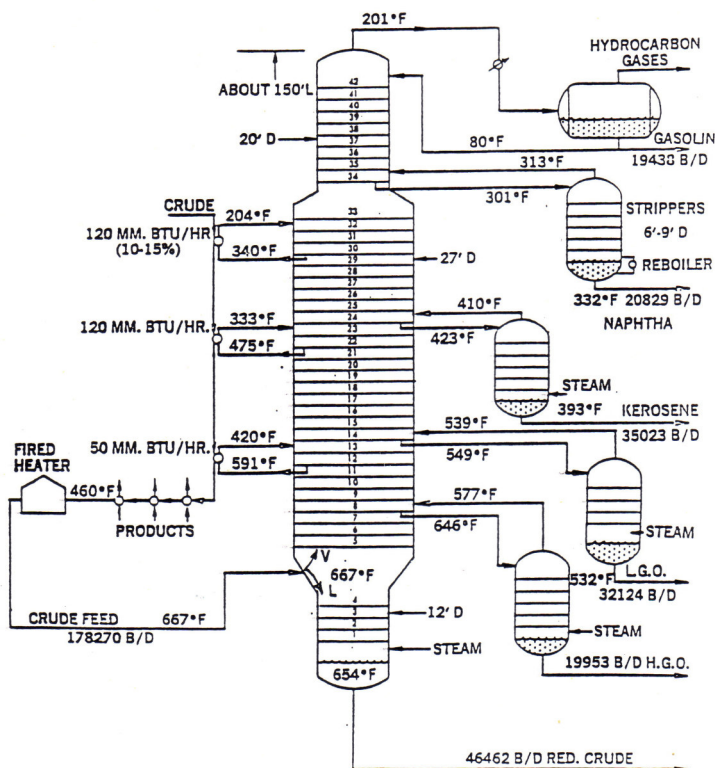


Figure 5.3 Crude Tower

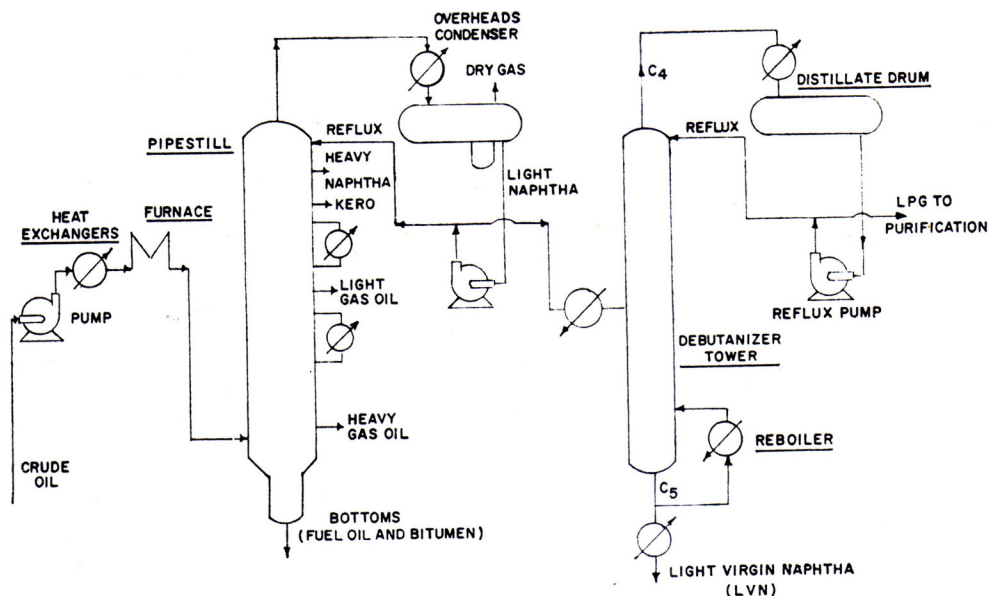


Starting at the top we will trace the design and operating concepts of the tower. The upper section of the tower is designed with the appropriate number of trays to separate the light naphtha (or gasoline) and lighter components from the heavier components in the crude. Vapor is removed, partially condensed, and a portion of the condensed liquid is pumped away as light straight run gasoline. It will be charged to the reformer to raise its octane. The remainder of the condensed liquid is pumped back to the column as reflux.

The temperature at the top is the major factor in determining the highest boiling components in the vapor. In other words, at the pressure and temperature in the top of the column only the lighter materials will be at or above their boiling points and will be in the vapor state. Heavier materials will be liquid. If the concentration of heavy material is too high, more reflux is returned to the column to cool it, and less product is withdrawn. As the top of the column cools, less heavy material will go overhead as vapor and will remain as liquid internal reflux.

Conversely, if the light gasoline is too light, we reduce the reflux and draw more products. The top becomes hotter, allowing heavier components to go overhead as vapor. Composition of the top product in a crude tower is usually controlled by top temperature, which is controlled by varying the reflux rate.

In addition to overhead and bottom products, three other fractions are drawn from the side of the tower. Each of these fractions passes through a stripping column that uses steam to remove light components. Vapors from the stripping columns are reintroduced to the tower at a point above the draw-off tray.



**Figure 5.4 Recovery of LPG from Crude Oil**

## 5.3 RECOVERY OF LPG FROM REFINERY CONVERSION PROCESSES

These are listed in Table 5.1 and it will be noted that they yield by-product LPG in varying quantities.

<i>Process</i>	<i>Feed</i>	<i>Prime product</i>	<i>Yield of LPG (wt % on feed)</i>
Catalytic reforming	Light virgin naphtha	Aromatics, gasoline blendstock	5–10
Catalytic cracking	Gas oil	Ethylene, propylene (for petrochemicals)	15–20
Steam cracking	Gas oil or naphtha	Ethylene, propylene	23–30
Polymerization/ alkylation	Butane-unsaturated gases	Gasoline	10–15
Thermal cracking	Gas oil, fuel oil	Gasoline	10–20
Coking/vis-breaking	Heavy gas oil, residuum	Coke	5–10

**Table 5.1 Refinery Conversion Processes**

Most oil refineries operate only one or two of the above processes and, depending on whether catalytic and steam cracking form part of the overall processing scheme, yields of LPG from an oil refinery will vary within a fairly wide range.

### 5.3.1 Catalytic Reforming

Perhaps the commonest conversion process-source of LPG is catalytic reforming. The real object of the process is to produce  $C_6/C_7$  aromatics either as chemical intermediates or more often, as a gasoline blendstock. The feedstock is virgin naphtha obtained from the crude oil fractionating tower or specially purchased for the purpose (imports). The scheme of operations is shown in Figure 5.5.

The fixed bed 'reforming' process is one of converting paraffinic and naphthenic hydrocarbons present in the naphtha to aromatics by cyclization and dehydrogenation reactions occurring simultaneously.



A refinery which includes only atmospheric distillation (no vacuum step) and catalytic reforming (no cracking reactors) among its main processing features is often called a 'hydroskimming' refinery. In this, the twin tributary LPG streams from the distillation and reforming units, suitably purified, join for separation into propane and butane products in the depropanizer tower.

### **5.3.2 Catalytic Cracking**

'Cat crackers' are installed along with catalytic reformers at so called 'integrated' oil refineries for the purpose of cutting down on the production of middle distillates and producing motor gasoline and unsaturated gases which serve as intermediates for further chemical processing. The feedstock is usually heavy gas oil, even wax, which is cracked at high temperature in the presence of a silica-aluminate catalyst. Many large, modern 'cat crackers' are based on the 'fluid catalytic' principle in which case, the feedstock and fresh make-up catalyst are fed continuously to the reactor tower from which, at the same time, catalyst is being withdrawn to a vessel regeneration for reactivation by hot-air treatment. The entire effluent from the reaction vessel is fractionated in a primary separator into so-called 'light ends', middle distillate and heavy fractions. LPG, together with methane, ethane and catalytically cracked gasoline are taken off as an overhead stream and separated in an absorption tower by means of light absorbing oil into a noncondensable gas stream (methane, ethylene and ethane) and an absorbed fraction consisting of LPG and gasoline. The saturated absorbent, sometimes referred to as 'fat oil' is stripped of its light end content and the latter separated into a gasoline fraction and LPG overhead in a 'debutanizer' tower. The propylene and butene components are removed from the LPG stream by further fractionating or chemical means but, depending on the supply requirements of the separate petrochemicals business at a given time, both saturated and unsaturated C<sub>3</sub>/C<sub>4</sub> gases may find their way into the domestic or industrial LPG tankage.

The feedstock to the catalytic cracking plant is normally not sweetened prior to cracking, and therefore the LPG produced in this process contains mercaptans and other sulphur compounds, which have to be removed. 'Cat cracker' LPG is also passed sometimes to a 'polymer' plant in which the unsaturated components react over an acidic catalyst (phosphoric or hydrofluoric acid) to produce a 'polymer gasoline'. The unreacted tail gas, or excess feed gas previously sweetened by caustic washing, also contributes to refinery LPG production.

One variant of the fluid catalytic cracking process is known as 'hydrocracking', which can take naphtha, light or heavy gas oils as feedstock along with a hydrogen-rich diluent gas to suppress overcracking and polymerization side reactions.

Cracking processes yielding LPG as a by-product which are mainly noncatalytic in operation include steam cracking (naphtha or gas oil feedstock with steam), thermal cracking (naphtha feed), visbreaking, delayed coking and fluid coking, both being operated mainly for the production of petroleum coke.

The butane stream may also be passed to a superfractionating tower known as the 'de-isobutanizer' where it is split into separate isobutane (overheads) and n-butane (bottoms) products for use as pure chemical intermediates.

Although LPG production in catalytic reforming processes in the past has taken very much second place behind the need to produce aromatic gasoline components, this is no longer the case when using a recently developed catalyst which, it is claimed, is shape selective, and converts normal paraffins into propane and butane, whereas isoparaffins and aromatics remain unaffected. The Mobil Selectoforming process thus produces not only high octane motor spirit but, in addition, between 9 and 13% of LPG.

## **5.4 PURIFICATION OF LPG**

### **5.4.1 Sweetening**

The process is one of removing sulphur compounds from the sour streams contributing to LPG production. The object is to produce a non-corrosive, non-toxic gas which is acceptable to domestic and industrial markets. The impurities to be removed include hydrogen sulphide, methyl and ethyl mercaptans and, occasionally, elemental sulphur. The processes adopted at the present time, whether the LPG be natural gas or crude oil-derived, include the following:

H <sub>2</sub> S	: caustic soda wash
H <sub>2</sub> S and elemental sulphur	: mono- or di- or tri-ethanolamines extraction (Girbotol process)
Mercaptans	: caustic soda wash
	: "Merox" extraction
H <sub>2</sub> S/light mercaptans	: Absorption on 'molecular sieves'

**Caustic Wash**

The caustic solution (NaOH or KOH) reacts with the  $H_2S$  which is dissolved in the liquid LPG.  $H_2S$  is a weak acid, and its removal is nearly quantitative even in a single stage.

The extraction of mercaptans, however, is equilibrium-limited and is dependent on the strength of alkali used, the ratio of alkali to LPG, the operating temperature and pressure and the molecular weight of the mercaptans, etc. Twin towers may be used in series, the first to remove the bulk of the  $H_2S$  and the second to deal with the mercaptans. Commonly used is a 5-20% strength caustic solution. Spent caustic solution is not usually regenerated and its disposal often presents a problem to the oil refiner. Measures adopted to cut down on caustic consumption include partial recycle of spent solution to the wash tower and batch washing with intermittent replacement of caustic rather than a continuous countercurrent flow operation.

**Girbotol Process**

If a relatively large amount of  $H_2S$  is present in the sour LPG, it may conveniently and more economically be removed by extraction with monoethanolamine (MEA) or diethanolamine (DEA), which is regenerated by heating at  $95^\circ C$  in a separate vessel, followed by stream stripping and recycle to process. Extraction takes place at  $40-60^\circ C$  under vapour pressure in a packed tower, countercurrent fashion. This amine solution method avoids the use of aqueous alkali, effectively removes carbon dioxide and, if present, also removes elemental sulphur, but is not very effective in removing mercaptans. Hence, a refinery LPG sweetening package may be found to comprise an amine extraction tower followed by a caustic trimming washer and a 'Merox' unit (for mercaptans removal).

**Merox Extraction**

The Universal Oil Company's (UOP) Merox process is one of oxidation of the mercaptans with air and a relatively small amount of alkali in the presence of chelated iron compound catalysts. The mercaptans are converted to disulphides which are relatively odorless, non-corrosive compounds. A small amount may remain in the treated LPG but the bulk is transferred with the caustic to a regenerator where sulphur compounds are stripped by hot-air treatment and the alkali returned to process along with some make-up solution.

**Molecular Sieve Adsorption**

The use of a dry 'molecular sieve' process obviates the caustic disposal or recovery problems.

Molecular sieves are synthetic metal aluminosilicates having a three-dimensional pore structure and a one to three micron particle diameter. They are manufactured as pellets sized 1/16 in or 1/8 in for easy handling and use. The size and position of the metal ions in the crystal control the effective diameter of the interconnecting channels. The 13X (Linde) or 10A (Grace) types which are used in many LPG sweetening plants will absorb molecules with critical diameters of up to 10 Angstrom units (10 Å). H<sub>2</sub>S and mercaptans, and LPG hydrocarbons themselves all fall into this category. The separation of the sulphur compounds depends therefore on selective adsorption due to the higher polarity of these compounds rather than on conventional molecular sieve action. The adsorptive capacity of H<sub>2</sub>S is about 1% by weight and for the lower mercaptans, 0.5%. Higher sulphides and disulphides are not removed.

The plant consists of twin towers alternating the processes of adsorption and bed regeneration. The cycle might be, typically, 8 hr service at 30°C followed by 8 hr regeneration (using sweet product gas or refinery gas, or nitrogen, heated to 260°C) and 8 hr cooling to adsorption temperature. Sour regeneration gas is flared.

LPG sweetened by molecular sieves will at the same time be dried by the same process of adsorption. The preferred feedstock is an LPG stream containing saturated hydrocarbons, the H<sub>2</sub>S and a relatively small amount of mercaptans. Typically, a regenerative unit might be sized for 40 gal/min throughput with a product specification of 1-2 ppm H<sub>2</sub>S or mercaptans and 10 ppm maximum outlet water concentration.

**5.4.2 Drying**

The object is to produce LPG which do not deposit the dissolved water left over from an aqueous sweetening process on liquid temperature reduction or vapour expansion. Not all LPG need to be dried but those marketed in cold climates, propane grades in particular, invariably are. The process is one of percolating the liquid LPG through solid absorbents for water. The cheapest is often found to be a once-through system using calcium chloride. Other absorbents in common use on a regenerative basis in refineries at the present time are alumina, silica gel or 4A molecular sieves. In all such absorption processes, the packed towers are protected from slop water carry over by upstream separator-cum-coalescer drums.

Refinery LPG which is stored at atmospheric pressure, as distinct from at its saturated vapour pressure, has to be refrigerated to near its true boiling point. For this purpose, the LPG needs to be dried by an absorption process.

### **Drying with Calcium Chloride**

The liquid LPG to be dried passes into one of two drying towers connected in series. Initially, dissolved water is removed in the first tower and the second has no effect. As the desiccant in the first tower is used up, dissolving to form heavy brine containing about 25% calcium chloride, the second tower takes over. At this point, the first tower is recharged with fresh calcium chloride containing about 72% calcium chloride, and the flows are reversed. The brine formed during operation is normally drained off once per eight-hour shift.

The amount of calcium chloride required can be calculated from the original and final water concentrations in the LPG, the water content of the saturated absorbent and a predetermined bed life, say six months. On the basis of reducing an inlet water concentration of 300 ppm weight in propane at 100°F to 20 ppm outlet water concentration, the weight of water to be removed is 0.5 lb (0.25 kg) approximately per ton of LPG. Taking the calcium chloride content of fresh and spent calcium chloride as 72 and 25%, respectively, the consumption of drying agent works out at one pound per pound of water, i.e. 0.5 lb/tonne of propane (45 lb/1000 barrels).

### **Regenerative Drying**

The twin tower principle is employed with the service tower on drying duty for, say, 24 hr and the other engaged for a similar time on regeneration and cooling. During regeneration, hot purge gas (which can be vaporized LPG) removes liquid LPG and water from the spent service tower. The effluent is cooled and the LPG separated and re-used. Alternatively, one or more service towers are fitted with internal steam coils which are brought on during regeneration after the liquid LPG has been removed by pressure reduction, this being usually achieved by means of a steam ejector.



**Chapter 6**  
**COMPOSITION AND**  
**CHEMICAL PROPERTIES**

## **Chapter 6 Contents**

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## Chapter 6

## Composition and Chemical Properties

### 6.1 INTRODUCTION

In this chapter, we discuss chemical composition of LPG in terms of major and trace components, and chemical properties from the standpoint of the more important chemical reactions which the main components are known to undergo.

The main components are hydrocarbons which impart to LPG its physical characteristics (vapour pressure, dew point, etc., see Chapter 7). The trace components are the remnants of sulphur compounds, etc., which though seldom present in amounts greater than a few parts per million can cause certain application problems if their nature is not properly understood.

A review of the chemical reactions undergone by LPG is tantamount to a study of the processes which support the vast petrochemical industry. Our aim is to indicate the key reactions of the  $C_3$  and  $C_4$  hydrocarbons only. The hydrocarbons included are propane, n-butane, isobutane, propylene and the butenes. Though some may regard the unsaturated hydrocarbons solely as feedstocks for the chemical industry, they are included here because (as we have shown) they can feature in sizeable proportions in LPG sold to the domestic and industrial markets.

### 6.2 MAIN COMPONENTS

As discussed in Chapter 5, LPG can derive from the condensate fraction of natural gas wells or from the light end fractions of crude oil. LPG is recovered at crude oil refineries in almost every country of the world. Not every natural gas-producing centre, however, gives rise to a recoverable amount of LPG.

Both types of LPG are similar in one respect. The bulk consists of hydrocarbons containing three or four carbon atoms per molecule, respectively. However, in detail of hydrocarbon type as well as trace impurities present, LPG derived from natural gas can differ from its refinery counterpart.

LPG as marketed in most countries rarely consists of pure propane or butane. Rather is LPG, whether of refinery or natural gas origin, a mixture of liquefied or liquefiable saturated and unsaturated hydrocarbons in the  $C_3$  and  $C_4$  boiling range. Commercially, LPG is sold to domestic and industrial customers in four grades:

- As LPG propane when it consists mainly of propane and/or propylene.
- As LPG butane when it consists mainly of n-butane, isobutane and/or the butylenes.
- As LPG mixture when it consists of a variable amount of all the C<sub>3</sub>/C<sub>4</sub> hydrocarbons previously mentioned.
- As high purity propane containing about 95 % of this single hydrocarbon.

<i>LPG propane, mol %</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>G</i>
Methane	0.05	—	—	—
Ethane	2.8	1.0	1.9	0.9
Ethylene	—	—	—	—
Propane	87.0	98.6	61.1	33.8
Propylene	9.0	—	36.3	64.0
<i>n</i> -Butane	0.1	0.1	0.1	0.2
Isobutane	1.0	0.3	0.4	0.9
Isobutene/butene-1	—	—	0.1	0.2
<i>trans</i> Butene-2	—	—	—	—
<i>cis</i> Butene-2	—	—	—	—
Pentanes and higher	—	—	—	—

<i>LPG butane, mol %</i>	<i>D</i>	<i>E</i>	<i>F</i>
Methane	—	—	—
Ethane	—	—	0.3
Ethylene	—	—	—
Propane	2.5	2.1	26.1
Propylene	—	0.1	10.4
<i>n</i> -butane	66.8	39.6	52.2
Isobutane	29.7	37.2	10.2
Isobutene/butene-1	0.2	14.4	0.5
<i>trans</i> Butene-2	—	5.7	—
<i>cis</i> Butene-2	0.1	0.4	0.2
Isopentane	0.5	0.05	0.1
<i>n</i> -Pentane	0.2	0.25	—
Hexanes	—	0.2	—

A Belgian refinery	B German refinery	C French refinery
D German refinery	E French refinery	F Italy, trade
G Sweden, trade		

**Table 6.1 Main Components Present in Refinery LPG**

The distribution of main components which can occur in refinery LPG is illustrated by the analyses of samples of European origin shown in Table 6.1.

The examples represent one refinery or trade depot in each of the countries mentioned. In the propane series, a spread is seen from 98.6% propane, nil propylene to 64% propylene, 34% propane. In the butane series, the saturated C<sub>4</sub>'s range from 96.5% with only 0.3% C<sub>4</sub> unsaturates through 77% butanes with 20.5% butylenes to 62.4% butanes with only 0.7% butylenes but 10% propylene and 26% propane.

The chemical formula, molecular weight and boiling point of these main component gases are noted in Table 6.2 together with similar data for certain trace contaminants which can occur in LPG.

<i>Component</i>	<i>Chemical formula</i>	<i>mol wt</i>	<i>B.P. °C 14.7 lb/in<sup>2</sup> abs.</i>
Ethane	C <sub>2</sub> H <sub>6</sub>	30.06	-88.6
Ethylene	C <sub>2</sub> H <sub>4</sub>	28.05	-103.7
Propane	C <sub>3</sub> H <sub>8</sub>	44.09	-42.1
Propylene	C <sub>3</sub> H <sub>6</sub>	42.08	-47.7
n-Butane	C <sub>4</sub> H <sub>10</sub>	58.12	-0.5
Isobutane	C <sub>4</sub> H <sub>10</sub>	58.12	-11.7
n-Butene(-1)	C <sub>4</sub> H <sub>8</sub>	56.10	-6.47
Isobutene	C <sub>4</sub> H <sub>8</sub>	56.10	-6.9
trans Butene-2	C <sub>4</sub> H <sub>8</sub>	56.10	0.9
cis Butene-2	C <sub>4</sub> H <sub>8</sub>	56.10	3.7
n-Pentane	C <sub>5</sub> H <sub>12</sub>	72.15	36.1
Iso Pentane	C <sub>5</sub> H <sub>12</sub>	72.15	27.9
TRACE CONTAMINANTS			
n-Hexane	C <sub>6</sub> H <sub>14</sub>	86.17	69.0
Iso Hexane	C <sub>6</sub> H <sub>14</sub>	86.17	60.2
Hydrogen sulphide	H <sub>2</sub> S	34.08	-60.7
Methyl mercaptan	CH <sub>3</sub> SH	48.11	5.8
Ethyl mercaptan	C <sub>2</sub> H <sub>5</sub> SH	62.13	36.7
Dimethyl sulphide	(CH <sub>3</sub> ) <sub>2</sub> S	62.0	37.3
Elemental sulphur	S	32	444.4
Dimethyl disulphide	CH <sub>3</sub> -S-S-CH <sub>3</sub>	94	117
Carbonyl sulphide	COS	60	-47.5 (50.2)

**Table 6.2 Nature of Main and Trace Components found in LPG**

## 6.3 TRACE COMPONENTS IN LPG'S AND THEIR ORIGIN

These compounds may be present in the parent natural gas or crude oil and survive the most efficient purification processes which can be economically justified at the present time. They may also be introduced after the LPG has left the manufacturing point, i.e. by contamination during transportation to the user. This group of compounds includes not only hydrocarbons, sulphur compounds and elemental sulphur (see Table 6.2), but also involatile oils and polymeric residues, water, halogens, ammonia and other minor contaminants.

### 6.3.1 Hydrocarbon Impurities

Those that may not be completely removed by the 'topping' and 'tailing' processes employed during fractionation include:

- $C_2^-$  ; ethane, ethylene
- $C_5S'^{+}$  ; n-pentane, isopentane, pentenes and hexanes
- $C_3H_4$  ; propadiene, methyl acetylene

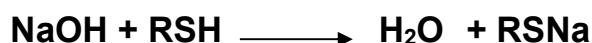
### 6.3.2 Sulphur Compounds

#### $H_2S$

This impurity is often present in raw natural gas or crude oil LPG. At refineries, it can also be introduced into the light end processing streams by hydrogenation of the naturally occurring sulphur compounds during the sweetening process. The bulk of it is removed by caustic wash, amine scrub or molecular sieve percolation but traces can remain.

#### *Mercaptans (RSH)*

The lightest members of these series, methyl and ethyl mercaptans are present both in natural gases and in crude oil. In refinery processing in particular, they may survive the hydrofining step and not be completely removed by caustic wash. This reaction is equilibrium-limited and the proportion solubilized by the reaction depends on the temperature, alkali treat rate, alkali concentration, proportion of spent alkali and the molecular weight of the mercaptans.



#### *Disulphides*

Disulphides may be formed during caustic sweetening by the action of dissolved air on the mercaptans present. Another source of sulphur impurity is the stenching agent added in particular to house-hold LPG to impart an unmistakable smell. The amount added is about 35 ppm by weight of the LPG. Odorants used for LPG include ethyl mercaptan, which may also be present naturally, dimethyl sulphide and tetrahydrothiophene (THT). Stenching agent may be omitted from LPG used for industrial applications.

**Carbonyl Sulphide (COS)**

One way in which this compound is formed is the reaction between carbon dioxide and hydrogen sulphide.



Thus it is conceivable that it can occur in LPG if  $\text{CO}_2$  containing flue gases are contacted with  $\text{H}_2\text{S}$ -rich refinery gases from which LPG is subsequently recovered.

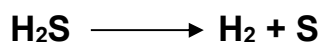
Carbonyl sulphide dissolves relatively slowly in caustic soda; hence it may pass through the product sweetening tower which is designed to remove  $\text{H}_2\text{S}$ . It then concentrates in the propane stream on account of its very low boiling point ( $-50^\circ\text{C}$ ).

**Elemental Sulphur**

Apart from the disulphides, the sulphur compounds already mentioned are termed volatile in the sense that they volatilize from the liquid phase under conditions of natural vaporization. In addition, involatile forms of sulphur are formed, i.e. those which deposit from the liquid when this is volatilized.

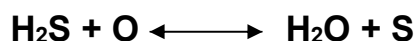
Among the possible ways in which elemental sulphur can be formed are the following.

(a) Thermal decomposition or pyrolysis of  $\text{H}_2\text{S}$



This reaction does not progress at temperatures below  $300^\circ\text{C}$  but proceeds rapidly at  $500^\circ\text{C}$  and above. The reaction could occur in refinery pipestill furnaces but not during subsequent distillation and processing where line temperatures are usually below  $300^\circ$ . Presumably it also occurs at below ground temperatures in natural gas wells, for  $\text{H}_2\text{S}$  is the common sulphurous contaminant in these gases and elemental sulphur often is an accompanying impurity which has to be removed at the well head.

(b) Reaction of  $\text{H}_2\text{S}$  with limited amounts of oxygen\*



\* The reaction is the basis of the well-known Claus process for producing sulphur by burning hydrogen sulphide with the stoichiometric proportion of air.

In homogeneous phase, this reaction proceeds at temperatures above about 500°C but it can be aided by the action of catalytic (metallic) surfaces at lower temperatures. The reaction could occur during caustic sweetening of refinery LPG by the action of oxygen dissolved in the alkali. Oxygen may also derive from the crude oil and be carried through the LPG system or, more likely, from limited air ingress. In product tankage, the reaction may be aided by the presence of bacteria particularly of the chlamydobacteriales family.

In natural gas, some air may find its way into reservoirs and tapping facilities. This may react with the hydrogen sulphide which is also present forming sulphur in the manner suggested.

If elemental sulphur is formed in natural gas, it may be removed in the amine scrubbing step prior to LPG removal. At those refineries which employ only a caustic sweetening step, the sulphur (being insoluble in alkali) is carried through. However, at some refineries, an amine scrub process is also applied ahead of the caustic sweetener. The object is to remove the bulk of the H<sub>2</sub>S and reduce the alkali consumption, but any elemental sulphur present is solubilized at the same time. Refineries which adopt the combined amine-caustic wash process seem to have less problems with elemental sulphur in product LPG than those which employ only the caustic step.

Despite modern refining methods and many precautions, elemental sulphur is a possible contaminant of LPG which often occurs at the production point and at customers' premises. Table 6.3 shows some examples of the distribution of sulphur compounds.

	H <sub>2</sub> S	Sulphur compounds	Elemental sulphur
<i>Refinery samples</i>			
1. Propane	<1	0.4	<1
2. Propane	<1	1.7	30.0
3. Butane	<1	5.0	<1
4. Butane	<1	20.0	127.0
<i>Trade samples</i>			
5. Propane	<1	6.0	<1
6. Propane	<1	18.0	25.0
7. Butane	<1	15.0	<1
8. Butane	<1	115.0	165.0

**Table 6.3 Distribution of Sulphur Compounds in LPG (ppm wt)**

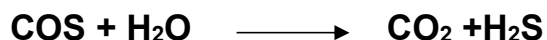


### 6.3.3 Sulphur Compounds and the Causes of Corrosivity

Sometimes, LPG is found to be corrosive towards copper or other metals. The causes of corrosiveness are not fully understood, but one is certainly the presence of traces of H<sub>2</sub>S which, at a level of about 3 ppm by weight, can begin to corrode copper.

Other agents thought to be active in this respect include volatile sulphur compounds and elemental sulphur. In some recent studies, elemental sulphur was confirmed as being corrosive at levels of 5 ppm and above but most organic sulphur compounds in contrast were found to be non-corrosive. Very small quantities of mineral acids or alkalis also do not impart corrosiveness.

Carbonyl sulphide must also be mentioned as a possible cause of corrosion particularly in propanes (see sub-section 6.2.3). This compound slowly hydrolyses with water to form CO<sub>2</sub> and H<sub>2</sub>S which is the active corrosion.



### 6.3.4 Lubricating Oil in Refinery LPG

Although many gas compressors and liquid transfer pumps in present-day use are of the non-lubricated type, some of the integral crankcase type of compressors in particular (e.g. those used aboard ship for assisting in butane unloading operations) can leak lubricating oil into the LPG. LPG flowing through a greased valve or swing joint will inevitably pick up some oil. Thus an LPG, though virtually free from oil in refinery storage, can be appreciably contaminated with lubricating oil after it has passed through a series of transfer operations into a customer's tank.

Another instance of lube oil contamination came to light in the course of an investigation into sea shipments of butane. At the refinery end, the residue content of the butane was virtually nil. After transfer to the customer's tank by sea, the butane contained 120 ppm by weight of lube oil. Using thin layer chromatographic analysis and infra-red spectroscopy, this oil was found to contain the same zinc additive as did the ship's compressor oil.

### 6.3.5 Water in LPG

Water is a likely contaminant both of natural gas and crude oil derived LPG. In the former, the water is present naturally, and in refinery LPG caustic washing in particular ensures water saturation of the hydrocarbon phase. If the LPG is to be stored in refrigerated conditions, i.e. at low temperatures and only slightly above atmospheric pressure, much of the native water will have to be removed by percolation through a bed of alumina immediately ahead of the storage vessel. Even for pressure storage, i.e. at ambient temperatures and superatmospheric pressure, some refineries produce a dry LPG (below 10 ppm weight of water) by filtration of product streams through beds of molecular sieve (zeolites), alumina or calcium chloride. Other refineries do not chemically dry their LPG.

The exact amount of water dissolved in an LPG depends on its composition, the temperature and whether the liquid or vapour state is considered.

It is seen from Table 6.4 that solubility increases markedly with temperature in both liquid and vapour phases. Regarding the effect of hydrocarbon type, the solubility of water in liquid butane is less than in propane. The solubility in isobutane, however, is appreciably greater than in n-butane and about equals that in propane at matching temperatures. The solubility of water in liquid commercial butane (mixture of n-and iso- isomers) is about 190 ppm by weight at 60°F compared with 280 ppm in propane at the same temperature.

	<i>ppm by weight</i>	
	<i>Liquid phase</i>	<i>Gaseous phase</i>
<i>Propane</i>		
32°F	65	1100
70	140	1500
100	280	2200
130	550	3000
160	1100	4200
190	2400	6000
<i>n-Butane</i>		
32°F	16	1500
70	60	3300
100	150	5000
130	330	7800
160	680	10,100
190	1400	10,800
<i>Isobutane</i>		
32°F	16	
70	155	
100	248	
120	500	

**Table 6.4 Solubility of Water in LPG**

At the refinery run down line to storage, the liquid temperature may be as high as 43°C (110°F), at which temperature the solubility of water in propane for example is 320 ppm wt. If the liquid subsequently stands and cools to 0°C (32°F), the solubility is much reduced (65 ppm), and free water separates at the bottom of the tank. If this is not periodically run off, it may find its way into the loading arm for customers' deliveries. Also, if the standing time is long enough, the separated water sometimes freezes and may block the liquid LPG discharge pipe.

### 6.3.6 Other Trace Contaminants

The following completes our list of occasionally reported trace contaminants in refinery LPG.

- **Ammonia**, used as corrosion control agent at refineries, or more often, introduced by switch loading of ammonia and LPG in common vessels.
- **Oxygen** and **nitrogen** (air entrainment).
- **Sodium** (from caustic sweetening step).

**Warning:** High concentrations of moist ammonia are thought to cause stress corrosion in brass or bronze components or fittings included in some storage vessels, e.g. the valve seat at the inlet of the pressure regulator. The underlying cause is the reaction between ammonia and zinc (in brass) or aluminium (in bronze). If LPG is to be loaded into a transport vessel known to have previously carried ammonia, the interior space should first be flushed with water or cleaned with condensing steam, air or inert gas.

## 6.4 CHEMICAL REACTIONS OF LPG

Chemical reaction mechanisms of hydrocarbons are well covered in academic type textbooks and specialist publications. The reactions selected here for special mention are: dehydrogenation, cracking (both thermal and catalytic), oxidation, halogenation, steam reforming, and nitration. Some of these are discussed in greater detail in other chapters of this book, notably, oxidation as the basic mechanism in combustion and the generation of furnace atmospheres, steam reforming which is used in the town gas industry, and cracking as a means of producing feedstocks for the chemical industry.

### 6.4.1 The Order of Stability

It is generally accepted that the stability of hydrocarbons decreases with molecular weight, methane being the least reactive member of the entire class of paraffins:

Methane > ethane > propane > isobutane > n-butane > neopentane > n-pentane > isopentane > n-hexane > 2-methyl pentane


  
Decreasing thermal stability (increasing reactivity)

This order of stability is reflected in the response of the hydrocarbons to thermal pyrolysis and to attack by chemical reagents, including oxygen. The thermal stability of the corresponding unsaturated hydrocarbons relative to the saturates depends on the temperature. As a general rule, however, attack by chemical reagents proceeds more easily, i.e. at lower temperatures in the case of unsaturates, and chemical reactivity increases also with carbon number, i.e. butenes are more reactive than propylene.

### 6.4.2 Dehydrogenation and Cracking Reactions

Thermal stability is a function of the free energy of the molecule. The lower the numerical value of the free energy at a particular temperature, the more stable the molecule is at that temperature. API Research Project gives values for the heat of formation of the lower members of the paraffin series from graphite and hydrogen over the temperature range 700-1000°K. The values given in Table 6.5 have been recalculated at the extreme temperatures to show how temperature can alter the order of thermal stability.

	1000°K	700°K
Methane	4580	−3070
Ethane	26,160	10,920
Propane	45,650	22,910
<i>n</i> -Butane	64,470	34,170
Propylene	43,430	30,590
Ethylene	8928	3348
1-Butene	63,070	42,730
<i>trans</i> Butene-2	62,660	41,450
<i>cis</i> -2-Butene	63,383	42,083
Isobutene	61,687	40,447

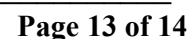
**Table 6.5 Free Energy of Formation ( $\Delta G$ ), g. cal/g. mol**

Propane and butane are now more stable than propylene and the butenes, respectively. Thus, in practice, propylene is found to pyrolysis to carbon fairly readily while being preheated to cracking temperatures. For the same reason, butane is less easy to dehydrogenate to the butenes than propane is to propylene. The cracking reaction (chain rupture) is favored by higher temperatures, dehydrogenation by low pressures and short residence time in the reaction zone.

Radically different reactions and products occur according to whether the oxidation reaction is carried out in the gaseous or liquid phase.

The order of difficulty of oxidation obeys the general stability order: methane > ethane > propane > isobutane > n-butane > n-pentane > isopentane.

The sequence of reactions, proceeding through the formation of chemical intermediates in the presence of a metal catalyst  $\text{MO}_2$  to the ultimate product of combustion,  $\text{CO}_2$ , is probably as follows:



The relative proportion of the chemical intermediates formed by partial oxidation is determined by the type of hydrocarbon feedstock, the temperature (about 450°C), pressure (up to 30 atm), the oxygen to hydrocarbon ratio and the nature of catalyst used (oxides of iron, nickel, copper etc.). Table 6.6 lists products formed from various hydrocarbons.

<i>Hydrocarbon feed</i>	<i>Oxygenated products in order of decreasing yields</i>	
C <sub>1</sub>	1,2	(1) methanol
C <sub>2</sub>	2,1,3	(2) formaldehyde
C <sub>3</sub>	3,2,1,4	
nC <sub>4</sub>	3,2,1,4	(3) acetaldehyde
iso C <sub>5</sub>	4,3,2,1	(4) acetone

**Table 6.6**

The direct oxidation of propane and butane to methyl alcohol etc. in this manner is a commercially viable process ('Celanese' process).

At atmospheric pressure and 650°C, the oxidation of propane can be stopped short by rapid quench at about 25% conversion to propylene. Isobutane is similarly dehydrogenated with some cracking at 625°C, n-butane at 608°, n-pentane at 604°, isopentane at 580°.

At as low a temperature as 190°C, propane in the presence of a trace of HBr catalyst can be oxidized to give acetone; isobutane at 160°C yields tertiary butyl hydroperoxide but methane does not react.

### **Liquid Phase Oxidation**

The effect of a solvent or liquid diluent medium is to limit reaction temperatures to relatively low levels, i.e. to decrease the reactivity of the hydrocarbon with oxygen. Thus in the LPG range, commercially interesting reactions are limited to the butanes.

A useful commercial process for the manufacture of acetic acid is based on n-butane which is dissolved in glacial acetic acid and oxidized with enriched air at about 175°C and 60 atm pressures. The reaction is aided by dissolved catalysts of the cobalt and manganese type (Huls process).

# **Chapter 7**

# **PHYSICAL PROPERTIES OF LPG**

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- 7.2.4 Vapour Pressure
- 7.2.5 Latent Heat
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## Chapter 7

# Physical Properties of LPG

### 7.1. INTRODUCTION

The physical properties of a mixture are largely a function of its chemical composition.

Propane must be considered to refer to the pure paraffinic hydrocarbon  $C_3H_8$ , whereas butane may apply to the isomer and n-butane, the branched-chain isomer, isobutane, or to a mixture of the two. Likewise propylene refers to the unsaturated hydrocarbon  $C_3H_6$  and butenes to any of the unsaturated isomers, butene-1, butene-2 and isobutylene, which bear the chemical formula  $C_4H_8$ .

LPG propane on the other hand, as distributed in various parts of the world, though it may consist predominantly of  $C_3$  hydrocarbons (propane and/or propylene, can contain smaller amounts of the  $C_4$  hydrocarbons (butanes and butenes). Similarly LPG butane may contain 95% or more of the normal isomer, or of iso-butane, or it may comprise a mixture of butanes and butenes with a relatively small proportion of the  $C_5$  hydrocarbons.

The point to be made here is that an exact physical property can only apply to any one of the pure hydrocarbons previously mentioned. If a property such as vapour pressure or specific volume, etc, is required to be known for a given LPG, a chemical analysis should first be made and the required property then calculated from knowledge of the composition and the data known for the pure components. Nevertheless, for practical purposes, since the data do not vary greatly for the pure hydrocarbons in the  $C_3$  and  $C_4$  classes, 'rule-of-thumb' numbers can be quoted from experience as applying to what are termed 'commercial propane' or 'commercial butane'.

We propose therefore to list in this chapter physical data for the major components of the  $C_3$  and  $C_4$  hydrocarbons as well as typical values for the two groups of commercial LPG.

Another feature of LPG which has already been stressed is its existence in two phases, liquid and gaseous. From the point of view of distribution and supply, one requires knowing the properties of the liquid phase; from a burner or furnace feedstock angle, it is usually the gaseous phase that has to be defined. However, the user of domestic or camping gas which is sold as bottled LPG may wish to know about some properties of both phases, e.g. specific gravity of the liquid, yield of gas from the liquid, heating value of the

gas, etc. For these reasons, the physical properties of the two phases, which are numerically very different, will be quoted separately. A distinction is also drawn between the properties of saturated vapour, i. e. that existing above the liquid at vapour pressure, and those of LPG which has been expanded to standard conditions of temperature and pressure (1 atm, 15°C).

It is proposed also to focus attention on all those properties which bear significantly on the ways in which LPG are handled and used in practice and on any problems that arise in consequence. Thus, although values for all the usually quoted physical properties are given collectively in Appendix 7, certain groups of properties are discussed in the text, as indicated below:

### **Liquid Phase**

#### **(a) Mechanical properties**

- Specific gravity (weight and volume relationships)
- Specific volume (gas production from liquid)
- Vapour pressure (design of containers)
- Viscosity (calculation of pressure drops, sizing of liquid and vapour transfer equipment)

#### **(b) Thermal properties**

- Coefficient of expansion (container filling ratios)
- Enthalpy and specific heat capacity (design of vaporizers)
- Latent heat (liquid evaporation rates)
- Gaseous Phase

#### **(c) Mechanical properties**

- Specific gravity (design of vapour distribution systems)
- Viscosity (pipe sizing)
- Dew points (condensation phenomena)

#### **(d) Combustion properties**

- Calorific value and Wobbe Number
- Air required for combustion
- Combustion products
- Limits of inflammability
- Ignition temperatures
- Flame temperatures
- Flame speed

On the other hand, certain physical properties can conveniently be discussed with reference to specific topics which are important in LPG technology. The following provide us with an opportunity so to elaborate in later sections of this chapter.

- Compressibility and Liquefaction
- Critical constants
- Departure from ideal gas laws
- Icing
- Freezing of separated water
- Icing of expanded gas
- Formation of hydrates
- Vaporization and Component Separation
- Separation of mixed LPG into 'light' and 'heavy' components on natural vaporization
- Effect on offtake rates from bottled gas

Numerical values for the physical properties which are discussed in the text of this chapter are given mainly in metric units. Factors for conversion to other units in common use are provided in Appendix 1.

## **7.2 PROPERTIES OF LIQUID PHASE**

### **7.2.1 Molecular Weight, Boiling Point & Critical Conditions**

Since LPG boil at relatively low temperatures (propane,  $-42^{\circ}\text{C}$ ; n-butane,  $-0.5$ ; isobutane,  $-11.7$ ) (see Table 7.1), they exist in the gaseous state at normal atmospheric temperatures, unless they are contained under pressure or refrigerated; hence their generic title, 'liquefied petroleum gases'. The pressure required to liquefy propane for example at ambient temperature ( $15^{\circ}\text{C}$ ) is its vapour pressure (7.3 atm). As the temperature is increased, the pressure required to maintain propane in the liquid state also increases (i.e. its vapour pressure increases). At  $96.67^{\circ}\text{C}$  the required pressure is 41.94 atm. above this temperature, propane ceases to exist as a liquid even when the applied pressure is raised above 41.94 atm. The critical temperature for propane is  $96.67^{\circ}\text{C}$  and 41.94 atm is the critical pressure. The values of the critical constants vary widely for the separate pure LPG.

	<i>Propane</i>	<i>n-Butane</i>	<i>Isobutane</i>	<i>Typical propane</i>	<i>Commercial butane</i>
Molecular weight	44.097	58.124	58.124	44	58
Boiling point, 1 atm, °C	-42.045	-0.50	-11.72	-45	-7
Critical temp., °C	96.67	152.03	134.99	95	150
Critical pressure, atm	41.94	37.47	36.00	~40	~35
Critical volume, lit./mole	0.203	0.255	0.263	~0.20	~0.26

**Table 7.1 Molecular Weight, Atmospheric Boiling Point & Critical Conditions**

## 7.2.2 Density, Specific Volume & Specific Gravity

The values quoted in Table 7.2 for liquid density are in the usual terms, weight per unit volume at standard temperature, 15.5°C (60°F). The reciprocal is, of course, specific volume. The value for propane (2 m<sup>3</sup>/tone) indicates that anyone providing for a 10 day storage capacity with an average daily process demand of 0.5 tones requires a vessel capacity of at least 10 m<sup>3</sup> exclusive of reserve bottoms.

	<i>Propane</i>		<i>n-Butane</i>		<i>Isobutane</i>		<i>Commercial propane</i>		<i>Commercial butane</i>	
	<i>Liquid</i>	<i>Vapour</i>	<i>Liquid</i>	<i>Vapour</i>	<i>Liquid</i>	<i>Vapour</i>	<i>Liquid</i>	<i>Vapour</i>	<i>Liquid</i>	<i>Vapour</i>
<i>At vapour pressure</i>										
Density, kg/m <sup>3</sup> , 15°C	507	15.9	584	4.8	563	7.0	510	15.3	580	5.62
Specific volume, m <sup>3</sup> /tonne, 15°C	1.975	63.0	1.712	209.0	1.78	141.5	1.96	65.0	1.73	1.78
<i>At atmospheric pressure (760 mmHg)</i>										
Density, 0°C kg/m <sup>3</sup>	—	2.03	—	2.67	—	2.67	—	2.0	—	2.6
Density, 15°C kg/m <sup>3</sup>	—	1.96	—	2.60	—	2.60	—	2.0	—	2.5
Specific volume, 0°C m <sup>3</sup> /tonne	—	500	—	374	—	374	—	500	—	380
Specific volume, 15°C m <sup>3</sup> /tonne	—	509	—	385	—	385	—	500	—	400
Specific gravity, 15/4°C	0.5077	—	0.5844	—	0.5631	—	0.510	—	0.575	—
Specific gravity (air = 1)	—	1.5464	—	2.0698	—	2.0656	—	1.5	—	2.0

**Table 7.2 Density, Specific Volume & Specific Gravity**

The specific gravities related to the density of water at 4°C (1000 kg/m<sup>3</sup>) indicate liquid LPG to be about half as heavy as water.

As with other liquids, LPG volume increase in temperature by an amount given by the coefficient of cubical expansion.

The precise variation alters slightly with the temperature. The effect of temperature rise is to decrease the density of the liquid and to increase that of the vapour state (see Table 7.3).

<i>Temperature, °C</i>	<i>Propane</i>		<i>n-Butane</i>		<i>Isobutane</i>	
	<i>Liquid</i>	<i>Vapour</i>	<i>Liquid</i>	<i>Vapour</i>	<i>Liquid</i>	<i>Vapour</i>
−40	567	2.585				
−20	558		620		602	
0	530	10.33	598	2.775	582	4.31
20	500		580		560	
40	470	28.7	556	9.31	533	13.83
80			502	25.1	473	36.0

**Table 7.3 Temperature Variation of LPG Density  
(at saturation pressure, kg/m<sup>3</sup>)**

Values of the coefficient of cubical expansion at 15°C are approximately 0.0015 for propane, 0.0012 for the butanes. These are significantly higher than those for higher boiling petroleum distillates such as gasoline or fuel oils, and are of an order of 100 times that for steel. The latter fact has to be taken account of in practice in arriving at the maximum filling density pertaining to liquid storage vessels. Filling density is the ratio of maximum liquid LPG content to the water capacity of the vessel. It allows for a rise in the liquid level with increase in temperature up to the maximum value expected for a given geographic region. The maximum per cent volume fill in temperate climates is about 90% (88% for propane vessels above 2 ton in size, 92% for butane tanks). (The filling density is often expressed in weight terms, for example kg LPG, liter vessel capacity 0.45 and 0.53 for the two types of LPG vessels, respectively.) Liquid volumes measured at any ambient temperature can conveniently be corrected to standard conditions (15°C) by means of factors which are set out in Appendix 2 for propane-butane mixtures of known standard specific gravity (see also Table 7.4 for an extract).

<i>Measured temperature, °C</i>	<i>Specific gravities at 15.6/15.6°C</i>		
	<i>Propane (0.5079)</i>	<i>n-Butane (0.5844)</i>	<i>Isobutane (0.5631)</i>
−40	1.142	1.099	1.110
0	1.044	1.030	1.033
+15.6	1.000	1.000	1.000
+20	0.986	0.991	0.990
+40	0.922	0.950	0.944

**Table 7.4 Liquid Volume Correction Factors  
(To obtain liquid volume at 15.6°C)**

The correction factor (Cf) appears in the formula for calculating vessel filling density, by way of compensating for the alteration in the specific gravity term with temperature.

$$\text{Filling density} = \frac{(0.97) \times (\text{Vessel water capacity}) \times (\text{S.G. of LPG at } t^{\circ}\text{C})}{(\text{S.G. of LPG at } 15.6^{\circ}\text{C}) \times (\text{Cf})}$$

Likewise, if standard volumes are to be converted to a weight basis, say for accounting purposes, the gravity at standard temperature (15°C) should be used. This can be obtained from the gravity at any observed temperature by means of standard tables.

### 7.2.3 Viscosity of Liquid under Vapour Pressure

The absolute viscosity of liquid LPG is shown together with that of LP vapours at atmospheric pressure in Table 7.5. It is seen that the viscosity of the liquids (~0.15 cp at 15.6°C) is much less than that of water, which is unity.

In common with most other fluids, the effect of temperature is to reduce the viscosity ( $\eta$ ) of the liquid phase and to increase that of the vapour phases. The magnitude of the effect is slight on the liquids (except near the critical temperature) but more pronounced on the vapours. Pressure in ordinary ranges does not greatly alter the liquid viscosity but it does result in a marked increase in the viscosity of the gases, especially above the critical pressure. The change in viscosity of a gas with pressure can be calculated.

<i>Temperature, °C</i>	<i>Propane</i>	<i>n-Butane</i>	<i>Isobutane</i>
<i>Liquid phase</i>			
boiling point (at atmospheric pressure)	0.21	0.21	0.21
15.6 (at vapour pressure)	0.106	0.180	0.163
37.8 (at vapour pressure)	0.086	0.142	0.125
<i>Vapour phase (atmospheric pressure)</i>			
boiling point	0.0065	0.0080	0.0075
37.8	0.0085	0.009	0.009
critical temperature	0.0103	0.0108	0.0104

† cP =  $6.72 \times 10^{-4}$  lb/ft s

**Table 7.5 Absolute Viscosity of LPG (cp)**

Turning to the usefulness of viscosity data for LPG, this lies in specifying pumps for liquid transfer and in predicting pressure losses pertaining for example to butane gas flow along the piped connection between upstream pressure regulator and the burner. Provided that the appropriate data are known (pipe diameter and length  $D$  and  $L$ ; flow velocity  $U$ ; fluid density  $S$  and viscosity  $\eta$ ) the Reynolds Number ( $DUS/\eta$ ), which is a well-known flow characteristic, can be derived. This, with the aid of standard charts can be correlated with the so-called 'Fanning friction factor' ( $f$ ) and the latter term is used in deriving the pressure drop  $\Delta p$ .

$$\Delta p = KfU^2SL / D$$

Where:  $K$  is a constant dependent on the units chosen.

### 7.2.4 Vapour Pressure

All LPG confined in a closed system above their boiling point readily form vapours in the space above the liquid level. When liquid is present, the vapour pressure is referred to as the saturation vapour pressure. This is equal to atmospheric at the boiling point and increases gradually towards the critical condition. Vapour pressure is a measure of volatility. It follows that at any given temperature, the lowest boiling LPG member (propane) has the highest vapour pressure, isobutane rather less and n-butane (the highest boiling LPG member) has the lowest vapour pressure (see Table 7.6).

°C	<i>Decreasing volatility</i>		
	<i>Propane</i>	<i>Isobutane</i>	<i>n-Butane</i>
-17.7	2.68	0.82	0.52
0	4.82	1.64	1.05
15.5	7.53	2.72	1.85
37.8	13.12	5.18	3.67
60	21.44	8.91	6.51

**Table 7.6 Saturated Vapour Pressures of LPG  
(kg/cm<sup>2</sup> absolute)**

FUEL		VAPOR PRESSURE Psig AT SEA LEVEL
Butane		37.5
90% B	10% P	53.6
80% B	20% P	69.6
70% B	30% P	86.6
60% B	40% P	102.0
50% B	50% P	120.0
40% B	60% P	132.0
30% B	70% P	145.0
20% B	80% P	162.0
10% B	90% P	174.0
Propane		190.0

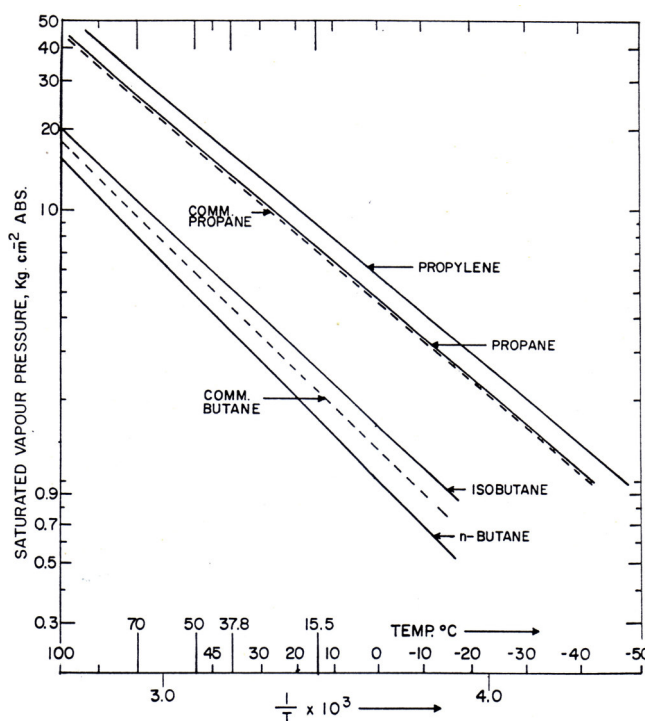
**Vapour Pressure of Commercial LPG Mixtures at 100 °F**



Usually one needs to know LPG vapour pressures for two reasons, first to ensure that the pressure of a given mixture is less than that which the steel shell of any containing vessel is designed to withstand at the highest service temperature; secondly, to ensure that the LPG is sufficiently volatile to provide for a prescribed gas offtake rate by natural vaporization.

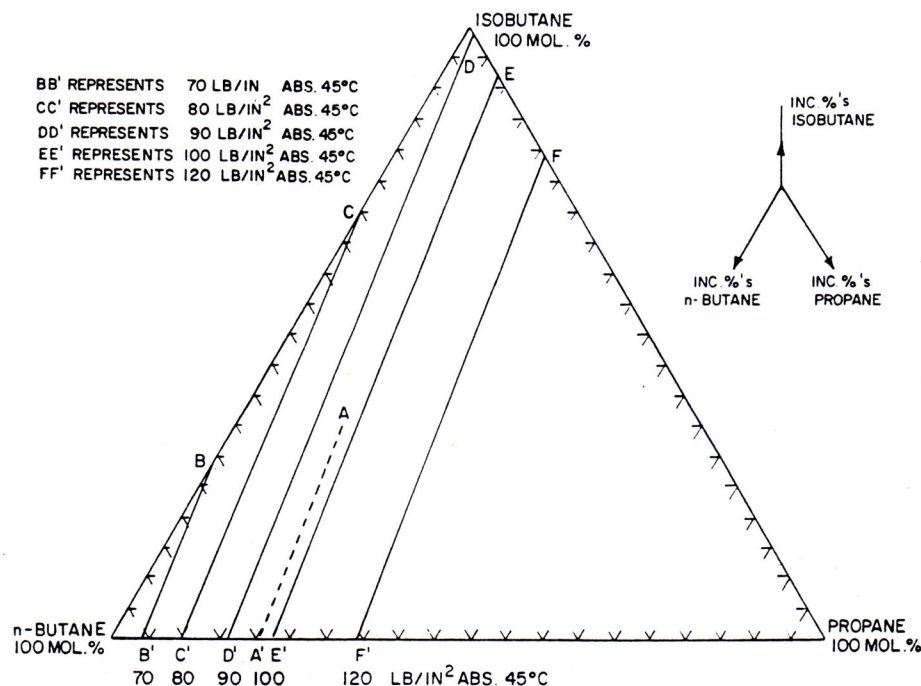
They are also expressed graphically between the boiling point and the critical temperature in Figure 7.1. This is a logarithmic-linear plot of vapour pressure ( $\text{kg}/\text{cm}^2$  absolute) versus the reciprocal of the absolute temperature ( $^{\circ}\text{K}$ ), and the relationship is a linear one approximately.

In the case of commercial LPG, the vapour pressure is, by Dalton's Law, the sum of the partial pressures of the  $\text{C}_3/\text{C}_4$  hydrocarbon components. These in turn are related by Raoult's Law to the mol fraction of each component in the liquid. The vapour pressure of LPG mixtures can therefore be calculated as well as measured directly.



**Figure 7.1 Saturated vapour pressure-temperatures Relationships for LPG**

When no cracked stock is present, the vapour pressure of commercial LPG will be determined by the concentration of the three principal components, propane, n-butane and isobutane. A triangular diagram which can be used to predict the vapour pressure of such mixtures at 45°C (a statutory specification item in the U.K.) is provided in Figure 7.2.



**Figure 7.2 Vapour pressures of mixtures of propane, iso-butane and n-butane lb/in<sup>2</sup> abs., 45°C**  
(Mixture ratios are in vol. per cent liquid phase)

The diagram is constructed by calculating the vapour pressure of certain boundary mixtures. Thus, the mixture represented by point B (70 vol. % liquid n-butane and 30% isobutane) has a vapour pressure of 70 lb/in<sup>2</sup> abs, at 45°C, and so does the mixture at point B' (96% n-butane, 4% propane). Similarly, all mixtures represented by points on the line CC are calculated to have a vapour pressure of 80 lb/in<sup>2</sup> abs.; on DD' 90, on EE', 100; on FF', 120, and so on.

Thus point A within the diagram (15 vol. % propane, 35% iso-butane, 50% n-butane), by drawing a line AA' to meet the horizontal base of the triangle and interpolating, is found to have a vapour pressure of 97.6 lb/in<sup>2</sup> abs. (6.6 atm).

The diagram also enables one to say that the 35% isobutane in mixture A can be replaced by an additional 6% of propane without affecting the vapour pressure.

## 7.2.5 Latent Heat

The latent heat of a liquid is the quantity of heat absorbed on vaporization at the normal boiling point, or conversely, it is the amount of heat given out when the vapour is condensed at atmospheric pressure. As the heat content of the liquid increases with temperature, the latent heat decreases as shown in Table 7.7.

The value of latent heat data lies in calculating the quantity of LPG that will be vaporized ( $Q$ ) at a given liquid temperature by a specified heat input  $H(Q = H/L)$ . Latent heat indirectly is also a measure of liquid volatility, the higher boiling LPG requiring more heat to boil than the lowest (propane) but all, as a class, requiring far less than a similar quantity of water, for example.

C°	Propane	n-Butane	Isobutane	Commercial		Water
				Propane	Butane	
At the boiling point (1 atm.)	101.76	92.09	87.58			
15				95	89	
25	81.76	86.63	78.63			
60	61.88	76.07	65.01			555.5

**Table 7.7 Latent Heat of LPG (under vapour pressure) (kcal/kg)**

## 7.2.6 Specific Heat of Liquid LPG

Specific heat is defined as the quantity of heat necessary to raise unit mass through a unit temperature interval. Numerically, the parameter is the same when expressed in metric or English units (kcal/kg/°C versus Btu/lb/°F).

As is seen in Table 7.8, the specific heat of both liquid and vapour phases is dependent on the temperature and therefore the figure used in practice should be related to the temperature level. Mean values appropriate to a wide temperature interval can conveniently be calculated from Mollier diagrams, of which more will be said later.

	Propane	n-Butane	Isobutane	Commercial	
				Propane	Butane
Liquid at constant pressure, 1 atm 25°C	0.6023	0.5748	0.5824	0.60	0.57
Vapour at atmospheric pressure					
Cp 0°C	0.359	0.342	0.372		
15	0.388	0.397	0.386		
100	0.456	0.438	0.438		
500	0.844	0.822	0.822		
Cv 15°C	0.343	0.361	0.348		

Table 7.8 Specific Heat of LPG (kcal/kg/°C (or Btu/lb/°F))

## 7.3 PROPERTIES OF THE GASEOUS PHASE, STANDARD CONDITIONS OF TEMPERATURE AND PRESSURE

### 7.3.1 Equation of State and Molal Volume

For an ideal gas, the general equation of state,  $PV = RT$  applies where  $V$  is the molal volume (379.5 ft<sup>3</sup>/lb, 60°F, 30 in. Hg; 22.41 m<sup>3</sup>/kg mol 0°C, 760 mmHg),  $P$  is the absolute pressure,  $T$  the absolute temperature and  $R$  is the so-called 'gas constant' expressed in consistent units. In the case of LPG which depart slightly from ideality a compressibility factor  $Z$  is introduced into the equation of state to allow for the fact that the molal volume at raised pressures is slightly less than that expected of ideal gases. Thus  $PV = ZRT$  for non-ideal gases where  $Z$  has a value below unity. The precise values of  $Z$  for LPG at standard conditions (15°C, 1 atm) are listed in Table 7.9.

	$Z$
Propane	0.9840
Propylene	0.9840
n-Butane	0.9690
Isobutane	0.9710
Butene-1	0.9690
cis Butene-2	0.9650
trans Butene-2	0.9650
Isobutene	0.9690

Table 7.9 Compressibility Factors for LPG  
(15 °C, 1 atm)

It will be seen that the molal volume of propane for example at standard conditions is  $22.41 \times 0.9840$ , that is  $22.05 \text{ m}^3/\text{kg mol}$ . Corrected molal volumes for the other LP component gases are listed in Table 7.10 in metric and British units.

	<i>Propane</i>	<i>n-Butane</i>	<i>Isobutane</i>
Volume of 1 kg mol at 0°C, 760 mm Hg ( $\text{m}^3$ )	22.05	21.71	21.76
Volume of 1 lb mol at 60°F, 30 inHg ( $\text{ft}^3$ )	373.40	367.74	368.49

† Ideal gas =  $22.412 \text{ m}^3 / \text{kg mol}$ ;  $379.50 \text{ ft}^3 / \text{lb mol}$ .

**Table 7.10 Molal Volumes of LPG (STP)†**

Another way of calculating the effects of pressure and temperature variation on non-ideal gases involves the introduction of Van der Waal constants ('a' and 'b') into the ideal gas relationship.

$$\left(P + \frac{a}{v^2}\right) \cdot (V - b) = RT$$

Values of 'a' and 'b' for LPG are as follows:

	<u>'a'</u> †	<u>'b'</u> ‡
Propane	8.664	0.08445
Isobutane	12.87	0.1142
n-Butane	14.47	0.1226
Propylene	8.379	0.08272

† Expressed in litres<sup>2</sup> atm/mole<sup>2</sup>.

‡ Expressed in litres/mole.

The effect of non-ideality in the case of LPG is to decrease slightly the specific volume and thereby to increase the density of saturated vapour above the value expected of an ideal gas under equal conditions of pressure and temperature.

### 7.3.2 Gas to Liquid Volume Relationship

From the molal volume, the gas to liquid weight relationships at standard conditions of temperature and pressure can be calculated. Thus one pound of liquid propane, wholly vaporized at atmospheric pressure and 15°C, occupies 373.40/44.097 (8.47 ft<sup>3</sup>). Likewise, in metric units, 1 kg occupies 22.05/44.097 (0.500 m<sup>3</sup>). This of course is also the specific volume of the gas at standard atmospheric conditions. Similar numbers can be calculated for the other LPG by dividing the molal volumes by the respective molecular weights, as shown in Tables 7.2 and 7.11.

	<i>Propane</i>	<i>n-Butane</i>	<i>Isobutane</i>	<i>Commercial</i>	
				<i>Propane</i>	<i>Butane</i>
Vol./Vol. 0–15°C, 760 mmHg	267·4	229·8	222·3	274·0	233·0
ft <sup>3</sup> /lb 60°F, 30 inHg	8·47	6·33	6·34	8·6	6·5
m <sup>3</sup> /kg 0°C, 760 mmHg	0·500	0·374	0·374	0·50	0·39

**Table 7.11 Gas-Liquid Relationships**

### 7.3.3 Density

The density of the expanded vapour at standard conditions of temperature and pressure is, of course, the reciprocal of the specific volume, i.e. for propane it is 1/0.500 or 2.0 kg/m<sup>3</sup>, 0°C, 760 mmHg pressure (see Table 7.2), or in English units 0.118 lb/ft<sup>3</sup>, 60°F, 30 in Hg. For convenience this value is often quoted as the weight in pounds of one hundred cubic feet of gas that is 11.8 lb /100 ft<sup>3</sup>.

### 7.3.4 Specific Gravity

The specific gravity of a gas is normally defined as the ratio of its density to that of air at the same temperature and pressure (taken as unity). The values given in Table 7.2 indicate that LPG is 1½ to 2 times as heavy as air. Leaking LPG will sink to ground level rather than rise to atmosphere as does natural gas, a fact which necessitates extra safety precautions in handling.

### 7.3.5 Viscosity

The value for LPG vapour at atmospheric pressure and 15.5°C is about 0.008 cp or 0.04 Stokes. Temperature change has a relatively slight effect. The significance of viscosity in calculations of gas flow has already been discussed (see sub-section 7.2.3).

### 7.3.6 Specific Heat and Sensible Heat

In the particular case of the gaseous state, the value of the specific heat is dependent not only on the mean temperature (see sub-section 7.2.6) but also on whether the pressure ( $C_p$ ) or the volume ( $C_v$ ) is constant during a change in temperature. Usually, it is the constant pressure value which is used in practical calculations. The sensible heat of a gas is the heat required to raise unit mass from a reference value, usually 0°C and atmospheric pressure, to the given conditions. Since specific heat is temperature dependent, though not a linear function, an approximate sensible heat value can be calculated by assuming an average value at constant pressure over the temperature range in question.

For accurate calculations, however, the function  $C_p \cdot dt$  must be integrated. Effects of dissociation of LPG at high temperatures can be ignored for the purposes of sensible heat calculations. Values for the three main gases at any particular temperature do not differ greatly (see Table 7.12).

°C	<i>Propane</i>	<i>Butane</i>
0	0	0
100	50	50
500	300	300
1000	770	770

**Table 7.12 Sensible Heat (k cal/kg) of LPG Vapour  
at Atmospheric Pressure (above 0°C)**



### 7.3.7. Combustion Properties

#### Calorific Value and Wobbe Index

The calorific value or heat of combustion is defined as the amount of heat released when a unit quantity of the gas is burned at atmospheric pressure and at ambient temperature (25°C). The gross value is obtained when the contribution from the latent heat of condensation of the water vapour formed is recovered: the net calorific value is a more realistic parameter pertaining to practical conditions when flue gases are usually maintained above 100°C. However, the gross heating value is the standard adopted almost universally for the calculation of thermal efficiencies of fuel burning appliances.

	<i>Propane</i>	<i>n-Butane</i>	<i>Isobutane</i>	<i>Commercial</i>	
				<i>Propane</i>	<i>Butane</i>
Calorific value, 25°C					
Gross, kcal/kg	11,943	11,742	11,714	11,900	11,800
Net, kcal/kg	10,989	10,837	10,810	11,000	10,900
Gross, kcal/m <sup>3</sup>	23,700	30,600	30,500	24,000	30,200
Net, kcal/m <sup>3</sup>	22,250	29,400	29,200	22,600	29,000
Wobbe Number†					
Gross, kcal/m <sup>3</sup>	19,100	21,290	21,180	19,200	21,000

$$\dagger \text{ Wobbe Number} = \frac{\text{Gross calorific value}}{\sqrt{(\text{specific gravity})}}$$

**Table 7.13 Calorific Value and Wobbe Numbers**

The Wobbe Index defined as the gross calorific value divided by the square root of the specific gravity is a measure of the heat flow to an appliance and the degree of aeration required to prevent 'yellow tipping'. Thus, an appliance with 'an appropriately sized burner injector and governed pressure will accept either of two hydrocarbon fuels, without noticeable effects on heat input or combustion performance, if the Wobbe Indices do not differ by more than about 5% (see also Chapter 9). Values for Wobbe Index are needed when consideration is given to replacing natural or town gases by LPG-air mixtures without resorting to burner and appliance conversions.



The calorific value and Wobbe Indices of both pure and commercial LP grades are given in Table 7.13. The figures quoted for commercial grades can only be regarded as typical of what is commonly encountered in practice, and if accurate values are required for design purposes, these can be obtained by calorimetric determination or by calculation from the composition (see Chapter 8).

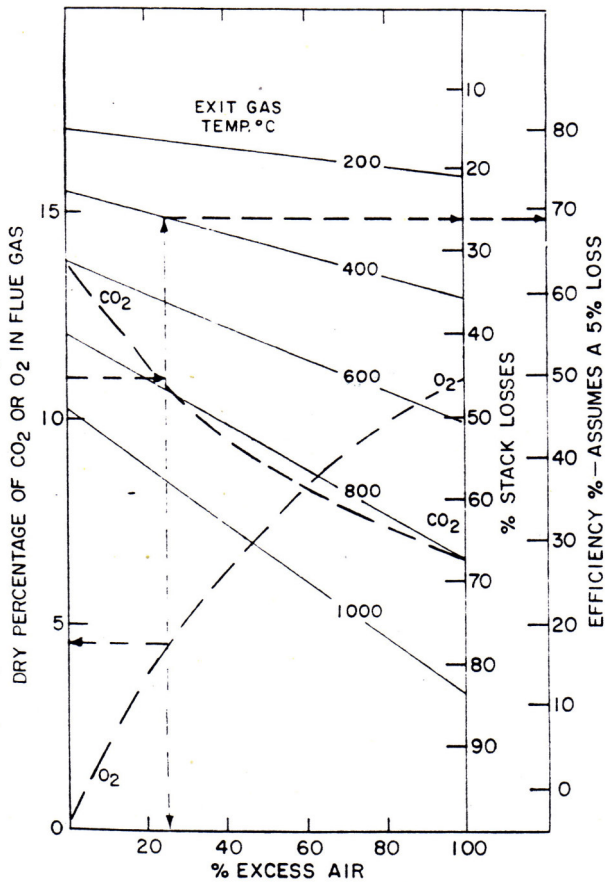
### **Other Combustion Data**

The data most commonly required for calculations of combustion and process efficiencies are: stoichiometric air requirement, flue gas volume, ultimate CO<sub>2</sub> content, burning velocity, ignition temperature, flammability limits and flame temperature. This information is given in Table 7.14 along with similar data for natural gas (methane).

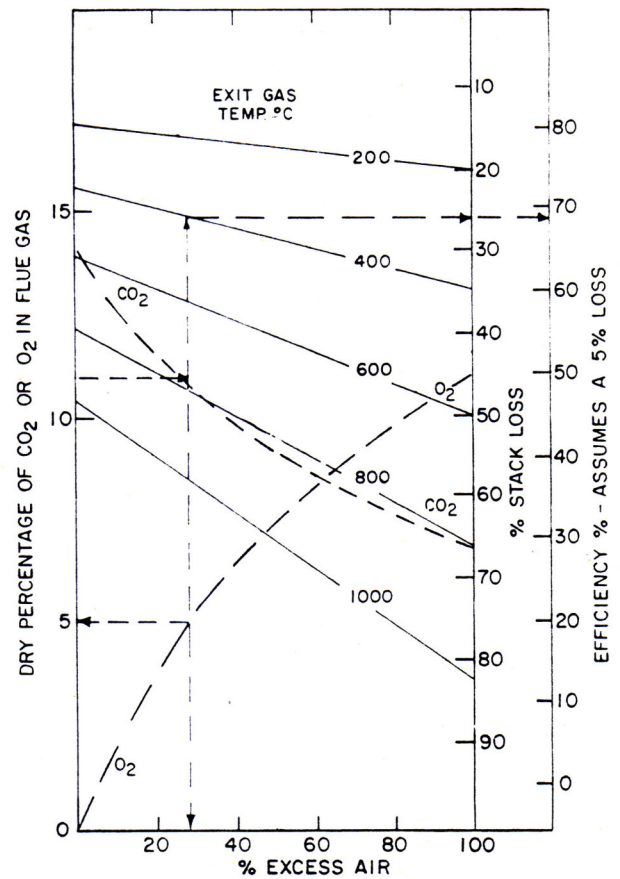
	<i>Propane</i>	<i>n-Butane</i>	<i>Isobutane</i>	<i>Commercial</i>		<i>Natural gas</i>
				<i>Propane</i>	<i>Butane</i>	
m <sup>3</sup> air required per m <sup>3</sup> gas for combustion	23.8	31.0	31.0	24	30	9.5
Products of combustion (m <sup>3</sup> ) per m <sup>3</sup> of gas						
CO <sub>2</sub>	3.0	4.0	4.0	3.0	4.0	1.0
H <sub>2</sub> O	4.0	5.0	5.0	4.0	5.0	2.0
N <sub>2</sub>	18.8	24.5	24.5	18.8	24.5	7.5
Ultimate CO <sub>2</sub> in flue gas (%)	13.7	14.0	14.0	13.8	13.9	11.8
Maximum burning velocity (1 in tube) cm s <sup>-1</sup>	39.0	37.9	37.9	38.5	38.0	33.8
Ignition temperature, min, °C in air	466	405	462	450	420	537
Flammability range gas/air, vol. %						
Lower limit	2.10	1.86	1.80	2.0	1.8	5.0
Upper limit	10.10	8.41	8.44	10.0	8.5	15.0
Flame temperature °C in air	1970	1975	1975	1970	1975	1918

**Table 7.14 Additional Combustion Data for LP and other Fuel Gases**

A convenient summary of the combustion data required for the estimation of boiler and furnace stack losses, and also of combustion efficiency, is provided in chart form in Figures 7.3 (propane) and 7.4 (butane).



**Figure 7.3 Combustion Data Chart  
for Propane**



**Figure 7.4 Combustion Data Chart  
for Butane**

As an example, instrumental measurements on a butane-fired furnace give:

**CO<sub>2</sub> in the dry flue gas = 11%;  
Exit gas temperature = 400°C**

Starting from the 11% of CO<sub>2</sub> point on the left-hand scale (Figure 7.4), read across to the broken CO<sub>2</sub> line. The excess air is 28% and the amount of oxygen in the flue gases is 5.1%. Then, taking the point where the vertical line crosses the temperature line, 400°C, read horizontally, to obtain:

**Stack losses = 26%  
Actual efficiency = 69%  
Therms input for 1 therm output = 1.45 (net basis)**

Optimum fuel efficiency requires the lowest possible excess air together with as low an exit gas temperature as can be attained. The amount of excess air is governed by the need for complete combustion, and depends on the burner and combustion chamber geometries. The flue gas temperature is governed by stack height considerations and also by the need for the furnace stack gases to remain slightly above the water dew point temperature.

### 7.3.8 Dew Points of LPG

The dew point temperature is that at which Raoult's Law holds, namely,

$$\sum_i \frac{Y_i}{p_i^*} = \frac{1}{\pi}$$

Where  $Y_i$  is the mol fraction of component 'i' in vapour,  $p_i^*$  is the vapour pressure of pure component 'i' and  $\pi$  is the total pressure.

The dew point of the vapour at atmospheric pressure is close to the normal boiling point. Increase of pressure raises the dew point of LPG very markedly but addition of air has the opposite effect. Butane, being the higher boiling LP gas, is of course more prone to condense than propane. In practice therefore, transfer lines carrying butane or butane-propane mixtures under pressure need to be lagged and heated, or else diluted with air, to prevent liquid condensation (see also Chapter 11). Table 7.15 illustrates the magnitude of the effects of raised pressure on the dew points of LPG, and of LPG-air mixtures, respectively.

	<i>Dew point, °C</i>				
	<i>1 atm</i>	<i>2 atm</i>	<i>3 atm</i>	<i>4 atm</i>	<i>5 atm</i>
<i>LP gases</i>					
Propane	−42	−25	−14	−6	+2
<i>n</i> -Butane	−1	21	32	42	
Isobutane	−11.7	6.1	20	29.5	36
<i>LPG-air mixtures</i>					
50/50 propane-air	−56.5	−42.8	−32	−25	−19
50/50 <i>n</i> -Butane-air	−25	0	+10	+18.5	+25
50/50 isobutane-air	−29	−12.2	−1	+7.2	+14.5

**Table 7.15 Effect of Pressure on the Dew Point of LPG**

## 7.4 PROPERTIES OF THE SATURATED VAPOUR

### 7.4.1 Density, Specific Gravity, Specific Volume

Under saturation conditions, LP vapour is in coexistence with liquid LPG, i.e. the system pressure is at least equal to the vapour pressure at the temperature in question. At 15.5°C, for example, the vapour pressure of propane is 7.5 kg cm<sup>2</sup> (see Table 7.6). Therefore, the specific volume of saturated propane vapour in a container at 15.5°C is not 0.509 m<sup>3</sup>/kg as at atmospheric pressure but

$$0.509 \times 1.033 / 7.53 \times Z'/Z_0$$

Where  $Z'/Z_0$  is the ratio of the compressibility factors at 15°C and 0°C, respectively, that is, it is 0.063 m<sup>3</sup>/kg or 63.0 m<sup>3</sup>/tonne as shown in Table 7.2. The value of the density of saturated vapour at 15.5°C, being the reciprocal of the specific volume, becomes 1/0.063 or 15.9 kg/m<sup>3</sup>. Values of specific volume and density of the saturated butane vapours can be calculated similarly (see Table 7.2).

### 7.4.2 Enthalpy and Entropy

The Enthalpy of saturated liquid is the heat required to raise the temperature of unit mass from a datum temperature, being that at which the heat content of the liquid is taken to be zero. For the liquid, enthalpy is the sum of the sensible heat plus heat of fusion. Similarly, for the saturated vapour, it is the sum of the enthalpy of the liquid plus the latent heat of vaporization. Enthalpy is usually expressed as kilocalories per kilogram (kcal/kg) (or Btu/lb). The enthalpy or total heat content of the saturated liquid or vapour is an important concept used, for example, in calculations of design and thermal rating of liquid vaporizers.

The entropy of a liquid or vapour is its enthalpy divided by the absolute temperature. It is expressed as kilocalories per kilogram per degree centigrade (kcal/kg/°C) and remains constant while the liquid or vapour volume changes without absorption or release of heat. However, entropy increases or decreases if the material receives or surrenders heat from or to its surroundings. Over an infinitely small change in temperature, the increase or decrease of entropy, when multiplied by the absolute temperature gives the heat absorbed or lost by the fluid. Table 7.16 provides enthalpy data.

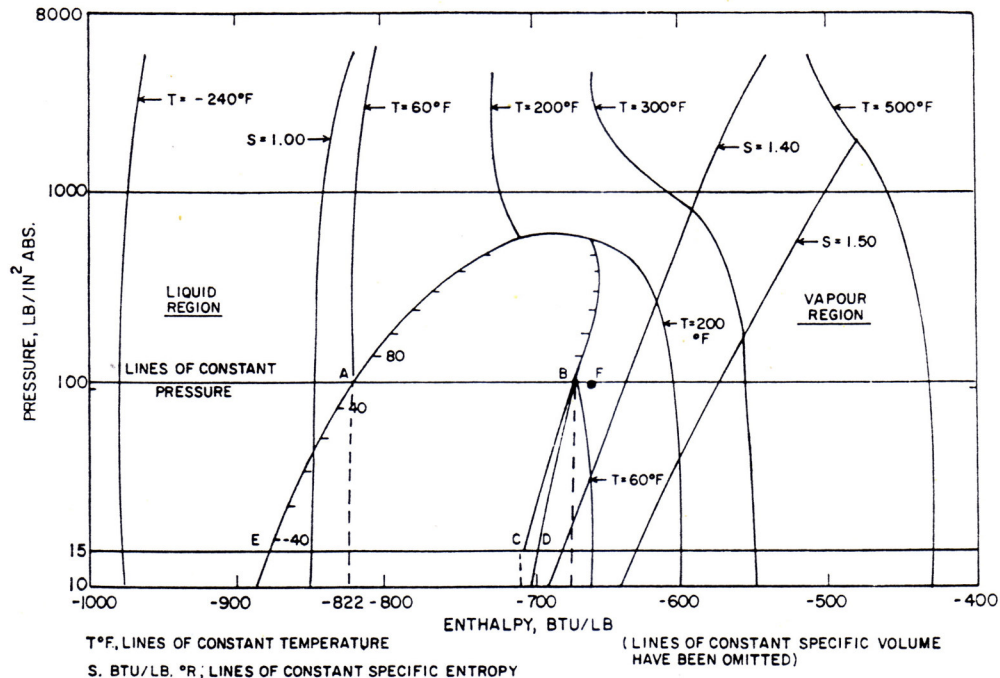
<i>Temperature, °C</i>	<i>Pressure, kg cm<sup>-2</sup></i>	<i>Enthalpy, kcal/kg</i>	
		<i>Liquid</i>	<i>Vapour</i>
-42.1	1.033	64.6	166.4
-9.9	3.51	81.8	174.8
12.8	7.03	95.7	181.0
28.2	10.54	105.6	184.9
40.3	14.06	113.7	187.6
50.3	17.57	120.8	189.4
58.7	21.09	127.8	190.8
66.3	24.60	134.1	191.5
73.1	28.12	140.0	191.6
79.3	31.63	145.3	190.8
84.9	35.15	150.3	189.4
90.2	38.66	155.5	187.3
93.9	41.33	161.0	185.1
95.3	42.18	164.7	183.8
96.8	43.37	175.0	175.0

**Table 7.16 Enthalpy of Propane at Saturated Conditions**

In dealing with practical conditions involving changes in liquid or vapour state (for example liquid flow along pipes, liquid compression, vaporization at the liquid boiling point, superheat of vapour, expansion or compression of vapour) one requires to have knowledge of heat content (or enthalpy) outside the saturated boundaries. For this purpose, recourse has to be made to graphical relationships of enthalpy with a wide range of pressure or temperature, often wrongly called Mollier diagrams (the true Mollier diagram relates enthalpy to entropy).

Useful pressure-enthalpy diagrams for propane and n-butane have been published recently by Starling and are reproduced in Appendix 3. These diagrams refer to datum conditions of zero enthalpy and entropy at 0°R and 0 lb/in<sup>2</sup> abs. Consequently, the enthalpy values do not relate to those quoted elsewhere. Nevertheless, since in practice one is usually concerned with changes in entropy rather than in absolute values, differences in datum temperatures are of little consequence. Examples of the ways in which practically valuable data can be extracted from the enthalpy diagrams are supplied in the following.

Consider the case of propane at vapour pressure undergoing total vaporization (see Figure 7.5)



**Figure 7.5 Pressure-enthalpy diagram, propane (illustrative only)**

Point A which represents a natural vapour pressure of 107 lb/in<sup>2</sup> abs. at 15.4°C (60°F) can be taken as a starting point. The enthalpy of liquid is – 822 Btu/lb. Vaporization occurs at constant temperature and pressure along the line AB. The heat content of the vapour at the other side of the boundary of saturated conditions (point B) is – 671 Btu /lb. AB represents the heat which has to be supplied to effect vaporization, and is the latent heat at 60°F that is, – 671 to – 822 or 151 Btu/lb.

If now the saturated vapour is expanded adiabatically to atmospheric pressure along the line BC (line of constant entropy), it arrives at point C where its temperature is decreased to – 42°F. The position of C inside the envelope of saturated conditions shows that some condensation of liquid will occur, the dryness factor (q) being given by the equation:

$$\text{Heat content at C} = \text{Heat content at E} + q (L)$$

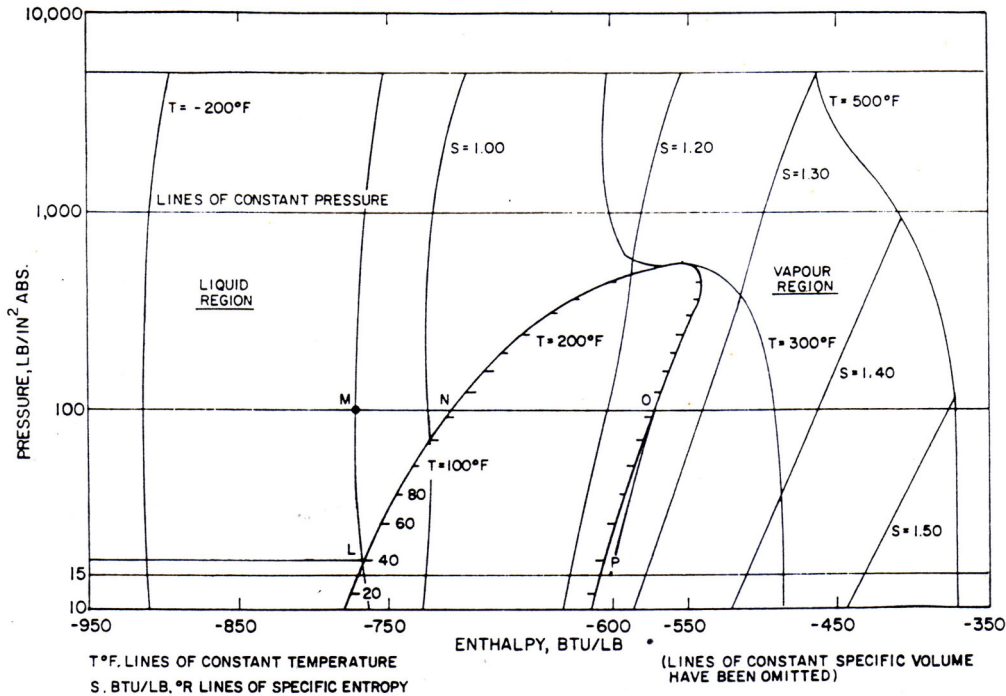
Where: L is the latent heat at the true boiling point (182 Btu/lb). Thus,

$$\begin{aligned} -710 &= -880 + q (182) \\ q &= 170/182 \\ &= 0.935 \end{aligned}$$

that is, 6% by weight of the total vapour will condense.



On the other hand, if the saturated vapour represented by B were superheated to point F, that is, raised to a temperature of 85°F where its enthalpy is - 660 (necessitating an addition of 11 Btu/lb sensible heat), adiabatic expansion to atmospheric pressure will take the vapour to point D. This is situated on the boundary of the saturated envelope, indicating that the vapour will remain 'dry'. Incidentally, the specific heat of the propane vapour in this region can be calculated by dividing the heat absorption per pound (11 Btu) by the temperature rise (25°F), which is 0.44.



**Figure 4.6 Pressure-enthalpy diagram, n-butane (illustrative only)**

Let us now turn to the case of n-butane which, being a low-pressure liquid usually is withdrawn from tankage by a pump and delivered to a vaporizer at a raised pressure to allow for subsequent line losses or to provide for sufficient heat at the vapour exit to overcome dew point difficulties. At (5°C) 40°F, n-butane (see point L in Figure 7.6) has a vapour pressure of 17.7 lb/in<sup>2</sup> abs. If it is to be pumped up to 100 lb/in<sup>2</sup> abs. before vaporization at the boiling point, the quantity of sensible heat represented by the line MN (-710 to -772 = 62 Btu/lb) has to be supplied as well as latent heat (NO = 137 Btu/lb). And on adiabatic expansion to atmospheric pressure along the line OP, the vapour arrives at P which is situated just outside the envelope. The temperature is (5°C) 40°F approximately and the vapour is 'dry' (boiling point of n-butane at atmospheric pressure = 31.1°F).

## 7.5 ICING PHENOMENA

It has already been pointed out in Chapter 6 that water is soluble to a slight extent in LPG, the effect being most marked in propane and in the vapour phase at raised temperatures. The presence of water may reveal itself at low temperatures in what can collectively be termed 'icing phenomena' in a number of ways: separation of free water because of reduction in solubility of water in LPG as the liquid temperature falls (see Table 6.7 for solubility data): freezing of the separated water in storage tanks, still liquid lines, vaporizers, etc.: separation and freezing of water in LPG vapour as the liquid is expanded through a pressure reducing valve (see also sub-section 7.4.2): icing of water vapour in ambient air as LPG liquid is expanded through an open valve, with the consequent lowering of temperature; formation of hydrocarbon 'hydrates' at low temperatures and medium pressures or at elevated pressures and higher temperatures. Hydrates are in the nature of solid solutions (white crystals) of water in the hydrocarbon, the bonding forces being of the loose physical, rather than firm chemical, type. If conditions of temperature and pressure are suitable, and if enough water is present in the system, the formation of solid hydrates is a continuing process which leads to the plugging of valves, pipelines and regulators. Design of process equipment for the handling of wet propane in particular requires accurate prediction of the limiting conditions at which hydrates are formed. Stable hydrates can also be formed from isobutane, and from mixtures of n-butane with smaller molecules.

A mixture of ice and solid hydrate crystals is formed from propane over the temperature range 10 to 32°F with pressures of 15 and 25 lb/in<sup>2</sup> abs., respectively, i.e. below the saturated vapour pressure of the liquid. Between 32 and 42°F and at pressures above 25 lb/in<sup>2</sup> abs. (and up to 520 lb/in<sup>2</sup> abs.), as would be the case with pumping liquid propane at elevated pressure from storage in winter-time conditions to a vaporizer, hydrate formation is accompanied by the separation of a water-rich liquid. After the liquid vaporizer in a gas-making plant, the temperature of the LPG vapour will be too high (i.e. above 42°F) to allow hydrates to form. Hydrates of butane may form at atmospheric pressure and up to its vapour pressure at temperatures below 32°F.

The precautions which can be taken to guard against ice or hydrate formation in process equipment are as follows; drying of the LPG at source by filtration through water-absorbing agents such as calcium chloride, silica gel, alumina or zeolites; raising of the liquid temperature above 32°F for butane and 42°F for propane, respectively; adding methyl alcohol to the liquid at a minimum dosage rate of 0.1 vol. % (1 pint per 100 gallons), a step which reduces the ice and hydrate formation temperatures. Reduction of operating pressure (if above vapour pressure) is also a palliative.



## 7.6 VAPORIZATION AND COMPONENT SEPARATION

In the case of a pure, liquid hydrocarbon, the chemical composition of the liquid and vapour phases will be identical, but the proportion occurring in the two phases is related to its volatility. The more volatile a liquid is, the larger will be the equilibrium or 'K' factor at a particular temperature, as defined by:

$$K_i = \frac{y_i}{x_i}$$

Where ' $y_i$ ' is the mole fraction in the vapour phase; ' $x_i$ ' is the mole fraction in the liquid phase.

With a mixture of two or more hydrocarbons, as for example propane and n-butane in an LPG mixture, the relative proportion of each in the vapour and liquid phases, respectively, is related to their relative volatility, the vapour being rich in the most volatile (propane) and the less volatile (n-butane) being concentrated in the liquid phase. In fact as has been explained in Chapter 6, LPG can comprise a mixture of propane and the two butanes with smaller amounts, say, of propylene, ethane and pentanes. Thus, vaporization of such a liquid, as for example by vapour withdrawal from domestic LPG bottles or external heating of the liquid in industrial vaporizers, will simulate the process of a single plate fractionation whereby the lightest components (propane, propylene, ethane) are concentrated in the vapour phase and the heavier components (butanes and pentanes) in the liquid phase.

In the case of bottled gas withdrawal for example, the gas pressure at any interval of time is determined by the sum of the partial pressures of the individual hydrocarbon components (Dalton's Law). The partial pressures of any component 'i' are in turn related by Raoult's Law to its mole fraction in the liquid phase ( $x_i$ ) and saturated vapour pressure ( $P_i$ ). Thus:

$$\begin{aligned} x_i P_i &= p_i \text{ (Raoult's Law)} \\ \text{and} \quad x_i P_i &= \pi y_i \end{aligned}$$

Where  $\pi$  is the total vapour pressure of the system. Hence

$$\pi = (p_i)_1 + (p_i)_2 + \dots + (p_i)_n \quad \text{for 'n' components}$$

$$\pi = \left[ \left( \frac{x_i}{y_i} \right) P_i \right]_1 + \left[ \left( \frac{x_i}{y_i} \right) P_i \right]_2 + \dots + \left[ \left( \frac{x_i}{y_i} \right) P_i \right]_n$$

It must be mentioned that application of Raoult's Law holds only for ideal mixtures but may be regarded as valid for hydrocarbon homologues in the LPG range (C<sub>2</sub>-C<sub>5</sub>) at moderate pressures. (In order to improve the accuracy in predicting vapour-liquid equilibrium constants for hydrocarbons at higher pressures, some prefer to substitute the concept of 'fugacity function' for vapour pressure.)

Adhering to Raoult's Law, the vapour-liquid equilibrium diagrams for two component mixtures, namely propane + n-butane and propane + propene, respectively, at a given temperature (60°F) are shown in Figure 7.7.

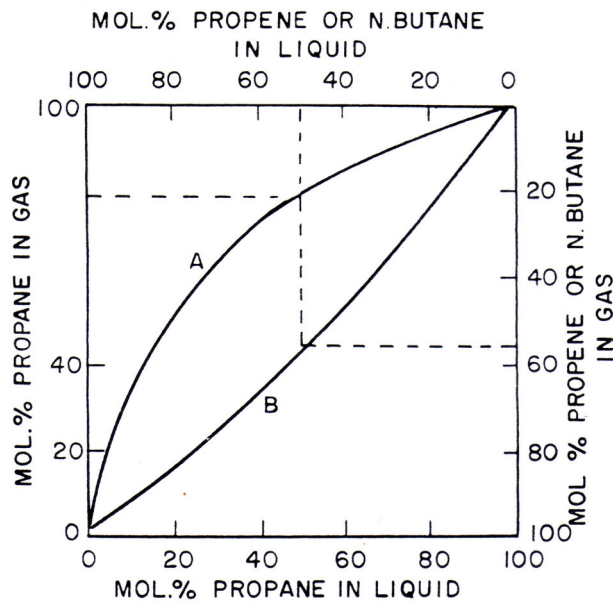
The diagram is constructed as follows.

$x_i$		$P_i$		Partial pressures ( $x_i P_i$ )		$\pi$	Vapour composition†	
Propane	n-Butane	Propane	n-Butane	Propane	n-Butane		Propane	n-Butane
0.8	0.2	105	26	84.0	5.2	89.2	0.94	0.06
0.5	0.5	105	26	52.5	13.0	65.5	0.80	0.20
0.2	0.8	105	26	21.0	20.8	41.8	0.50	0.50
0.1	0.9	105	26	10.5	23.4	33.9	0.31	0.69

$$\dagger y_i = \frac{x_i P_i}{\pi}$$

The propane-propylene curve is constructed in the same way using the appropriate vapour pressure data. It is seen then that LPG liquid containing 50 mol % propane with the less volatile n-butane yields gas containing 80% propane and 20% n-butane whereas one containing 50% propane with the slightly more volatile propylene provides a gas composition of 55% propylene, 45% propane.

Although the LPG composition, and therefore the gas pressure, inside a bottled gas system at any point in time in part determines the rate at which further quantities of gas can be withdrawn from the bottle, this rate is also affected by other factors which greatly complicate the calculation.



A; PROPANE- N. BUTANE SYSTEM

B; PROPANE-PROPENE SYSTEM

**Figure 7.7 Equilibrium compositions of liquid and gaseous LPG's**

Two important conclusions concerning bottled gas composition can be drawn from this work. The first is that increasing the butane content reduces the possibility of being able to empty LPG bottles at low temperatures; the second is that in sub-tropical climates, adding propane to butane in order to increase the gas pressure affords little advantage in increasing average offtake rates.

It must be added that although mixing butane with propane may adversely affect gas withdrawal rates in certain conditions, the variation in the composition of gas obtained makes little or no difference to combustion in the usual type of appliances that are designed for use with LPG.

**Chapter 8**

**QUALITY CONTROL**

**AND**

**ANALYTICAL METHODS**

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## Chapter 8

# Quality Control and Analytical Methods

### 8.1 INTRODUCTION

We propose to begin this chapter with a discussion on the reasons for imposing some form of quality control on marketed LPG. These reasons will be apparent from an outline of the main outlets for LPG and of features which are required to ensure trouble-free operations. Since in practice the optimization of LPG quality is brought about within the framework of specifications, we continue with a critical review of certain international LPG specifications, i.e. of those quality items which are selected for control in the form of concentration limits, e.g. a maximum sulphur content, a minimum propane concentration, etc. Because this critique shows up certain anomalies and differences between specifications which are accepted by producers and users alike at the present time.

Specifications are meaningless without prescribed test methods which permit the particular quality feature to be determined accurately at the specified level of concentration. Therefore, the chapter ends with a brief description of analytical procedures which, in practical experience, have proved to be the most useful for this particular purpose.

### 8.2 WHY IS CONTROL OF QUALITY IMPORTANT?

As noted in Chapter 6, LPG rarely consists of pure C<sub>3</sub> or C<sub>4</sub> hydrocarbons alone. Rather, is it a refined light portion of crude oil or natural gas condensate, specially tailored at the refinery to suit a particular field of applications. It follows that commercial LPG is a mixture of hydrocarbons with possibly some impurities left over from the refining process or introduced between the points of manufacture and consumption. Quality control therefore becomes a matter of matching properties to applications, or applications to properties, and minimizing impurities without unduly increasing the product price.

The nature of established uses for LPG gives a clue to some of the properties which are either necessary or desirable for this product to possess. These outlets are discussed at length in later chapters. For the present, the main ones can be summarized along with desirable LPG properties as follows:

### **8.2.1 Bottled Gas**

- Maximum vapour pressure commensurate with the container design stress
- Natural vaporization at year-round temperatures
- No corrosion of container walls
- No blockage or fouling of pressure regulator
- No toxic impurities in the gas
- Minimum non-vaporizable residues
- Protection against icing on expansion of the vapour
- Detectable smell

### **8.2.2 Industrial Gas (burner and furnace requirements)**

- No corrosive action of liquid, or formation of deposits or residues in storage tanks, transfer lines, vaporizer, pressure regulators
- No corrosion or fouling of burner tips
- Controlled combustion characteristics (calorific value, Wobbe Index, flame speed)
- No catalyst fouling impurities (endothermic gas generators)
- No toxic impurities (agriculture and food industries)
- No freezing of separated water preventing liquid offtake or blocking gas ports, etc.

This outline of applications indicates that some form of control over many aspects of LPG quality is necessary if trouble-free operations are to be guaranteed.

Control over product quality is exerted in two ways. One is by the product distributor or the user setting a specification which suits the equipment or process into which the LPG is fed. Such a specification usually names a potentially harmful impurity and sets a limit on the concentration which can be tolerated. The other way is by the LPG producer setting his own manufacturing specification to match the user's requirements and by continuously testing quality by means of stream analyzers or laboratory checks. Both of these quality control methods are usually adopted in practice.

## 8.3 WHAT ARE THE IMPORTANT SPECIFICATION ITEMS?

The more important items for quality control are evident from the foregoing outline of applications. They can be grouped together and summarized as follows: vapour pressure; icing propensity; odour and toxicity; corrosiveness; non-vaporizable residues and certain other trace impurities.

### 8.3.1 Vapour pressure control

Is readily understood to be a matter of balancing the content of the main C<sub>3</sub>/C<sub>4</sub> hydrocarbon components against lower and higher boiling homologues, e.g. of specifying limits as follows:

#### Composition

- Maximum content: ethane, ethylene, pentanes
- Minimum content: propane, propylene, butanes, butenes

### 8.3.2 Icing troubles

Icing troubles are due to the presence or accumulation in LPG of water which may separate and freeze if the liquid temperature is low enough, or combine with the hydrocarbons or vapour to form relatively high melting gas hydrates. If the pressure is high enough, the presence of water also leads to rusting of non-stainless equipment and rust, in turn, can add to the residues problem. Therefore, a limit is usually placed on the content of water in one or all of three possible forms.

#### Water

- Free or entrained: 'none visible'
- Dissolved: maximum content

Another way of inhibiting icing problems is by the addition to LPG, more particularly to propane, of an anti-icing agent such as methanol. This lowers the temperature at which water can separate from the ternary hydrocarbon-water-methanol system. Thus, recommendations are often made regarding the concentration of methanol to be incorporated in LPG, particularly during the winter season.

Methanol content:

- minimum content (to prevent under-dosing)
- maximum content (to avoid contamination problems)



### 8.3.3 Toxicity and odour control

Toxicity and odour control is a matter of minimizing the content of hydrogen sulphide but allowing, in commercial grades, a very small proportion of certain volatile sulphur compounds such as ethyl mercaptans or dimethyl sulphide to impart a detectable odour. (For the highest purity grades, e.g. aerosol propellant LPG, the smell may have to be minimized by eliminating these sulphur compounds as well as any other odoriferous compounds such as unsaturated hydrocarbons.

#### ***Odour and toxicity***

##### **H<sub>2</sub>S:**

- maximum content (toxicity)

##### **Mercaptans** (volatile sulphur compounds):

- minimum content (detectable smell)
- maximum content (catalyst poisoning, no odour)

### 8.3.4 Corrosion

Corrosion of metal equipment is of course controlled by limiting the corrosivity of the product. Two methods of control are adopted in practice. One is to specify the degree of corrosion which is allowable under standardized test conditions, namely a slight discoloration of a copper strip immersed in liquid LPG for a specified time and at a prescribed temperature (e.g. 1 hr, 37.8°C). Copper is chosen because it is the most sensitive of metals likely to be encountered by LPG in ordinary process equipment. The other method is to limit the concentration of known corrosive agents which could be found in LPG. These agents are mainly H<sub>2</sub>S and elemental sulphur. Additionally, in very critical circumstances, control over corrosivity may have to be extended to cover trace impurities which could conceivably cause corrosion over extended periods. Such impurities or contaminants could include carbonyl sulphide, water, oxygen, ammonia, caustic alkali and dissolved chlorides.

#### **Corrosivity**

As to ***non-volatile residues***, these can comprise a miscellany of compounds ranging from incompletely separated refinery fractions such as pentanes and hexanes to the higher boiling contaminants such as lubricating oil, as well as certain sticky deposits from rubber hoses which were described in Chapter 3. They also include other forms of involatile material such as rust, dirt and elemental sulphur. As has been mentioned, the lighter ends (C<sub>5</sub>'s, C<sub>6</sub>'s) and also elemental sulphur are specified separately for other reasons.

## 8.4 WHAT SPECIFICATIONS EXIST?

- Such specifications as exist at the present time derive from many authorities, e.g. national (U.K., U.S.A., European, etc.), the LPG supplier (natural gas producer or oil company), industry (i.e. association of LPG interests) and user. They all relate to the type of LPG (propane or butane) which is used, to the type of application in question (e.g. domestic, industrial, chemical or automotive) and to the product grade (commercial or high purity).

	(a)	(b)	(c)	(d)	(e)
<i>Composition</i>					
acetylenes	—	—	✓	—	—
C <sub>2</sub> 's	—	—	✓	—	—
Ethylene	—	—	✓	—	—
Propylene	—	✓	—	—	—
Propane	—	✓	—	—	—
Propane + propylene	—	—	—	✓	—
C <sub>4</sub> and higher	✓	✓	✓	—	—
<i>Vapour Pressure</i>	✓	✓	✓	✓	✓
<i>Volatility</i> (95% evaporated)	✓	✓	—	—	—
<i>Residues</i>	✓	✓	—	✓	—
<i>Copper corrosion</i>	✓	✓	—	—	✓
<i>Sulphur compounds</i>					
H <sub>2</sub> S	—	—	✓	✓	—
Volatile sulphur	✓	✓	✓	✓	✓
Elemental sulphur	—	—	—	✓	—
Elemental sulphur + carbonyl sulphide	—	—	—	✓	—
Water, free	✓	✓	✓	✓	✓
Ammonia	—	—	—	✓	—
Alkali	—	—	—	✓	—
Hydrogen + nitrogen + oxygen + methane	—	—	—	✓	—

**Table 8.1 Specifications for Propanes**

- (a) NGPA, commercial  
 (b) NGPA, high purity  
 (c) British Standard Specification 4250  
 (d) Deutsche Normen 51622  
 (e) French Ministry of Industry & Agriculture CSR—15A  
 ✓ Item included in specification

A comparison of these specifications in terms of the items specified and the limits imposed are shown in Appendix 4, Tables 4(a) and 4(b) for propane and butane grades, respectively. Here, it is sufficient to highlight the fact that specifications differ in detail from country to country (see Tables 8.1 and 8.2).

The only items which are common to most specifications are vapour pressure, mercaptan-type sulphur compounds and free water. Some authorities also control corrosivity by inserting the copper strip test with a permissible discoloration limit; others adopt the indirect method of imposing limits on the corrosive agents, normally  $\text{H}_2\text{S}$ .

	(a)	(c)	(d)	(e)
<i>Composition, mol %</i>				
Propane	—	—	—	—
Butanes + butenes	—	—	✓	—
$\text{C}_5$ 's and above	✓	✓	—	—
Dienes	—	✓	—	—
Acetylenes	—	✓	—	—
<i>Vapour Pressure</i>	✓	✓	✓	✓
<i>Volatility (95% evaporated)</i>	✓	✓	—	✓
<i>Residues</i>	—	—	✓	—
<i>Copper corrosion</i>	✓	—	—	✓
<i>Sulphur compounds</i>				
$\text{H}_2\text{S}$	—	✓	—	†
Volatile sulphur	✓	✓	✓	†
Elemental sulphur	—	—	✓	—
Elemental sulphur + carbonyl sulphide	—	—	✓	—
<i>Water, free</i>	✓	✓	✓	✓
<i>Ammonia</i>	—	—	✓	—
<i>Alkali</i>	—	—	✓	—
<i>Hydrogen + nitrogen + oxygen + methane</i>	—	—	✓	—

**Table 8.2 Specifications for Butanes**

(a) NGPA, commercial

(c) British Standard Specification 4250

(d) Deutsche Normen 51622

(e) French Ministry of Industry & Agriculture

† Pass on \*Doctor Test\* required to indicate freedom from  $\text{H}_2\text{S}$  and mercaptans

✓ Item included in specification

The impurities most commonly omitted from user and some suppliers' specifications are many of those included in DIN 51622, i.e. elemental sulphur, corrosivity and oily residues and elements such as fluorine, chlorine, caustic soda, ammonia, oxygen, nitrogen, etc. However, it must be emphasized that a very restrictive specification serves no useful purpose unless the process concerned is known to be especially sensitive to certain aspects of fuel quality.

## **8.5 A GUIDE TO SPECIFICATION THINKING**

### **8.5.1 Composition**

LPG is primarily required to be a source of fuel gas. The bulk composition of the LPG will determine the combustion characteristics of the gas. If the liquid LPG is to be vaporized naturally as in the case of bottled gas, the LPG should have a high content of either C<sub>3</sub> or C<sub>4</sub> hydrocarbons or else the composition of the gas will be markedly different according to whether the bottle is near-full or empty. For industrial purposes, however, the liquid is always vaporized by external heating so that the characteristics of the gas remain constant as long as the liquid composition does not vary. In the latter case therefore, it is unnecessary to specify the exact composition of LPG propane or butane in terms of C<sub>3</sub>/C<sub>4</sub> contents. In both cases though, pentanes and hexanes should be limited to minimize residues. For propanes, the restriction could be 'nil C<sub>5</sub>'s and above', and for butanes 'nil C<sub>6</sub>'s and above' with a 2% maximum on C<sub>5</sub>'s and higher. The unsaturates content might be qualified in respect of critical applications such as, possibly, catalytic reforming processes and automotive fuel outlets.

It must also be mentioned here that the so-called 'volatility' specification test which measures the temperature at which 95% by volume of the propane or butane is evaporated is, in fact, an index of composition. In the particular case of commercial propane, the limit usually placed on this temperature is – 38.3°C. If this limit is to be met, the content of 'C<sub>4</sub>' and above' cannot amount to much more than 2.5 vol. %. Unless therefore the propane is particularly required to have a minimum content of 95% C<sub>3</sub>'s approximately, it will be found convenient to omit this test from specifications.

### 8.5.2 Vapour Pressure

A maximum vapour pressure is essential to ensure that LPG meets the requirement of pressure vessel design codes which apply in the countries concerned with handling the product. A minimum value may also be required to provide for a satisfactory gas flow rate by natural vaporization at low ambient temperatures. In very cold climates, a minimum vapour pressure may also be required to guard against vacuum conditions developing inside storage tanks containing a high content of normal (n) butane. This in turn would entail ensuring a minimum content of propane in butanes.

### 8.5.3 Sulphur Compounds and Corrosivity

The common practice of restricting corrosivity as judged by the copper strip test is a convenient means of limiting by the same token the concentration of the two types of corrosive sulphur compounds, namely  $H_2S$  and elemental sulphur. These may therefore be omitted from quality specifications unless specifically demanded for some aspects of process control. When required, levels recommended range up to 2.5 ppm weight ( $H_2S$ ) and 2 ppm (elemental sulphur), respectively. This leaves volatilisable sulphur compounds like mercaptans to be specified for odour control, a level of 25 ppm is adequate for this purpose and a reasonable maximum is 50 ppm, though some existing specifications allow up to 180 ppm weight total sulphur compounds.

### 8.5.4 Residues

A convenient limit to place on oily residues as judged by an evaporation procedure is 500 ppm by volume. This can be tolerated without undue nuisance to the user of residues building up in liquid vaporizers, though in some critical instances, the 50 ppm weight limit already advised in certain specifications may be found appropriate.

### 8.5.5 Water

The final specification item is water and two forms should be mentioned, free or entrained, and dissolved. The former should be related to a bottoms LPG sample from tankage and specified as 'non visible'. Dissolved water has to be determined by analysis. For full protection against the most critical icing conditions, the limits should be 10 ppm weight (propanes) and 20 ppm (butanes), respectively. If the LPG is not refrigerated or dried to provide for this low water content, a recommendation should be included for the addition of compensative methanol (usually 0.05 vol. % min). Restrictions on trace impurities should be imposed only if they are known to cause a particular application problem.

## 8.6 TEST PROCEDURES AND ANALYSERS

It is pointless to include a limit in specifications which cannot be measured accurately by either party involved in a dispute about LPG quality. Therefore, it is necessary to discuss existing analytical procedures for all the specification items previously mentioned. Where alternative methods exist, it is also necessary to pinpoint the most satisfactory technique as far as sensitivity, accuracy and repeatability are concerned.

### 8.6.1 The Importance of Sampling

Quality control starts at the point of production. Any departure of quality from an optimum or specified level is made evident by onstream analysers with the necessary corrective measures taken either manually or by means of an automatic signal from the analyser back to process. Unfortunately, automatic on-stream analysers are expensive, sometimes unreliable, and require frequent inspection and maintenance. Therefore, they are not viewed as favourably in practice as perhaps they should be. Recourse is made instead to intermittent sampling and laboratory analysis. This means that there is always a lag between actual and measured LPG stream composition.

The origin of the sample is very important, and the point and moment of sampling must be chosen in relation to the purpose for which the analysis is being carried out.

Another important point is size of sample. It has pointed out that reducing the liquid level of LPG inside a sample container increases the vapour volume. This in turn increases the mass of a volatile impurity (such as ethyl mercaptans or water) in the vapour phase and correspondingly decreases its concentration in the liquid phase. Thus analysis of successive liquid samples for volatile components can be expected to show diminishing concentrations. The best solution is, therefore, to use a sample container whose volume is large in proportion to the quantity required for analysis and not to further divide this sample into separate containers. Alternatively, one should take a fresh sample from the bulk source (refinery stream or tank) for each successive analysis, i.e. to work on a 'one test, one sample' basis.

Some further confusion can arise from the selection of either liquid or vapour phase LPG for analysis and the formulation of results, on a weight, mole or volume per cent basis.

Most analytical methods for LPG are based on gaseous samples, although the bulk of industrial users are more concerned about the quality of the liquid LPG which is supplied to them. Therefore it is essential to carry out every analysis on a totally vaporized, liquid sample. This ensures that no high boiling components of the liquid are left unaccounted for. It also prevents any bias due to preferential concentration of volatile impurities in vapour standing above the liquid, as in bottled (domestic) LPG. It is also suggested that results are most conveniently expressed on a weight basis, i.e. as weight per cent (wt %) or parts per million (ppm).

### **8.6.2 Sample Containers**

Two main types of sample containers are used. One is the stainless steel double-valve, cylindrical 'bomb' which ranges in size from 5 ml to 4.5L water capacity. The other is the free-standing domestic-type bottle, with single or twin gas valves, taking samples ranging in size from 3 to 50 kg. For replicate determinations of any single specification item 200 ml 'bombs' are suitable. For multiple determinations of a full range of items, a 25 kg bottle provides the requisite quantity without undue loss of components from liquid into the vapour phase between analyses.

Connections between LPG source and sample container should be made in stainless steel or aluminium tube. Nylon tubing is satisfactory in small diameters but flexible rubber or plastic (PVC/polythene) connections are not recommended on account of the leaching effect of the LPG on soluble components (i.e. plasticizer). Containers should be thoroughly cleaned and purged between samples.

'Bombs' are sometimes fitted with outage or 'ullage' tubes to ensure at least a 20% volume free vapour space to allow for liquid expansion with temperature rise. In sampling refrigerated propane, the ullage space should be increased to 30% for increased safety. If no outage tube is fitted, the maximum fill can be calculated and provided for by weighing the bomb before and after filling. The sampling procedure is to hold the bomb upright with the outage tube suspended from the top valve. Introduce a small quantity of liquid LPG through the bottom valve and crack open the top one so as to cool the bomb by liquid vaporization. Continue filling until liquid escapes from the top. Close both valves disconnect from sample line, open top valve, until only gas (no liquid) escapes.

If the vaporized LPG is to be sampled on industrial plants, water-cooled steel or ceramic suction probes are recommended for insertion into the flow lines. Gas can be withdrawn into water-filled glass sample tubes, aspirator bottles or metal gas holders. Plastic balloons are suitable only for short-term storage of gas samples and if 'chalked', may eliminate any acidic impurities before analysis.

### 8.6.3 Analytical Procedures

#### **Hydrocarbon Composition**

The most common method used is gas chromatography. A routine volatility check method which reports the temperature at which 95% by volume of the LPG is evaporated also indicates composition, as has already been explained.

In gas chromatography, a liquid LPG sample is vaporized in a stream of inert gas and passed through a gas-liquid partition column, maintained at a given temperature, which separates the LPG vapour into its component hydrocarbons. The components are detected in the effluent gas by means of a thermal conductivity or flame ionization detector, or similar detection device, using pure hydrocarbons as a check on relative retention times. In this way a series of 'peaks' are obtained in a chromatogram, each peak representing a pure component whose concentration is proportional to the area under the peak.

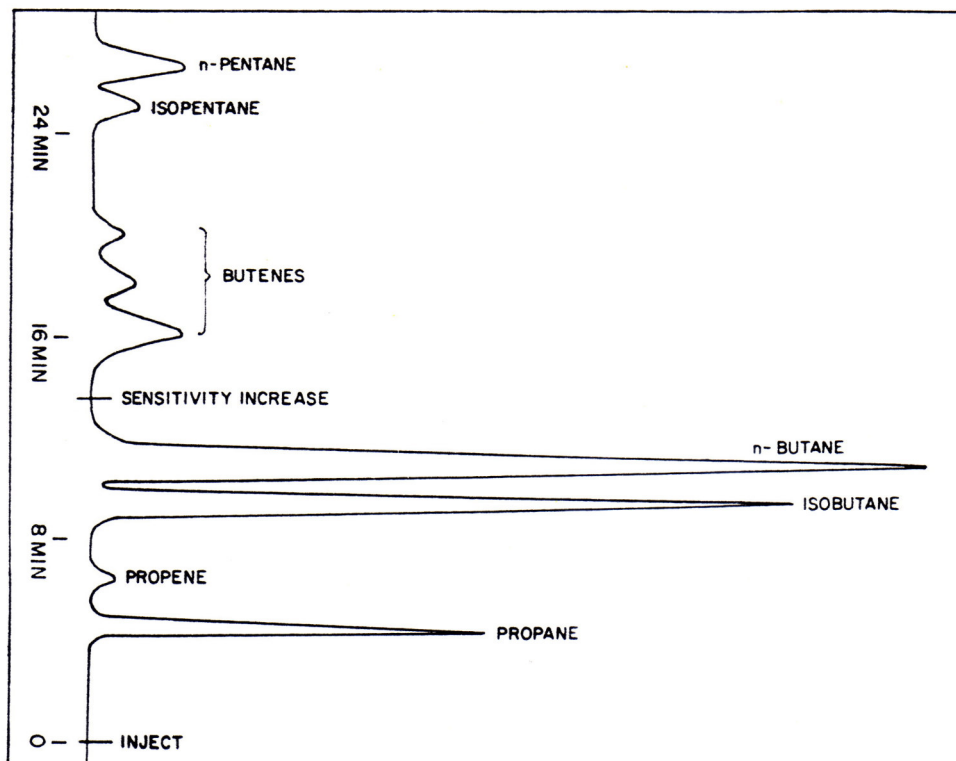
Squalene can also be used successfully when only saturates are present, and propylene carbonate if unsaturates have to be resolved. Thus, LPG can readily be analysed to 0.01 mol % of the following components; methane, ethane, ethylene, propane, propylene, n-butane, isobutane, butene-1, isobutylene, *cis*-butene-2, *trans*-butene-2, isopentane, n-pentane, hexanes. A typical LPG chromatogram is shown in Figure 8.1.

Laboratory gas chromatographic practices have also been applied to process control of LPG stream composition. In the case of a propane-butane splitter, this means resetting temperature and reflux ratio.

***The NGPA volatility test*** (ASTM D 1837) is used with a maximum of  $-38.3^{\circ}\text{C}$  for the 95% evaporation temperature in the case of propanes and  $+2.2^{\circ}\text{C}$  for butanes. Correlation work shows that the  $-38.3^{\circ}\text{C}$  temperature is met if the content of 'C<sub>4</sub>' and higher is not more than 2.5 %; if the butanes content in propane were 10% for example (as is allowed in B.S. 4250), the evaporation temperature would rise to  $-23.9^{\circ}\text{C}$ .



The limit of +2.2°C is met by all butanes containing not more than 2% of 'pentanes and higher', a composition which is typical of most commercial butanes.



**Figure 8.1 Gas chromatogram of LPG (British Gas Corporation)**

### **Vapour Pressure, Specific Gravity and Heating Value**

The compositional analysis of an LPG provides a convenient basis for calculating several properties, namely vapour pressure, specific gravity, motor octane number and heating value. The method uses the fact that any of these properties can be summed from the partial contributions of the various hydrocarbon components, e.g. in the case of the mean vapour pressure at 37.8°C ( $v$ ), allowing for main components only

$$v = av' + bv'' + cv''' \quad .$$

Where  $a$ ,  $b$  and  $c$  are the molar fractions of propane, n-butane and isobutane derived from the gas chromatographic analysis;  $v'$ ,  $v''$  and  $v'''$  are the respective vapour pressures of the pure components at the reference temperature (see Table 8.3). The other properties are calculated in similar fashion.

	<i>Vapour pressure, kg cm<sup>-2</sup> abs 37.8°C</i>	<i>Specific gravity† 15.6°C</i>		<i>M.O.N.‡ Blend value</i>	<i>Gross heating value k cal/kg 760 mm Hg, 25°C</i>
		<i>Liquid</i>	<i>Vapour</i>		
Propane	13.12	0.5077	1.5464	95.6	11,940
<i>n</i> -Butane	3.67	0.5844	2.0698	89.0	11,740
Isobutane	5.18	0.5631	2.0656	96.8	11,710

† The compositional analysis must be referred to either the liquid or the vapour phase, as required.

‡ M.O.N.: Motor Octane Number.

**Table 8.3 Factors for Calculation of Physical Properties**

In strict terms, summing of partial values applies only to ideal gases. For real gases such as propane and the butanes, account should be taken of their compressibility. Thus the true heating value for example,  $H'$  is obtained by dividing the apparent value derived from the compositional analysis ( $H$ ) by the mean compressibility factor applying to the mixture ( $Z$ ), which can be calculated from the component values thus:

$$H' = H / Z$$

Apart from calculation methods, vapour pressure can be measured directly using a thermostatted bomb, suitably 'ullaged' to allow for liquid volume expansion between sampling and measurement temperatures, connected to a pressure gauge.

Specific gravity of the liquid phase LPG can be determined using a pressure hydrometer.

### **Hydrogen Sulphide**

Two types of method for assessing  $H_2S$  concentration can be used. One is an inferential method based on the staining of lead acetate paper. The other is quantitative and is carried out by converting the  $H_2S$  to a mineral sulphide and estimating the same either calorimetrically or titrimetrically.

For regular monitoring of LPG production, the authors recommend using a vaporized liquid sample and testing the gas by a stain procedure selected from those described according to the detection limit required—with occasional use of the colorimetric methylene blue method for checking the actual  $H_2S$  content.

**Total Sulphur**

The so-called 'total' sulphur content of LPG is only a measure of volatile sulphur compounds ( $\text{H}_2\text{S}$ , light mercaptans and low boiling sulphides, etc.) which pass into the gas phase when the liquid test sample is evaporated at about  $80^\circ\text{C}$  into a test burner. This technique takes no account of elemental sulphur or relatively involatile forms of sulphur compounds which may be present in the liquid LPG.

An alternative method preferred by the authors involves electrometric titration of an alkaline solution of the mercaptans using silver nitrate solution, with a glass/silver sulphide electrode system to indicate the end point. The procedure enables hydrogen mercaptan ( $\text{H}_2\text{S}$ ) to be determined separately from other mercaptans (methyl, ethyl, etc.) which are determined collectively.

**Elemental Sulphur and Involatile Sulphur Compounds**

There are four main methods, the mercury test, the Sommer test, a colorimetric method and a combustion technique. All four depend on the preliminary extraction of the sulphur by bubbling a known weight of the LPG through toluene. The toluene solution is heated to remove any remaining LPG or volatile compounds.

**Oily Residues**

A number of test methods are available but selection depends on the type of residue that is to be determined.

As already mentioned, gas chromatographic analysis is available to measure the amount of low boiling  $\text{C}_5/\text{C}_6$  residues present in LPG. If the technique could be extended to include the higher boiling residues in the  $\text{C}_6$  to  $\text{C}_{30+}$  range, which are sometimes encountered in practice, it would be highly recommendable. Unfortunately, this is not yet at this stage.

In the industry, residues are usually taken to refer to 'oily residues', i.e. evaporated residues after removal of  $\text{C}_5/\text{C}_6$  fractions leaving mainly lubricating oil. One test method entails the evaporation of about one liter of the LPG at room temperature and the further heating of the residue on a steam bath for five minutes in order to remove unwanted pentanes and hexanes. The final residue is weighed. The drawback of this test is that the residue will contain all non-evaporated material boiling above heptane, i.e. gas oil as well as lube oil in addition to any elemental sulphur, dirt and rust present in the sample.

A more reliable measure of the lube oil content can be obtained by '*infra-red spectroscopy*'.

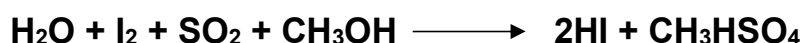
In all these residue methods, a word of caution needs to be added. The use of plastic or rubber connecting tube should be avoided. What might pass as a mineral oil residue often turns out to be a plasticizing compound such as phthalates or ricinoleates leached out by the LPG from plastic tubing used in the sampling or test equipment. Before reporting, therefore, the identity of the residues should be checked by infra-red examination.

### **Water**

A number of different methods are available. They include the following:

1. Chemical reaction with Karl Fischer reagent
2. Colour change with an indicator such as cobalt bromide
3. Dew point method
4. Gas chromatography
5. Instrumental techniques giving an instantaneous reading on a calibrated scale
6. 'Valve freeze' method

The **Karl Fischer method** is reliable and accurate down to 20 ppm of water in LPG. A known volume of LPG vapour is passed through anhydrous methanol. The water absorbed is titrated with Karl Fischer reagent, i.e. a mixture of iodine, sulphur dioxide and pyridine. The main reaction, in which the pyridine does not take part, is:



**Gas chromatographic** techniques have already been outlined for determining hydrocarbons. Water can be separated from the hydrocarbons on a column containing polyethylene glycol on a polystyrene bead support.

### **Trace Impurities**

**Ammonia:** A number of different methods have been proposed, namely titrimetric, colorimetric and indicator.

**Chlorine:** Total chlorine comprising both inorganic and organic forms is determined by reaction with sodium diphenyl dissolved in toluene. The method is sensitive down to the 1 ppm level.

**Fluorine:** The basis of the method is again the removal of fluorides and fluorine compounds from the sample by bubbling the gas through a toluene solution of sodium diphenyl.

**Carbonyl Sulphide:** This can be determined down to 0.1 vppm by gas chromatography using a Porapak-Q column.

**Oxygen and Nitrogen:** These gases can be analysed at the 1 ppm level by gas chromatography using 60-80 mesh 13 molecular sieve and a thermal conductivity detector.

# **Chapter 9**

# **COMBUSTION OF LPG**

## **Chapter 9 Contents**

### **9.1 OXIDATION OF HYDROCARBONS**

- 9.1.1 Chemistry of Oxidation Reactions
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### **9.2 COMBUSTION OF GASES**

- 9.2.1 Premixed and Diffusion Flames
- 9.2.2 The Bunsen Burner
- 9.2.3 Combustion Characteristics of Gases
- 6.2.4 Interchangeability Concepts

### **9.3 EFFICIENCY OF LPG COMBUSTION**

- 9.3.1 Stack Losses
- 9.3.2 Other Heat Losses
- 9.3.3 Heating Efficiency

## Chapter 9

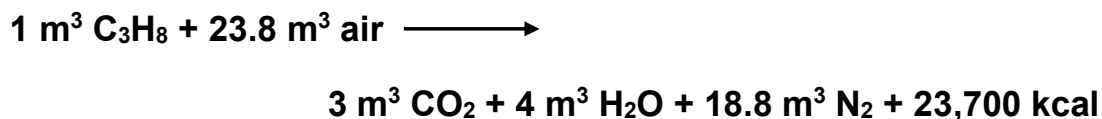
# Combustion of LPG

In this chapter, it is proposed to discuss high-temperature hydrocarbon oxidation processes with special reference to the combustion of LPG. We propose to deal with the chemistry and thermochemistry of the oxidation/combustion reaction, with the characteristics of diffusion and premixed hydrocarbon flames and the particular problems of gaseous flames and combustion. The chapter continues with a discussion of the combustion characteristics of gases and of the concept of gaseous interchangeability, and concludes with a review of combustion efficiency.

## 9.1 OXIDATION OF HYDROCARBONS

### 9.1.1 Chemistry of Oxidation Reactions

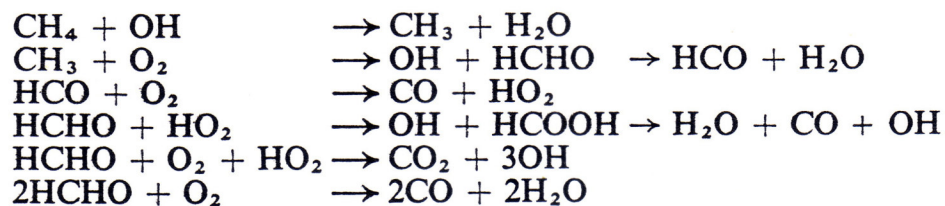
In its simplest form, the oxidation of propane follows the path indicated in Chapters 6 and 7. From these, it will be gathered that the burning of 1 m<sup>3</sup> of propane results in the liberation of 23,700 kcal of heat. Furthermore, it indicates that five volumes of oxygen or nearly 24 volumes of air are required in order to ensure complete combustion of one volume of propane to form three volumes of carbon dioxide and four volumes of water. Implied in the figure for heat evolution is that this water vapour is condensed and that the latent heat of the steam is given up; in other words, 23,700 kcal /m<sup>3</sup> is the gross calorific value of propane. The following volumetric balance applies:



In actual fact, this equation is an over-simplification: first it is difficult to ensure complete combustion with the exact equivalent (stoichiometric) of oxygen or air. It is necessary to provide a slight excess of oxidant in order to ensure complete oxidation. If excess air or oxygen is not available, some of the fuel will not burn to CO<sub>2</sub> and partial oxidation products will be formed. These include principally carbon monoxide and hydrogen, but frequently unsaturated hydrocarbons, formaldehyde and sometimes elemental carbon are also found. If combustion stops at these intermediate stages, the heat evolution is substantially reduced, and to ensure complete conversion into partial oxidation products, it may be necessary to introduce heat, rather than withdraw it from the reaction.



A further complication in the combustion of hydrocarbons is the fact that the reaction proceeds by way of a chain of intermediates which are formed before the final oxidation product appears. These intermediates are short-lived chemical entities or radicals; but they have the power to propagate combustion and to ensure that a flame, once it has started, also continues to burn. An example of a chain reaction involving the combustion of methane is shown in Table 9.1.



**Table 9.1 Chain Reactions- Methane Combustion**

A further aspect of the combustion of LPG, are the limits of composition beyond which it is impossible to propagate a flame. Although the actual fuel concentration required ensuring ignition depends on a number of factors such as direction of burning, size and shape of vessel, intensity of igniting mechanism, humidity, etc., there is a distinct difference for any given set of conditions between the inflammability limits of different hydrocarbons. It will be gathered from Table 9.2 that propane and the two butanes only burn over a relatively narrow range of concentrations: flammable mixtures of hydrogen or town gas and air cover a much wider area, and even methane is ignitable over a wider range.

	<i>Lower limit</i>	<i>Upper limit</i>
Hydrogen	4.1	74
Methane	5.3	14
Acetylene	2.5	80
Ethane	3.2	12.5
Propane	2.4	9.5
Butane	1.8	8.4

† Upward propagation in 5 cm diameter tubes.

**Table 9.2 Flammability Limits † Vol. % in air, 75°C, 1 atm**

The stoichiometric volume of oxygen or air consumed by a flame can be shown to be an approximate measure of its thermal output. As shown in Table 9.3 both air and combustion gas volumes in terms of unit heat of combustion differ very little over a wide range of gaseous fuels, a phenomenon due to the similar heat of combustion of one carbon atom to  $\text{CO}_2$  and of four hydrogen atoms to two  $\text{H}_2\text{O}$  molecules, each requiring one mole of  $\text{O}_2$ .

<i>Gaseous fuel</i>	<i>Calorific value gross—kcal/Nm<sup>3</sup></i>	<i>Stoichiometric volumes, Nm<sup>3</sup>/1000 kcal</i>		
		<i>Oxygen</i>	<i>Air</i>	<i>Flue gas (air)</i>
Hydrogen	3050	0.164	0.780	0.862
Methane	9572	0.209	0.995	1.10
Ethane	16,530	0.212	1.008	1.10
Propane	23,700	0.211	1.005	1.08
Butanes	31,510	0.206	0.981	1.03

**Table 9.3 Stoichiometric Ratios for Various Gases**

### 9.1.2 Physical Processes Involved in Oxidation

Although it is essential for suitable chemical species, i.e. fuel and oxidant, to be present for combustion to take place and for radicals to be formed to maintain the flame, it is also necessary for suitable physical conditions to prevail to enable one to ignite the gases and to maintain a hydrocarbon flame. Specifically, the flow of fuel and of oxygen or air must be such that the different molecules have an opportunity to make contact (collide) and that the energy created in these collisions and the subsequent reaction can be dissipated and passed on to other molecules to enable them to undergo the same reaction. There must therefore be good mixing of the two species either by diffusion of one gas into the other, or by some form of mechanical mixing.

The principal effect of oxidation reactions taking place is, of course, the release of energy, mainly heat. This, in conjunction with the volume increase of the gases caused by the raised temperature, will often produce pressure changes, and since combustion can be fast, these pressure changes can be explosive. In fact, the oxidation reactions, particularly of the fast-burning gases such as hydrogen or acetylene, are often of an explosive nature, and can result in damage to or destruction of the confining vessels. Similarly, an excessive increase in temperature can melt burners, refractory and heat transfer surfaces.

### 9.1.3 Hydrocarbon Flames

Although oxidation of hydrocarbons can take place at different temperatures, the more usual concept of a flame is one in which oxidation takes place at a temperature of 500°C or more with the simultaneous production of heat and light. When oxidation occurs at lower temperatures, it results in so-called cold flames, which often precede the ignition and oxidation of a hydrocarbon fuel. Although cold flames differ from high-temperature reactions, particularly in their rate and controllability, they may well involve the same short-lived intermediates which maintain the continuity of high-temperature flames.

It is worth bearing in mind that the majority of true flames only involve gaseous components; only carbon may be consumed directly by oxygen-containing gases and possibly burns as a solid on the surface; but even this is not altogether certain, since volatile carbon vapours which diffuse into the surrounding air also produce a gaseous flame. Liquid hydrocarbons are either completely vaporized before combustion or they are finely dispersed in an atomizer to form droplet flames. The droplets vaporize in the flame itself, and combustion occurs when the vapour contacts the surrounding atmosphere. In principle, therefore, a cloud of burning hydrocarbon droplets does not differ too much from the sort of gaseous diffusion flame which results from a stream of hydrocarbon gas mixing with atmospheric air.

Nevertheless, there are differences: a hydrocarbon droplet exposed to the heat and radiation of the surrounding flame will tend to decompose into carbon and hydrogen, a process referred to as cracking. The resulting solid carbon will not only be much more difficult to burn, but will also emit continuous radiation, typical of an incandescent solid. This means that liquid hydrocarbon flames will almost invariably be luminous due to the solid carbon particles formed in the flame; gaseous hydrocarbons, on the other hand, will rarely be exposed to flame radiation to such an extent that cracking of the hydrocarbon takes place. It will be more usual for the hydrocarbon vapours to burn direct, eventually to carbon dioxide and water. Their flames will consequently tend to be transparent, there being no solid particles present to provide luminous radiation.

## 9.2 COMBUSTION OF GASES

### 9.2.1 Premixed and Diffusion Flames

Whereas the combustion of liquid hydrocarbons involves vaporization, and therefore invariably the formation of a diffusion flame, which "can be laminar or turbulent, the combustion of gas, on the other hand, can take place in two distinct types of burner systems which show fairly basic differences. The so-called **premixed flame** involves blending of primary air with the fuel gas before ignition takes place. The extent of premixing varies, and can range from a few per cent up to 100% of stoichiometric oxidant requirement. A gaseous **diffusion flame**, on the other hand, burns at the interface between a stream of gas and the surrounding atmosphere. In other words, all the necessary air is supplied directly to the flame rather than mixed in with the gas. The combustion gases and oxygen have to diffuse in opposite directions away and towards the combustion zone, respectively.

It will be appreciated that such a flame will be essentially stationary as long as the rate of flow of the two gases remains unchanged. It will also be relatively quiet, and since it is easier to supply a sufficient volume of air to a low-molecular-weight hydrocarbon flame than to one consuming a more complex molecule, it will only be possible in practice to burn hydrogen and methane with atmospheric air in such a system, unless one is prepared to accept a high degree of turbulence and noise or incomplete combustion and carbon formation.

Atmospheric diffusion flames, particularly of the heavier gaseous fuels, will rarely be transparent (blue flames) and especially olefinic gases or aromatics will tend to produce yellow tips and may smoke, unless special provision is made, e.g. by induced turbulence or air preheat, to prevent cracking and to produce a non-luminous blue flame.

However, practically all gaseous fuels can be burned in premixed flames without producing luminosity or smoke. This will be assured by supplying part of the combustion air as primary air, before combustion takes place; however, the actual level of primary aeration necessary to prevent incomplete combustion will depend on the type of burner, the available space for gaseous combustion, the required burner turn-down ratio and the use to which the flame is to be put. From experience, it can be said that most gases burn best if 40-60% of the stoichiometric air requirement is added in the shape of primary air; higher levels often produce flash-back, lower degrees of aeration may result in yellow flame tips.

This level of primary aeration can quite easily be achieved by injecting either air or gas, usually the latter, through a jet into a venturi tube. The gas velocity change, as the gas issues from the injector orifice, produces a pressure drop which in turn is used to aspirate atmospheric air. The latter then mixes with the gas in the venturi or mixing tube and issues at the top of the tube as a partly premixed gas-air mixture.

The advantage of such burners is that only one of the gases need be supplied under pressure; and even that need only be a few inches water gauge for most gases to ensure complete mixing and satisfactory primary aeration. This simplifies and cheapens burner design, and in fact the vast majority of small burners and quite a few intermediate size burners employ the principles of gas injection, primary aeration and premixing.

Injector orifices can be selected from a standardized size range of diameters and areas to provide for a given gas flow rate (and consequently a given heat release on combustion) of propane or butane at a fixed gas inlet pressure. Such LPG orifice charts are often supplied by manufacturers of various types of burners. One example listing drill size numbers from 80 to 15 (orifice diameters 0.343 to 4.60 mm) and corresponding heat flows for the two LPG at 280 mm w.g. pressure is provided in Appendix 5.

## **9.2.2 The Bunsen Burner**

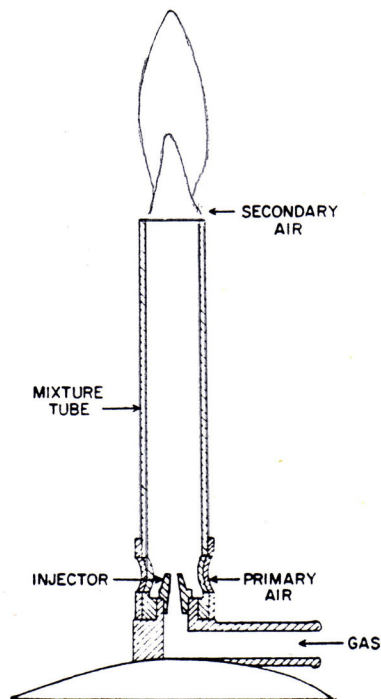
The first gas burner to use the above-mentioned principle of premixing and primary aeration dates back to the early nineteenth century and was invented by the German chemist, F. Bunsen; a modern laboratory Bunsen burner shown diagrammatically in Figure 9.1 only differs in minor details from Bunsen's original design.

The burner consists of an injection jet set into its base, through which the gas enters the vertical mixing tube. Air enters the latter through a cylindrical shutter mechanism, surrounding the injection jet, and this permits one to regulate the degree of primary aeration and thus to change the shape and character of the flame. Air and gas diffuse into each other while ascending through the mixing tube; the mixture burns when it leaves the tube as a result of the availability of secondary air, and also due to the slower rate of flow, which provides suitable conditions for the formation of a steady flame.

A precondition for flame stability is, of course, that the flow of gas-air mixture and the rate of combustion are reasonably well balanced. The flame which develops at the burner head consists of an inner cone which is usually blue and made up of unburnt gases, and of an outer, slightly luminous envelope of

burning fuel. Both cone and envelope are anchored to the circumference of the Bunsen head.

The Bunsen burner has remarkable flexibility; the mixing tube, for instance, need not be vertical but can be inclined or horizontal; gas injection can be in any direction and the air openings in the shutter could be either fixed or of variable size. Gas throughput can vary over a wide range, but it will be found that too low a flow of gas and air will result in flash-back; in other words, the flame, instead of being attached to the burner head, descends through the mixing tube and eventually burns on the injection jet. On the other hand, if gas flow is excessive, the flame may lift.



**Figure 9.1 Atmospheric partial premix (Bunsen) burners**

The tendency to either of these extremes can be reduced by subdividing the burner mouth into a number of small openings, the so-called flame ports.

The amount of primary air aspirated into the gas will affect the quality of the flame. Insufficient air will produce a soft and luminous diffusion flame; a high degree of aeration (over-aeration) will make the flame noisy and turbulent, but sharp and hard. Gas flow itself can be varied over a fairly wide range and flame length will clearly alter, as a result. With many gases turn-down ratios, particularly in modified Bunsen burners, can be as high as 10 or 15.

On the other hand, having chosen the injection jet to provide the required range of heat inputs for a given gas, it is not easy to change to another gas without affecting burner performance. In the light of the extensive use of premixed burners of this type, it is therefore important that any replacement gas substituted for a given reference gas should have combustion characteristics which should still be acceptable in a Bunsen burner which had been adjusted to operate on the original gas.

### 9.2.3 Combustion Characteristics of Gases

In order to ensure that the thermal output of a burner remains the same, it will be necessary for the flow of energy through the injector jet to be constant. Since the thermal energy of a gas is directly proportional to its calorific value, and the flow rate through an orifice is proportional to the square root of the pressure and inversely proportional to the square root of the gas density, a combined parameter known as the

$$\text{Primary aeration} = \frac{\text{Cal. value} \times \sqrt{\text{Pressure}}}{\sqrt{\text{Density}}} = W \times \sqrt{P}$$

is generally used to express heat flow. At constant pressure, the standard **Wobbe Index** (W), is a measure of the energy passing through a pipe or burner and is characteristic of any gas or gas mixture. The percentage of primary air entrained into the mixing tube, on the other hand, is inversely proportional to the heat flow, but directly proportional to the momentum of the gas emerging from the jet. Since the latter is proportional to the injection pressure of the gas, which is also called the gas modulus.

$$\text{Extended Wobbe Index} = \frac{\text{Pressure} \times \sqrt{\text{Density}}}{\text{Cat. Value} \times \sqrt{\text{Pressure}}} = \frac{\sqrt{P}}{W}$$

An interesting point emerges from this relationship. Since different gases and even LPG (propane) and LPG (butane) have quite different Wobbe Indices one cannot ensure the same thermal output and the same primary aeration by a change of supply pressure, as demonstrated in Table 9.4 opposite.

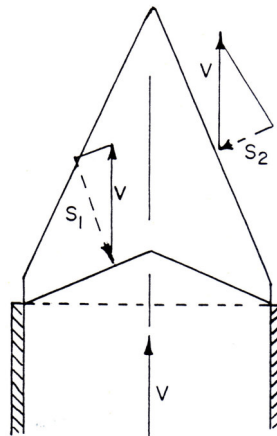
	<i>Wobbe</i>	<i>Supply pressures† for equal</i>	
		<i>Thermal input</i>	<i>Primary aeration</i>
Ethane	16,450	405	250
Propane	19,400	350	350
Butane	22,200	270	455
Pentane	24,450	220	555

† Based on 350 mm water gauge for propane.

**Table 9.4 Supply Pressures for LPG Component Gases (mm water gauge)**

It is worth noting that in some countries, local standards for butane and propane pressure regulation attach more importance to equal aeration, e.g. in Germany and Scandinavia, but in other areas they insist on equal thermal output, e.g. in the U.K. and France. Although this may be due to local differences in appliance sensitivity, it probably also follows that the same supply pressure for both propane and butane (say, 350 mm water column) should, as a rule, be capable of limiting variations in primary aeration and thermal output to an acceptable level.

**V = Velocity of Mixture Flow**  
**S<sub>1</sub> = Flame Speed (High)**  
**S<sub>2</sub> = Flame Speed (Low)**



**A Low Flame Speed Produces a Long Flame Cone**  
**A High Flame Speed, a Short Cone**

**Figure 9.2 Effect of burning velocity**



An important characteristic of a gas which is associated with its ability to maintain a steady flame in a premixed burner head is its **burning velocity**. From Figure 9.2 it will be clear that in order to balance a constant gas flow (velocity  $V$ ) through the mixing tube, the flame speed  $S$  and the component of  $V$  at right-angles to the flame must balance. Although the height of the cone will adjust itself to match minor fluctuations in gas mixture flow rate or burning velocity (the effective component of  $V$  equals  $V \times \sin \alpha$ , where  $\alpha$  is the cone angle with the horizontal), there must not be any major changes in flame speed of the gas or gas flow through the mixture tube, if flash-back or blow-off is to be avoided. From Table 9.5 it will be gathered that burning velocities of hydrocarbon gases do not vary widely: but hydrogen-containing gases and acetylene would strike back in burners designed for methane or LPG.

Two further gas combustion characteristics, the **yellow tipping index** and the **sooting index**, are of some significance when replacing one gas by another. Although a yellow flame will develop even without a change of fuel if the supply of primary air is restricted, some gases, especially the higher paraffins and olefins, are prone to yellow tipping and smoking, even if there is sufficient primary aeration.

Table 9.5 lists numerical values of all the above-mentioned combustion characteristics for the main components of LPG and for some other common fuel gases.

	<i>Cal. value gross, kcal/N m<sup>3</sup></i>	<i>Wobbe Index kcal/N m<sup>3</sup></i>	<i>Weaver flame speed factor</i>	<i>Delbourg Yellow tipping index</i>	<i>Sooting index</i>
Acetylene	13,970	14,685	60	252	—
Hydrogen	3050	11,570	100	0	—
Methane	9520	12,780	14	134	1.34
Ethane	16,820	16,450	17	279	2.03
Propane	24,120	19,400	16	386	3.21
<i>n</i> -Butane	32,000	22,240	16	472.5	3.05

**Table 9.5 Combustion Characteristics of Gases**

### 6.2.4 Interchangeability Concepts

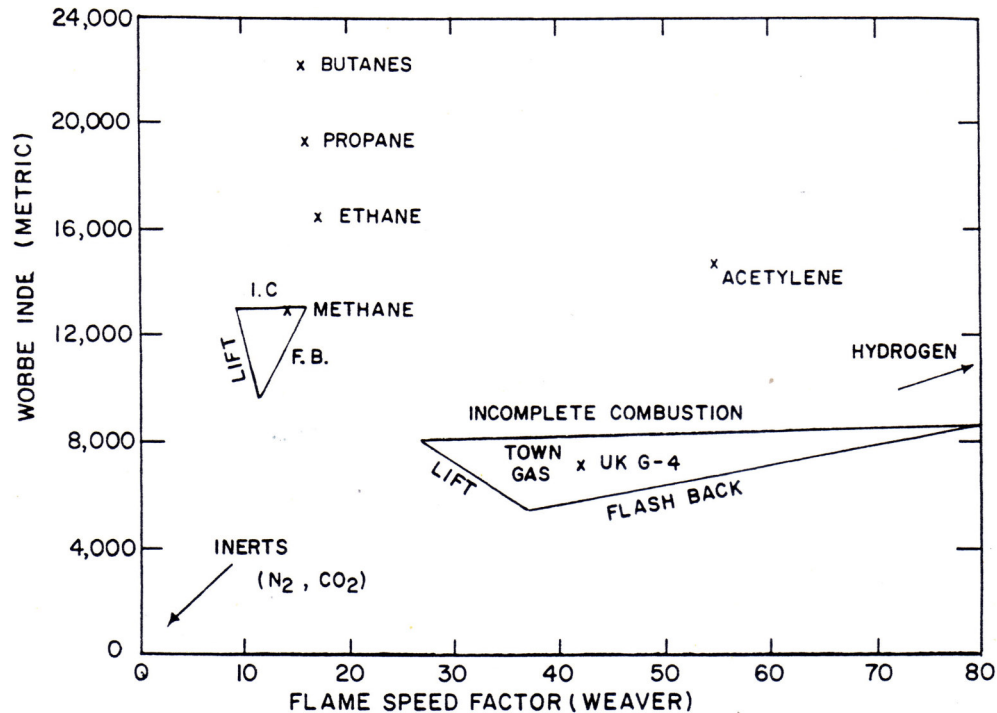
Since gaseous fuels are generally distributed over a wide area and used in a multiplicity of burners and appliances, it is essential that a gas of standard quality should at all times be supplied through the entire system. This maxim applies as much to the public piped distribution grid as to the sale of LPG in cylinders; changes in quality, even if the gas originates from different suppliers, will affect performance, economy and safety of both domestic appliances and industrial burners.

Since the bulk of gaseous fuels is used in air-aspirated premixed burners, it is highly desirable that gas supplies should vary as little as possible in regard to the combustion characteristics mentioned in the previous section; one would wish, for example, that all cylinder or grid supplies should have the same and if the gas is measured and charged by volume, it should also have a constant calorific value.

- Wobbe Index (or at least extended W.I)
- Gas modulus
- Flame speed
- Yellow tipping index
- Sooting index

The difficulty of maintaining all these parameters constant in spite of a possible change in gas composition is obvious. It is also clear that changes in combustion characteristics are permissible provided that they fall within the flexibility of the burner population to which the gas is supplied. To establish gaseous interchangeability it is, therefore, essential to study the demands of the burners and appliances, particularly of sensitive equipment, in the particular market.

A point worth bearing in mind is the interdependence of different combustion characteristics; in fact appliance flexibility can most easily be represented by a combustion diagram. Figure 9.3 shows the diagram used to estimate permissible variations in Wobbe Index and flame speed by Gilbert and Prigg. It also shows points representing pure gas components and the effects of blending nitrogen, hydrogen, and hydrocarbon gases into a gas of a given Wobbe Index and flame speed.



**Figure 9.3 Intel-changeability Diagram (Weaver-Gilbert-Prigg)**

The flexibility of a typical gas appliance population is shown by the two triangles for coal gas (first group of gases) and for natural gas (second group). LPG, it will be noted, can be made to match natural gases by blending with nitrogen or air, but can never become interchangeable with coal gas.

The boundaries of the interchangeability triangles are formed by the line of critical change in flash-back tendency, represented by the right-hand lower limit sloping upwards, beyond which either too high a flame speed or too low a Wobbe Index cause flame travel down the mixing tube; by the lifting line on the lower left hand sloping downwards, where a low burning velocity and a low Wobbe Index will result in flame lift; and finally by the almost horizontal incomplete combustion line which shows the effect of too high a Wobbe Index on carbon monoxide formation.

Other combustion diagrams use similar concepts such as combustion potential (the equivalent of flame speed) and a modified Wobbe Index, to replace the standard Wobbe Index defined here, in the Delbourg system, in which the simple Gilbert-Prigg triangle becomes a more complex shape, bounded by curved rather than straight lines.

## 9.3 EFFICIENCY OF LPG COMBUSTION

Although the combustion of LPG with stoichiometric or excess oxygen generates a given quantity of heat energy, i.e. does not vary in its efficiency, it is not possible to utilize the full amount of heat energy which is generated. There are, in fact, certain inherent losses, in all forms of heating, and the efficiency of a combustion process is the ratio of heat energy recovered in the operation to that supplied in the form of fuel.

Heat losses are of two kinds: first not all the heat which is generated will reach the material which is to be heated. Some energy will be required, e.g. to heat furnace refractory linings, insulation and the furnace structure itself; some heat will also be lost by radiation and convection from furnace roof and walls, through open doors or curtains, etc. Secondly, combustion gases will leave the furnace at elevated temperature and will entrain part of the heat energy of the fuel into the stack.

Although one cannot as a rule predict with accuracy how much heat energy will be lost by the first mechanism, since this type of loss depends on furnace construction, temperature distribution, ambient temperature and other factors, one can predict stack losses once operating conditions in a furnace have been established.

### 9.3.1 Stack Losses

Stack heat losses are a function of stack gas volume and stack gas temperature. It has been mentioned that stoichiometric combustion produces a volume of gas which, in the case of hydrocarbon gases, is mainly a function of the gross calorific value. Most LPG, unless they are highly unsaturated, will produce about 10.5 ft<sup>3</sup> of gas per 1000 Btu of fuel consumed (1.18 m<sup>3</sup>/1000 kcal). Excess air over and above that required for stoichiometric combustion will simply pass through the process, get heated to stack temperature and increase the volume of stack gas, thus reducing the overall efficiency by a corresponding amount.

Stack temperatures have to be maintained at a sufficiently high level to ensure buoyancy of the gases and a sufficient chimney draught. Furthermore, stack temperatures must not drop below the water dew point of the stack gases since condensation of water in the stack can cause corrosion and condensed vapour also results in a visible plume. Finally, if a combustion process is used to heat material to a certain temperature it is as a rule

unavoidable for the stack gases to be exhausted at a higher temperature (heat can only be transferred from a higher to a lower temperature level) and in a batch process the heat sink, particularly towards the end of the heating period, tends to be hot. In continuous processes one can sometimes cool combustion gases by countercurrent flow against freshly charged cold material. But in either process certain limitations on flue gas temperatures are imposed and there will always be a minimum stack temperature which has to be maintained.

Once stack temperature and volume of excess air are known, stack losses can be calculated with the aid of tables which allow for the specific heat of the flue gas components, itself a function of temperature, and of the composition of the flue gas, which depends on fuel make-up and excess air volume. Table 9.6 lists stack losses for a series of stack temperatures and excess air volumes for propane and butane combustion, the flue gases of which are close enough in composition to result in closely similar stack losses.

While it is theoretically possible to measure excess air volume, the accuracy of such measurements will generally be low. It is, therefore, common practice to calculate excess air from the composition of the flue gas and specifically from its carbon dioxide content.

<i>Stack temperature</i> † °C	<i>Excess air, %</i>			
	0	10	50	100
150	12.2	12.8	14.5	16.9
200	13.8	14.5	17.2	19.8
300	17.5	18.3	22.0	26.6

† Reference and ambient temperature 15°C throughout.

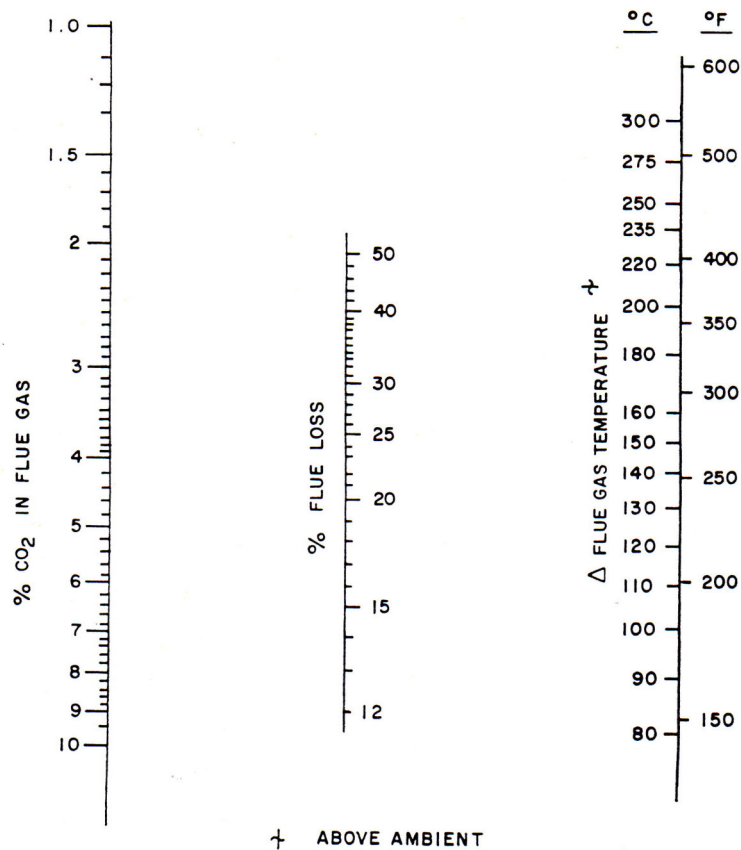
**Table 9.6 Per cent Stack Losses as a Function of Excess Air and Stack Temperature**

Provided that a minimum of stoichiometric oxygen is present all the carbon in the fuel will be converted into carbon dioxide, and Table 9.7 lists in its first numerical column the CO<sub>2</sub> concentrations which result from the stoichiometric combustion of various gases. The reduction in CO<sub>2</sub> concentration which results from excess air combustion listed in the remaining columns is shown to be sufficient to be used as a parameter for the determination of percentage excess air.

<i>Fuel</i>	<i>% Excess air:</i>	<i>Per cent CO<sub>2</sub></i>			
		<i>0</i>	<i>10</i>	<i>50</i>	<i>100</i>
Ethane		13.18	12.25	8.95	6.55
Propane		13.75	12.50	9.10	6.65
Propylene		15.05	13.10	9.40	6.90
Butanes		14.05	12.65	9.20	6.70
Butenes		15.05	13.10	9.40	6.90

**Table 9.7 Per cent CO<sub>2</sub> in Stack Gas as a Function of Fuel and Excess Air**

Thus, in practice, if one wishes to calculate stack losses in a combustion process one only has to measure flue gas temperature and CO<sub>2</sub> content of the gas at the furnace outlet. Alignment diagrams of the type shown in Fig. 9.4 are commonly used to simplify such calculations and to facilitate numerical interpolation. (See also Figures 7.3, 7.4).



**Figure 9.4 Alignment chart for calculation of flue gas losses**

### 9.3.2 Other Heat Losses

As already mentioned, the quantitative assessment of heat losses other than in the flue gases, on the basis of first principles, is extremely difficult. In practice repeated operation of a furnace under varying firing rates, while measuring both stack losses and useful heat transferred during a heating cycle, will enable one to calculate 'other losses' and ultimately to predict losses for other heating cycles. Experience in operating a furnace will ultimately lead to optimum firing rates in line with minimum heat loss and optimum throughput.

In addition certain elements of the 'other loss' total can be estimated: e.g. radiation loss from the furnace follows the Stefan-Boltzman Law, i.e. will be proportional to the fourth power difference between surface and ambient temperature.

$$\text{Loss}_{\text{rad.}} = K_1 \times A \times (T_1^4 - T_o^4)$$

Where:  $K_1$  is a constant and  $A$  is the surface area. Apart from radiation, heat will also be lost by convection, due to air currents round the furnace, and here the losses will be proportional to the first power difference.

$$\text{Loss}_{\text{conv.}} = K_2 \times A \times (T_1 - T_o)$$

Where:  $K_2$  is referred to as the convective heat transfer constant.

In batch heating processes, materials are charged into a cold furnace and in addition to heating the charge, the furnace itself, i.e. the refractory lining, the insulation and the metal structure, must be raised to their final equilibrium temperature. Approximate values for the heat required to do this can be estimated from the mass and specific heat of each structural component; however, it should be borne in mind that the final temperature will vary throughout the furnace and that the expression for the heat loss:

$$\text{Loss}_{\text{furnace}} = \sum_{i=0}^{i=n} m_i \int_{T_o}^{T_i} C_i dT$$

requires separate calculations for each element; of mass  $m_i$  specific heat  $C_i$  and ultimate temperature  $T_i$ , although a slight simplification, that is, the assumption that  $C_i$  is constant, results in a more manageable form, that is,

$$\text{Loss}_{\text{furnace}} = \sum_{i=0}^{i=n} m_i \times C_i \times (T_i - T_o)$$

### 9.3.3 Heating Efficiency

When defining the efficiency of a heating process it is worth recalling that heating values of fuels are normally expressed as gross calorific values, i.e. that one assumes that water vapour formed in the combustion of hydrogen is condensed and the heat recovered. Although this is not normally the case, both fuel heating values and heating efficiencies are commonly expressed on this basis.

The combustion efficiency in a particular heating process is, therefore, usually defined as that percentage of the gross calorific value of the fuel which is transferred to the material to be heated. From what has been said it will be clear that the following relationship should therefore hold:

#### Combustion efficiency

$$= 100 \times \frac{\text{Gross cal. Value} - \text{Stack loss} - \text{Other losses}}{\text{Gross cal. Value}}$$

### Combustion Equations

#### 1) Combustion of Liquid Fuels

Most fuels contain the following elements:

Element	Chemical symbol	Relative atomic mass	Relative molecular mass	Calorific value	
				Imperial units	SI units
Carbon	C	12	—	14 500 Btu/lb	33 730 kJ/kg
Hydrogen	H <sub>2</sub>	1	2	62 000 Btu/lb	144 200 kJ/kg
Sulphur	S	32	—	39 000 Btu/lb	90 700 kJ/kg
Oxygen	O <sub>2</sub>	16	32	—	—
Nitrogen	N <sub>2</sub>	14	28	—	—
Sand, Ash, etc.					

Nitrogen, sand and ash do not affect the process of combustion and remain after the process is completed.



## **Combustion of Carbon**

The combustion of carbon can be either complete or partial.

### **(a) Complete combustion of carbon**



1 molecule of carbon + 1 molecule of oxygen form 1 molecule of carbon dioxide and heat energy is liberated.

By mass	$\begin{array}{rcl} 12 & + & (16 \times 2) \\ 12 & + & 32 \\ 12/12 & + & 32/12 \end{array} \longrightarrow \text{CO}_2$
	$\begin{array}{rcl} & & = 44 \\ & & = 44/12 \end{array}$
Or	$\begin{array}{rcl} 1 & + & 2.60 \\ & & = 3.66 \end{array}$

1 kg of carbon + 2.66 kg of oxygen form 3.66 kg of carbon dioxide and this will liberate approximately 33 730 kJ (14 500 BTU/lb) of heat energy.

### **(b) Partial combustion of carbon**



2 molecules of carbon + 1 molecule of oxygen form 2 molecules of carbon monoxide and heat energy is liberated.

By mass	$\begin{array}{rcl} (2 \times 12) & + & (16 \times 2) \\ 24 & + & 32 \\ 24/24 & + & 32/24 \end{array} \longrightarrow 2\text{CO}$
	$\begin{array}{rcl} & & = 56 (2 \times 28) \\ & & = 56/24 \end{array}$
Or	$\begin{array}{rcl} 1 & + & 1.34 \\ & & = 2.34 \end{array}$

1 kg of carbon + 1.34 kg of oxygen form 2.34 kg of carbon monoxide and this will liberate approximately 10 470 kJ (4 500 BTU/lb) of heat energy.

## **Combustion of hydrogen**



2 molecules of hydrogen + 1 molecule of oxygen form 2 molecules of water vapour and heat energy is liberated.

By mass	$\begin{array}{rcl} (2 \times 1 \times 2) & + & (16 \times 2) \\ 4 & + & 32 \\ 4/4 & + & 32/4 \end{array} \longrightarrow 2\text{H}_2\text{O}$
	$\begin{array}{rcl} & & = 36 (2 \times 18) \\ & & = 36/4 \end{array}$
Or	$\begin{array}{rcl} 1 & + & 8 \\ & & = 9 \end{array}$

1 kg of hydrogen + 8 kg of oxygen form 9 kg of water vapour and this will liberate approximately 144 200 kJ (62 000 BTU/lb) of heat energy.

### **Combustion of sulphur**



1 molecule of sulphur + 1 molecule of oxygen form 1 molecule of sulphur dioxide and heat energy is liberated.

By mass	32	+ (16 x 2)	→	SO <sub>2</sub>
	32	+ 32	=	64
	32/32	+ 32/32	=	64
Or	1	+ 1	=	2

1 kg of sulphur + 1 kg of oxygen form 2 kg of sulphur dioxide and this will liberate approximately 90 700 kJ (39 250 BTU/lb) of heat energy.

### **Example 1**

A fuel oil contains by mass 86% carbons, 11% hydrogen, 2% sulphur and 1% oxygen.

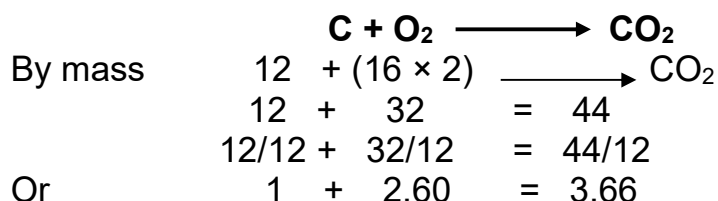
Calculate:

- (a) The theoretical mass of air required for the complete combustion of 1 kg of the oil;
- (b) If 10% excess air is provided, calculate the air-fuel ratio.

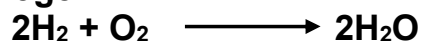
### **Solution**

(a) 1 kg of fuel oil contains 0.86 kg C, 0.11 kg H<sub>2</sub>, 0.02 kg S and 0.01 kg O<sub>2</sub>.

#### **1) Combustion of carbon (complete)**

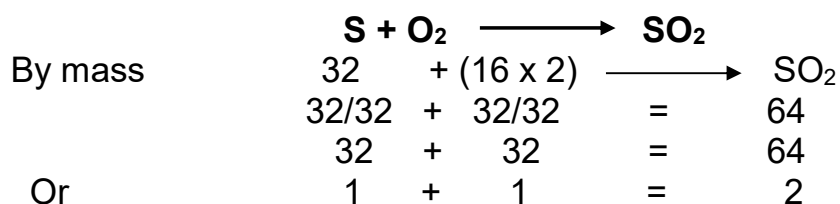


Therefore 1 kg of carbon requires 2.66 kg of oxygen, so 0.86 kg of carbon will require 2.66 x 0.86 = 2.29 kg of oxygen.

**2) Combustion of hydrogen**

$$\begin{array}{lcl} \text{By mass} & (2 \times 1 \times 2) + (16 \times 2) & \longrightarrow 2\text{H}_2\text{O} \\ & 4 + 32 & = 36 (2 \times 18) \\ & 4/4 + 32/4 & = 36/4 \\ \text{Or} & 1 + 8 & = 9 \end{array}$$

Therefore 1 kg of hydrogen requires 8 kg of oxygen, so 0.11 kg of hydrogen will require  $8 \times 0.11 = 0.88$  kg of oxygen.

**3) Combustion of sulphur**

Therefore 1 kg of sulphur requires 1 kg of oxygen, so 0.02 kg of sulphur will require  $1 \times 0.02 = 0.02$  kg of oxygen.

Total mass of oxygen required for combustion =  $2.29 + 0.88 + 0.02 = 3.19$  kg of oxygen; but fuel already contains 0.01 kg of oxygen and this must be subtracted from the oxygen required from the air, therefore oxygen required from the air =  $3.19 - 0.01 = 3.18$  kg of oxygen.

Air contains 23% oxygen by mass, hence theoretical mass of air required

$$\text{for combustion of 1 kg of fuel oil} = \frac{3.18 \times 100}{23} = 13.8 \text{ kg of air.}$$

(b) 10% excess air is supplied, therefore mass of air supplied =

$$13.8 + \frac{13.8 \times 10}{100} = 15.18 \text{ kg of air}$$

Air-fuel ratio = 15.18:1.

**Example 2**

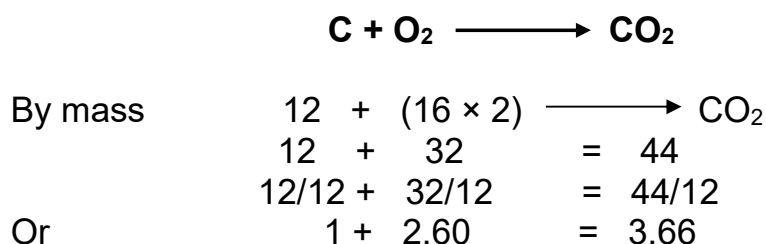
A gasoline (petrol) contains by mass 85% carbon and 15% hydrogen.

Calculate:

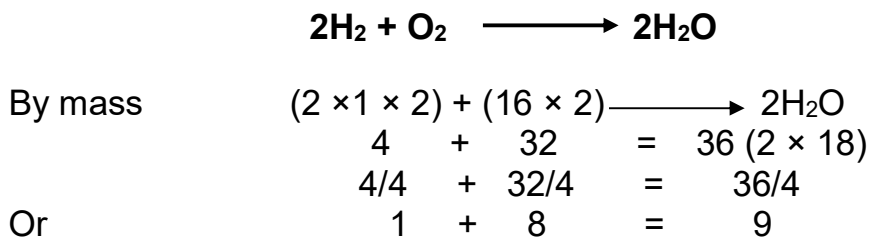
- (a) The theoretical mass of air required for the complete combustion of 1 kg of the fuel;
- (b) If 15% excess air is supplied, determine the air-fuel ratio.

**Solution**

(a) 1 kg of petrol contains 0.85 kg C and 0.15 kg H<sub>2</sub>.

**1) Combustion of carbon (complete)**

Therefore 1 kg of carbon requires 2.66 kg of oxygen, so 0.85 kg of carbon will require  $2.66 \times 0.85 = 2.26$  kg of oxygen.

**2) Combustion of hydrogen**

Therefore 1 kg of hydrogen requires 8 kg of oxygen, so 0.15 kg of hydrogen will require  $8 \times 0.15 = 1.2$  kg of oxygen.

Total mass of oxygen required for combustion =  $2.26 + 1.2 = 3.46$  kg of oxygen.

Air contains 23% oxygen by mass, hence theoretical mass of air required

$$\text{for combustion of 1 kg of gasoline (petrol)} = \frac{3.46 \times 100}{23} = 16 \text{ kg of air.}$$

(b) Excess air is supplied, therefore mass of air supplied as

$$15 + \frac{15 \times 15}{100} = 15 + 2.25 = 17.25 \text{ kg of air.}$$

Air-fuel ratio = 17.25:1.

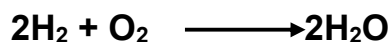
## 2) Combustion of Gaseous Fuels

A gas is normally measured by volume and the chemical equations are used in volume form.

Avogadro's hypothesis states that equal volumes of all gases contain the same number of molecules under the same conditions of temperature and pressure. Thus the volume of 1 molecule of  $H_2$  is the same as the volume of 1 molecule of  $O_2$  or  $N_2$  or any other gas at the same temperature and pressure.

Applying this hypothesis to the combustion equations:

### Combustion of Hydrogen ( $H_2$ )



2 molecules of  $H_2$  + 1 molecule of  $O_2$   $\longrightarrow$  2 molecules of  $H_2O$

Putting in volumes:

$$\text{So} \quad \begin{array}{ccc} 2 \text{ volumes} & + & 1 \text{ volume} \\ 2 \text{ m}^3 & + & 1 \text{ m}^3 \end{array} \longrightarrow \begin{array}{c} 2 \text{ volumes} \\ 2 \text{ m}^3 \end{array}$$

### Combustion of carbon monoxide (CO)



2 molecules of CO + 1 molecule of  $O_2$   $\longrightarrow$  2 molecules of  $CO_2$

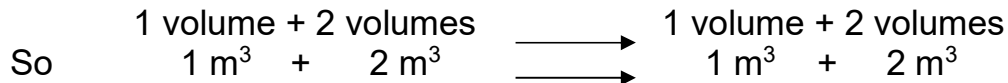
Putting in volumes:

$$\text{So} \quad \begin{array}{ccc} 2 \text{ volumes} & + & 1 \text{ volume} \\ 2 \text{ m}^3 & + & 1 \text{ m}^3 \end{array} \longrightarrow \begin{array}{c} 2 \text{ volumes} \\ 2 \text{ m}^3 \end{array}$$

**Combustion of methane (CH<sub>4</sub>)**

1 molecule of CH<sub>4</sub> + 2 molecules of O<sub>2</sub>  $\longrightarrow$  1 molecule of CO<sub>2</sub> + 2 molecules of H<sub>2</sub>O

Putting in volumes

**Example**

A fuel gas consists of the following chemical compounds, 60% methane (CH<sub>4</sub>) and 40% carbon monoxide (CO) by volume.

Calculate:

The volume of air required for the complete combustion of 1 m<sup>3</sup> of the fuel. If 10% excess air is supplied, determine the air-fuel ratio. Air contains 21% oxygen by volume.

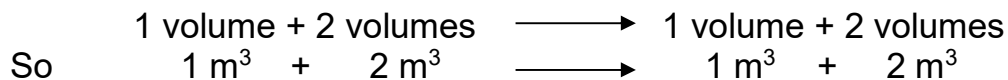
**Solution**

1 m<sup>3</sup> fuel gas contains 60% = 0.60 m<sup>3</sup> of CH<sub>4</sub> and 40% = 0.40 m<sup>3</sup> of CO.

**Combustion of methane (CH<sub>4</sub>)**

1 molecule of CH<sub>4</sub> + 2 molecules of O<sub>2</sub>  $\longrightarrow$  1 molecule of CO<sub>2</sub> + 2 molecules of H<sub>2</sub>O

Putting in volumes



1 m<sup>3</sup> CH<sub>4</sub> requires 2 m<sup>3</sup> of O<sub>2</sub>, so 0.6 m<sup>3</sup> will require  $2 \times 0.6 = 1.2 \text{ m}^3 \text{ O}_2$ .

**Combustion of carbon monoxide (CO)**

2 molecules of CO + 1 molecule of O<sub>2</sub>  $\longrightarrow$  2 molecules of CO<sub>2</sub>

Putting in volumes:

$$\begin{array}{rcll} & 2 \text{ volumes} + 1 \text{ volume} & \longrightarrow & 2 \text{ volumes} \\ \text{So} & 2 \text{ m}^3 + 1 \text{ m}^3 & \longrightarrow & 2 \text{ m}^3 \end{array}$$

$$\text{Therefore } 1 \text{ m}^3 + \frac{1}{2} \text{ m}^3 = 1 \text{ m}^3$$

1 m<sup>3</sup> CO requires  $\frac{1}{2}$  m<sup>3</sup> of O<sub>2</sub>, so 0.4 m<sup>3</sup> will require  $1 \times 0.4 = 0.2 \text{ m}^3 \text{ O}_2$ .

$$\text{Therefore total volume of O}_2 \text{ required} = 1.2 + 0.2 = 1.4 \text{ m}^3$$

$$\text{Volume of air required} = 1.4 \times (100 / 21) = 6.66 \text{ m}^3.$$

$$\begin{aligned} \text{Therefore air supplied, with 10\% excess} &= 6.66 + (6.66 \times 10 / 100) \\ &= 6.66 + 0.67 = 7.33 \text{ m}^3. \end{aligned}$$

Air-fuel ratio = 7.33:1.

**Chapter 10**  
**BULK DISTRIBUTION AND**  
**HANDLING OF LPG**



## **Chapter 10 Contents**

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**Chapter 10****Bulk Distribution and Handling of LPG****10.1 INTRODUCTION**

In this chapter we deal with the distribution and handling of propane and butane. By 'distribution' we mean the transfer of liquid LPG from the bulk supply tanks, situated at the oil refinery or natural gas liquid separation plant, to the user's storage vessels. By 'handling' we mean those operations which concern the conversion of the liquid LPG into a gaseous fuel at the point of application. 'Handling' covers therefore not only the bulk storage and vaporization of LPG but also the piping of LPG in liquid or gaseous phase, and the adjustment of the combustion characteristics of the fuel gas by mixing with air.

**10.2 DISTRIBUTION OF LPG**

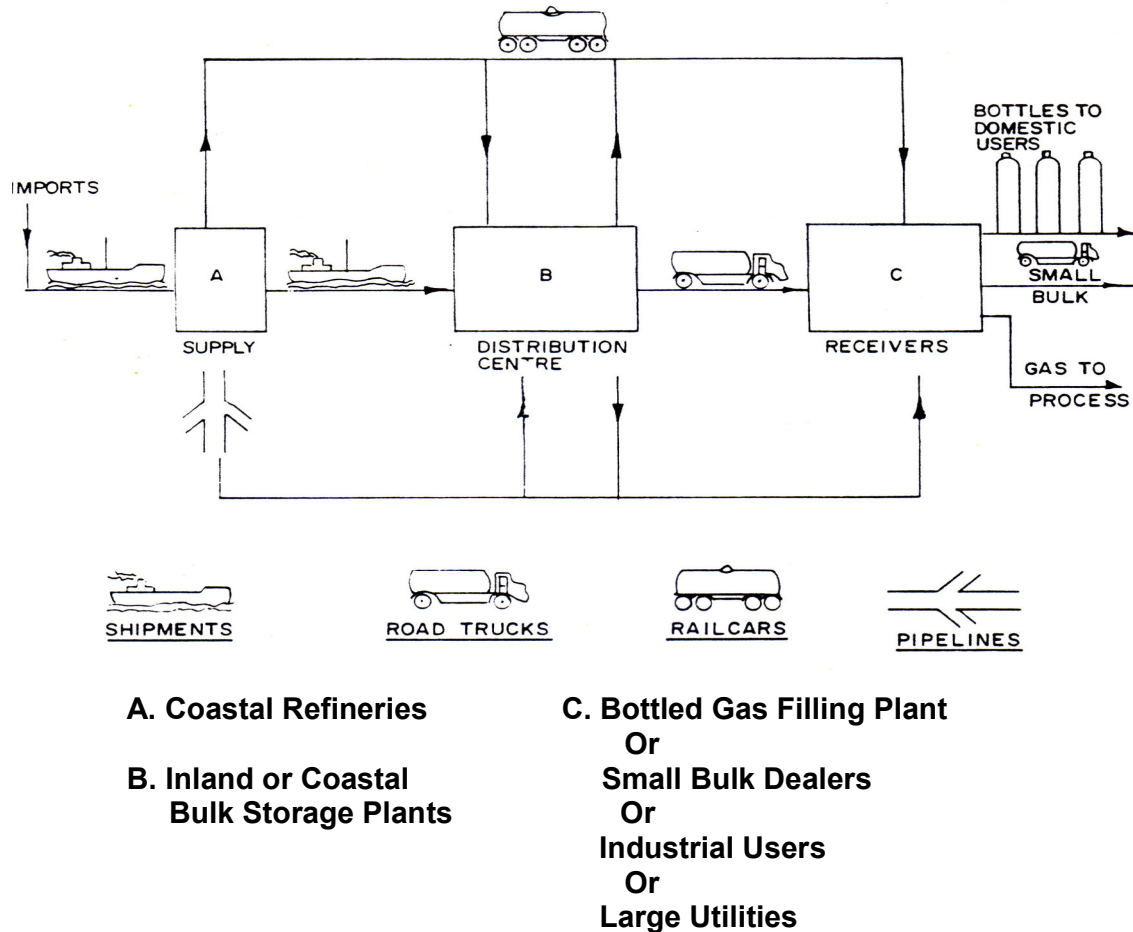
Product LPG is moved in four different ways, by pipeline, rail car, and sea or road truck.

**10.2.1 Pipelines**

Pipelines are used to transfer massive quantities of LPG from the refinery either to a secondary bulk supply plant situated in a highly industrialized area, or to a very large customer organization such as a modern gas works or power plant. Spur lines can be added to main trunk lines to serve subsidiary interests in close proximity.

**10.2.2 Rail Cars**

For quantities of LPG too small to be moved by pipeline, the preferred method of transportation is by rail. Train loads of 500 ton of product or more are made up of individual bogey cars each carrying up to about 50 ton butane or 40 ton propane. Deliveries can be made direct from refinery or bulk distribution plant into sidings located on the user's premises. Universally, rail cars are pressure vessels.



**Figure 10.1 LPG Supply and Distribution Systems**

They and their supporting frames are built to certain codes approved by the railroad authorities. Fittings on the vessel include relief valves, liquid fill and offloading lines, vapour return valve, safety relief valve, liquid level gauge, pressure gauge (which can also be used for product sampling purposes) and thermometer well. The relief valves are situated at the top of the vessel. The remainders are grouped together in recesses in either side of the car. Duplicate sets of side connections and fittings are provided because the car may arrive at the sidings in either direction. The recesses are closed by sliding doors which can be locked to prevent interference by unauthorized persons. The liquid and vapour lines terminate in self-sealing couplings. This means that very little LPG is released to atmosphere when the rail car is connected or disconnected, thereby minimizing the inflammable vapour hazard. In addition to the recessed level gauge, the rail car usually carries a contents gauge mounted centrally at one end.

### 10.2.3 Sea Transport

Propane and butane are conveniently transported between coastal refineries and customers with jetty offloading facilities, by sea. Storage vessels on coastal tankers are usually of the pressure type ranging in unit capacity up to 1000 m<sup>3</sup> (500 ton). Ocean-going ships can carry a total cargo of up to 40,000 m<sup>3</sup> (20,000 ton) of LPG in refrigerated condition, i.e. at temperatures down to -50°C. The same vessels, undesirably perhaps, often carry different liquefied gases, such as butane, propane, ammonia, butadiene and propylene, on consecutive journeys. There is a risk, therefore, of contaminating one product with another unless effective draining and purging procedures are adopted between loading operations.

### 10.2.4 Road Trucks

This is the most popular method of moving relatively small quantities of LPG in pressure vessels from refinery or secondary supply depot to locally placed customers (see Figure 10.1). Most of these trucks are equipped with unloading pumps to assist with deliveries to customers not provided with offloading facilities. Some also carry volumetric meters to record deliveries although the most accurate method of accounting is to weigh the smaller trucks at the supply source before delivery and on return, making due allowance for the amount of vehicle fuel consumed on the journey. Other fittings include vapour return connection, pressure, temperature and level gauges and relief valve.

Because of the hazards involved in transporting an inflammable liquid over the public highway, strict procedures are laid down for the safe handling and transport of LPG by road. In the U.K. the LPG ITA Code of Practice No. 2 is offered for guidance. This code details vessel design and capacity, filling considerations, accessories, inspections and maintenance procedures, electrical and fire precautions and instructions for the driver, and is based on the NFPA standard No. 58 (Division III), Truck Transportation of LPG.

Modern trucks comprise the rigid, conventional type, the larger articulated vehicles and small vehicles carrying skid-mounted vessels (1-5 ton water capacity) which can be parked separately from the truck at a customer's premises.

Filling and discharge hoses providing for both liquid fill/offtake and vapour balance are carried aboard the truck. These hoses are of the armored, flexible type but are not normally self-sealing. Furthermore, they usually remain full between uses and therefore are continually under high pressure. They must be inspected daily to ensure that they are in good condition, free from leaks and not damaged in any way.

### **10.2.5 Unloading Procedures**

The usual method involves a liquid pump although propane in some circumstances may not require mechanical assistance. Butane on the other hand in cold climates may need both pump and vapour compressor. If a compressor is used to unload the road truck, rail car or ship, it will withdraw vapours from the receiving vessel, compress and discharge them into the vapour space above the liquid in the delivery vessel. This action creates a pressure differential causing liquid to flow from one tank to the other. The preferred differential is of the order of 5-10 lb/in<sup>2</sup> gauge.

Liquid pumps will be of the centrifugal or positive displacement type with steel (not cast iron) body, mechanical seal rather than packed gland, and electrical, hydraulic or pneumatic drives. Road vehicles may use their own battery- or engine-driven pump or an external pump belonging to the user's installation. Vapour which is displaced from the receiving vessel during filling should be returned via the vapour balance arm to the supply tank.

There are a number of precautions which must always be taken during LPG transfer operations. First, propane must never be loaded into a vessel designed to house butane though the converse is allowable. Secondly, careful watch must be kept on the liquid level in the receiving vessel, thereby guarding against overfilling. During loading into rail cars at refineries, it is usual for the flow to be checked automatically at 97.5% weight of the product load. The remaining 2.5% is loaded at a slower rate to ensure accurate measurement of product and prevention of shock pressures as the valves are closed. A third precaution applies to prevention of static build-up. LPG rail sidings are inherently self-earthing, the rails being bonded to the loading or discharge pipes and earthed. Road trucks should be electrically bonded to an effective earthing point at the fixed installation before any LPG transfer operation is carried out. Hoses conveying liquid must have electrical continuity across flanged connections.

### 10.2.6 Vessel Filling

The appropriate directive for the U.K. is again based on NFPA standard No. 58 (Division V) and is given in the Home Office Code of Practice for the storage of LPG at fixed installations, and is based on the concept that:

- The maximum quantity of LPG filled into any tank should be such that the tank will become not more than 97% liquid full due to expansion of the contents with rise of temperature to the highest temperature which the contents will reach in service.
- The highest temperature is specified in accordance with vessel size, thus:
  - 42.5°C for tanks having a capacity not exceeding 5 m<sup>3</sup> (1100 gal approx.)
  - 38.0°C for tanks having a capacity exceeding 5 m<sup>3</sup> but not exceeding 30 m<sup>3</sup> (6600 gal)
  - 37°C for tanks having a capacity exceeding 30 m<sup>3</sup> but not exceeding 100 m<sup>3</sup> (22,000 gal)
  - 36° C for tanks having a capacity exceeding 100 m<sup>3</sup> (1 m<sup>3</sup> = about 0.5 ton LPG)
- The maximum LPG capacity of a vessel depends on its size and on the highest temperature specified for its size range, in accordance with the following equation.

$$\text{Filling capacity} = \frac{(0.97) \times (\text{Water capacity}) \times (\text{S.G. of LPG at } t^{\circ}\text{C})}{\text{S.G. of LPG at } 15.6^{\circ}\text{C} \times cf}$$

Where: S.G. is the liquid specific gravity,  $t^{\circ}$  is the highest temperature and  $cf$  is the correction factor which allows for difference in LPG liquid filling temperature from 15.6°C (see Table 7.4 and Appendix 2).

Examples of filling capacities allowable for some vessels at three levels of liquid filling temperatures are given in Table 10.1.

Filling temperatures, °C	Filling capacities		
	4	15.5	35
(a) Propane vessels			
<5 ton	85.3	88	93.6
10 ton	87.5	90.3	96.1
(b) Butane vessels‡			
<5 ton	89.6	91.5	95.3
10 ton	90.4	92.4	96.3

† Filling capacities expressed as per cent by volume of maximum water capacity.

‡ Taken as 50/50 mol% normal and iso forms.

**Table 10.1 Filling Capacities† of Propane and Butane Vessels**

The data in Table 10.1 is based on the following specific gravities and correction factors

Temperature, °C	Propane		Butanes	
	S.G.	cf	S.G.	cf
4		1.032		1.022
15.5	0.508	1.0	0.5732	1.0
35		0.940		0.960
38	0.473		0.5462	
42.5	0.461		0.5408	

Thus it appears that, in practice, the maximum filled volume of an LPG vessel will approximate to 90% of the total interior volume. Small sample containers of a liter or so in capacity are generally not filled to more than 80% volume of total capacity, thereby allowing an additional safety margin for handling and transportation.

In rating an LPG vessel, it is important not to confuse water capacity with weight of LPG allowed, and vice versa. Usually a 30 ton LPG tank can be taken to mean that the tank will hold 30 ton of LPG, i.e. either 30 x 440 Imperial gallons (13,200) of liquid propane or 30 x 390 Imperial gallons (11,700) of liquid butane. These maximum filled volumes will represent about 90% of the total interior volume of the vessel. Thus in the propane case, the total water capacity of the vessel is  $13,200 \div 0.9$ , that is, about 14,650 gal or 65 ton. Likewise if a vessel should be quoted as 30 ton water capacity, its maximum propane fill will be close to  $(30 \times 224 \times 0.9) \div 440$ , that is, 13.8 ton. Note that butane may be loaded into the higher pressure rated propane vessel but a butane vessel must never be filled with propane. If a 100 ton propane tank is filled with butane, the filled volume will then weigh  $100 \times 440 \div 390$ , that is, 113 ton, not 100 ton.

## 10.3 STORAGE AT FIXED LPG INSTALLATIONS

### (Refineries and User Plants)

#### 10.3.1 Types of Storage Vessels

LPG requires being stored in pressure vessels at ambient temperatures or in insulated tanks at near atmospheric pressure and reduced temperatures. Either of these forms is more expensive than storing a relatively involatile petroleum distillate such as naphtha in conventional tanks.

##### **Pressure Vessels**

LPG containers are to be fabricated in accordance with the rules for construction of unfired pressure vessels. The design pressure in the instance of propane vessels is 250 lb/in<sup>2</sup> gauge. Tanks should be designed and constructed for the following minimum design working pressures:

- Commercial butane 70 lb/in<sup>2</sup> gauge minimum
- Commercial propane 210 lb/in<sup>2</sup> gauge minimum

These pressures correspond to the maximum vapour pressures of the LPG at the highest temperature likely to be encountered in service. This temperature will be specified in accordance with vessel capacity. For vessels designed in accordance with these requirements, the highest temperature may be taken as:

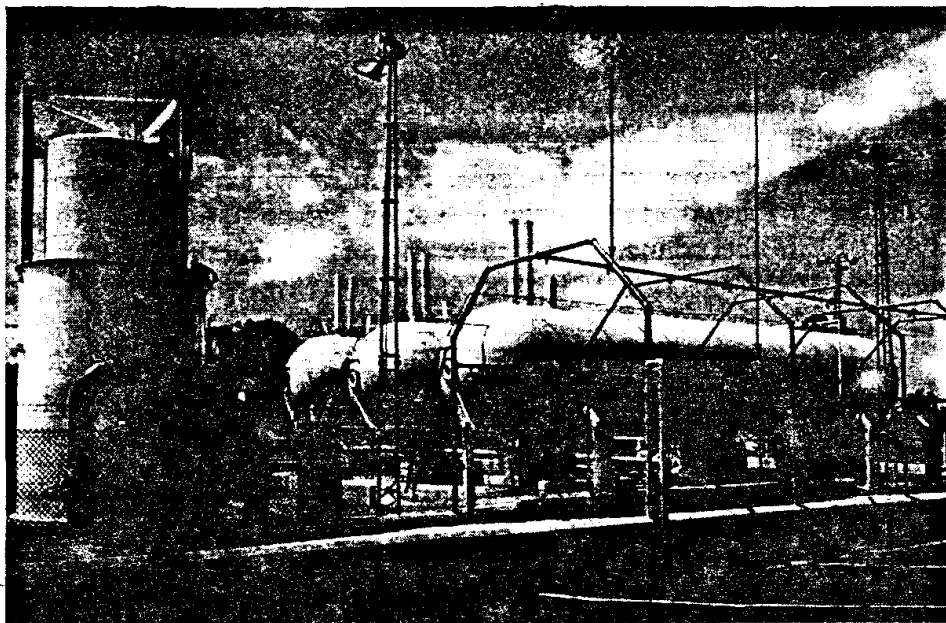
- 50°C for tanks having a capacity exceeding 130 L (approximately 28 gal) but not exceeding 1 m<sup>3</sup> (approximately 220 gal)
- 47.5°C for tanks having a capacity exceeding 1 m<sup>3</sup> but not exceeding 5 m<sup>3</sup> (approximately 1100 gal)

'†' Codes of Practice are intended as a guide for agreement between purchaser and manufacturer. They are enforced by official bodies which function with government authority and by insurance agencies which act on behalf of, and serve the interests of, the vessel user. Two important insurance agencies in the U.K., for example, are Associated Offices Technical Committee (AOTC) and Lloyds Register of Shipping.

- 42.5°C for tanks having a capacity exceeding 5 m<sup>3</sup> but not exceeding 30 m<sup>3</sup> (approximately 6600 gal)
- 41 °C for tanks having a capacity exceeding 30 m<sup>3</sup> but not exceeding 100 m<sup>3</sup> (approximately 22,000 gal)
- 40°C for tanks having a capacity exceeding 100 m<sup>3</sup>



Capacities of PG pressure vessels usually installed on industrial users premises range from 0.5 to 100 ton. The vessels themselves are cylinders with hemispherical or dished ends and can be mounted horizontally or vertically. Figure 10.2 shows three 100 ton horizontal 'bullets' situated in a plant supplying 78,000 ft<sup>3</sup>/hr of simulated natural gas.



**Figure 10.2 Butane Storage Vessels at a Plant Supplying 78,000 Ft<sup>3</sup>/Hr of Simulated Natural Gas (W. C. Holmes Ltd.)**

Above about 100 ton vessel capacity, a spherical shape becomes more economical for LPG pressure vessels and is therefore adopted for all such vessels installed at refineries and some of the larger inland LPG storage depots.

The relatively high boiling point of butane can lead to the creation of vacuum conditions inside pressure storage vessels in cold climates. If a low ambient temperature aided by intermittent, vapour withdrawal lowers the liquid temperature below 0°C for n-butane or below about -7°C for mixed butane isomers, the pressure inside the tank will fall below atmospheric. If such temperatures are likely, the storage vessel has to be designed for additional shell thickness and internal strengthening struts incorporated. Other safety measures which can guard against vacuum conditions are the use of propane and propane vessels only in cold climates, or else to 'spike' the butane grade with propane to the limit of the butane vessel design pressure (usually about 20 mol % propane with commercial butane is allowable).

An LPG pressure vessel is examined for external surface condition and incipient sources of leakage every five years. Ultrasonic tests are applied. A full internal examination is usually required every ten years.

### **Refrigerated Tankage**

When the vessel storage capacity increases above about 2000 ton capacity, refrigerated tanks lined with polyurethane foam insulation represent a cheaper means of storing LPG. Insulated LPG tanks at refineries have capacities as high as 10,000 ton and external LPG water removal and refrigeration facilities have to be provided as part of the complete package. Refrigerated propane is stored at temperatures in the region of  $-40^{\circ}\text{C}$ , butane at about  $0^{\circ}\text{C}$ .

An important facility in insulated tanks is allowance for vapour 'breathing' in accordance with small temperature changes. Vaporized gas resulting from a slight increase in temperature escapes from a pressure vacuum relief valve situated at the top of the tank. This is recompressed and the liquid, after cooling by partial flashing, is returned to the tank.

### **Underground Storage**

So far, we have been referring to above-ground storage. There remains to be mentioned the storing of LPG in buried steel tanks or in artificially created underground cavities. Pressure vessels are placed underground when there are cogent safeties or environmental reasons for doing so. However, they are required to be specially treated against external corrosion and mounted on masonry supports inside a concrete pit which provides for a one meter gap all round, this space being backfilled with fine sand. Hence, installation costs are increased. Furthermore, only small space savings are afforded since restrictions apply to the use of the ground space immediately above buried vessels. Liquid draw off is provided for either by burying the pump inside a special housing alongside the tank bottom and sleeving the pipe connections, or better (from a maintenance point of view) by mounting a suitable type of pump on the surface.

In this case, a self-priming centrifugal pump can be used and loss of suction due to vapour lock during running can be overcome by pressurizing the tank with superheated vapour returned from an external vaporizer (see sub-section 10.4.2).

As far as **artificial pits** are concerned, satisfactory LPG service has been obtained with salt dome caverns, mined caverns and refrigerated in-ground storage. The type used most extensively, particularly in the U.S.A. and Canada, is the salt dome cavern. The prime requisite is the availability of a high-purity salt formation into which a well is drilled. Water is then pumped in so as to dissolve the surrounding salt to a calculated amount. Subsequently, the bulk of the brine is removed by pumping in LPG under pressure. The brine is returned to the ground or else stored in salt producers.

**Mined caverns** are blasted from suitable quality rock formations, which must be impermeable to the ingress of water or to the escape of gas. Liquid LPG is pumped in after the cavern has been thoroughly purged of air. Such caverns have been used satisfactorily with pressure LPG over some twenty years or more in the U.S.A. and in Europe. They have also been used for storing refrigerated LPG, a recent example being the storing of propylene at  $-40^{\circ}\text{C}$  by Esso Chemical Co. Sweden in two 10,000 m<sup>3</sup> caverns.

**Frozen earth cavities** are proving more successful for storing LPG in refrigerated condition than for LNG (liquefied natural gas), due to a higher liquid temperature and less 'breathing' losses. During construction, a refrigerant is circulated through pipes inserted into the ground around the periphery of the proposed excavation. The frozen soil is then removed and an insulated roof is fitted over the cavity. Liquid LPG is pumped in through this roof and autorefrigerated by a small 'boil off' effect, as in the case with above-ground, insulated vessels.

### 10.3.2 Location of Storage Vessels at Users' Premises

Above about 5 ton capacity, LPG storage installations as a rule are located in specially prepared fenced compounds complete with water sprays and facilities for dealing with the rare event of gas or liquid leakage, fire or explosion. Guidance on such matters as location of tankage, spacing between vessels, distance from building and property lines, provision of safety facilities is given in a number of industry and official Codes of Practice.

Approved sitting distances for LPG storage vessels are given in Table 10.2. Some benefit is gained for underground vessels in terms of distances allowed from property lines.

Below the 5 ton size, vessels are often towed over the road for temporary sitting at a customer's site.

<i>Distance in Metres</i>					
<i>Storage Categories</i>		<i>Siting categories</i>			
<i>Water capacity of individual storage vessels (litres)</i>	<i>Nominal LPG capacity (tonnes)</i>	<i>From building property line or fixed point of ignition</i>		<i>Between vessels</i>	
		<i>Above ground</i>	<i>Under ground</i>	<i>Above ground</i>	<i>Under ground</i>
Up to 450	0-0.2	None	3	None	1.5
Over 450 to 2250	0.2-1.0	3	3	0.9	1.5
Over 2250 to 9000	1-4		3	0.9	1.5
Over 9000 to 135,000	4-60	15.0	3	1.5	1.5
Over 135,000 to 337,000	60-150	23	5	1.5 m or $\frac{1}{4}$ sum of diameter of adjacent vessels whichever is the greater	1.5
Over 337,000	150-	30.0	5		

<i>Distance in feet</i>					
<i>Water capacity of individual storage vessels in U.K. gal</i>	<i>Nominal LPG capacity (tons)</i>	<i>From building property line or fixed point of ignition</i>		<i>Between vessels</i>	
		<i>Above ground</i>	<i>Under ground</i>	<i>Above ground</i>	<i>Under ground</i>
Up to 100	0.2	None	10	None	5
Over 100 to 500	0.2-1.0	10	10	3	5
Over 500 to 2000	1-4	25	10	3	5
Over 2000 to 30,000	4-60	50	10	5	5
Over 30,000 to 75,000	60-150	75	15	5 ft or $\frac{1}{4}$ sum of diameter of adjacent vessels whichever is the greater	5
Over 75,000	150-	100	15		

Table 10.2 Location and Spacing of LPG Storage Vessels

### 10.3.3 Tank Fittings

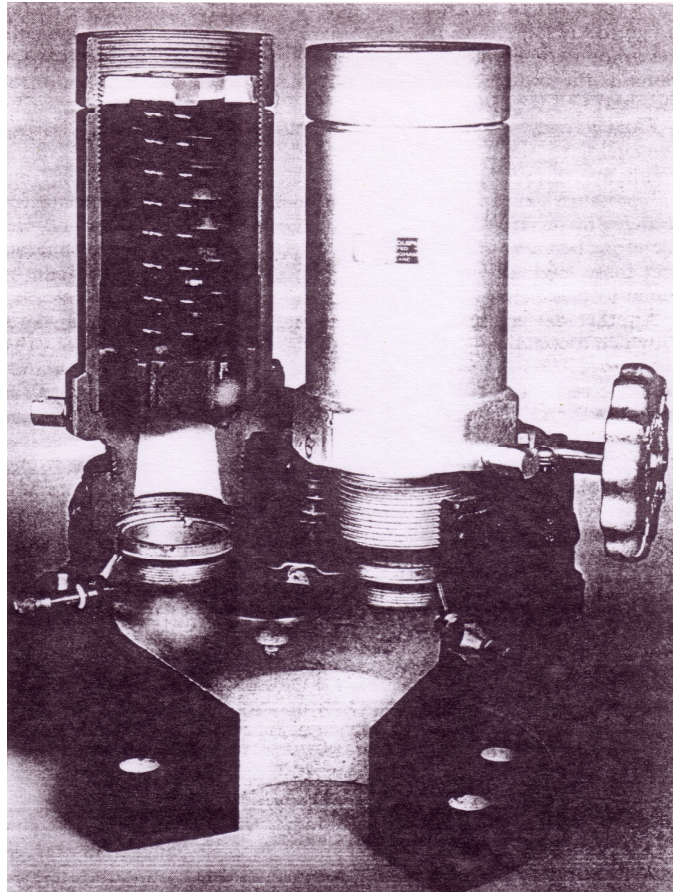
The full list of markings, fittings and instruments of LPG tanks comprises the following:

Inspection manhole, liquid fill line with non-return valve, vapour balance line, top vapour offtake line, bottom water draw-off valve, bottom liquid withdrawal line, safety relief valve, fixed liquid level indicator and contents gauge, pressure and temperature gauges, excess flow valves in liquid and vapour lines, and earth connection.

**The excess flow valves** have a maximum rating usually 130% of expected maximum flow. In the event of a downstream liquid or gas leak causing a fluid flow above the valve rating, this closes and remains closed as long as the low pressure persists downstream of the valve.

**The pressure relief valves** are designed to open when excessive temperatures cause the liquid vapour pressure to rise above the design working pressure of the tank. They are situated on top of the LPG vessel and may either be of the multiport type (see Figure 10.3) or the single pressure relief type. These valves usually have three settings; 70 lb/in<sup>2</sup> (butane vessels), 220 lb/in<sup>2</sup> (propane vessels) and 100 lb/in<sup>2</sup> (intermediate pressures). Care should be taken that the correct pressure setting is applied in the right circumstance.

For **measuring liquid contents**, rotary gauges, dip tubes, float gauges and differential pressure gauges are used. A rotary gauge consists of a curved dip tube which may be rotated until liquid spray appears at which position the gauge indicates a volume percentage fill or volume direct in a properly calibrated tank. A dip tube gauge is positioned on the top of the vessel. The liquid level is gauged by unscrewing the tube bleed valve and allowing liquid to blow out from the orifice. The tube is then lifted until vapour replaces liquid, at which point the bottom of the drip tube is level with the top of the liquid. The contents are then read off from an encircling calibrated scale. Differential gauges are dip tubes, one end of which communicates with the vapour, the other with the liquid space.



**Figure 10.3 Multi port relief valve manifold**  
(LP Gas Equipment Ltd)

Most convenient of all gauging devices used on LPG containers is the magnetic or float type gauge which shows at all times the volume per cent to which the container is filled. A float is located inside the container and as the liquid level changes; the movement of the float turns the shaft to which it is geared. The pointer on the face of the gauge follows the motion of the shaft and is calibrated to indicate the amount of liquid in the container. One unique feature of this gauge is the use of a permanent magnet to transmit the motion of the shaft to the pointer.

Float gauges give an accurate measurement of product level but conversion to weight of product, as with rotary gauges, must be done manually, using the correct temperature and specific gravity. Differential pressure gauges have the advantage that they compensate for changes in product temperature and gravity automatically and can therefore be calibrated directly in weight units. Experience suggests that these have a working accuracy of  $\pm 3\%$ , although they can be tuned to give better than 1%.

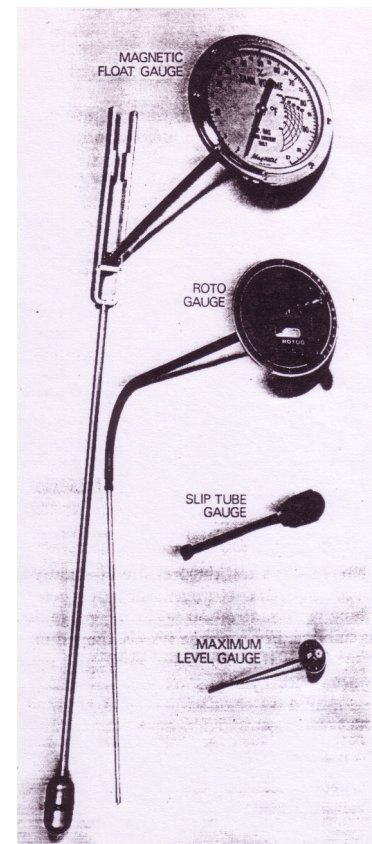


Another device is the fixed level gauge set to the maximum level to which a container can be filled. It has a tube with a bleeder valve at the top. The length of tube that is inside the tank is predetermined with the result that when the liquid level reaches the bottom of the tube, the liquid sprays out through the bleeder valve. Since this gauge has the limitation that it can indicate only one particular level, it is installed as an additional fitting to the regular gauge. Typical settings are 91 vol. % for butane vessels and 88% for propane tanks. These various types of liquid contents gauges are shown in Figure 10.4.

**The pressure gauge** is a very important fitting and is mandatory by all regulations irrespective of the type and size of the containers. Normally the 0-300 lb/in<sup>2</sup> range suffices. Since this gauge can easily be damaged if exposed to sudden liquid flow, it is usually installed with an excess flow check valve or flow limiting orifice, plus a manual isolating valve.

**The temperature gauge** is an optional fitting but is required for precise calculations of the maximum liquid fill, liquid gravity or weight of LPG. It is fitted into a socket situated low down on the hemispherical end of the vessel.

**Figure 10.4 Liquid LPG gauging devices**  
(LP Gas Equipment Ltd)



### 10.3.4 Vessel Commissioning

The term 'commissioning' implies the bringing of the entire gas-making plant into service on LPG fuel. Commissioning is an exercise which entails the following separate stages: inspection, tank pressure testing, leak testing, purging, initial tank fill with LPG, priming of the whole system with LPG, check on controls, instruments and safety devices, process light up, and an operational trial of about two days duration.

#### **Plant Inspections**

Overall inspection includes:

- The site, provision of safety facilities, such as water sprays, fire fighting equipment, proximity of other industrial premises or houses, ease of access for road tankers, etc.
- Liquid and vapour lines; provision of shut-off and excess flow valves
- Other provisions such as: absence of all flexible hose if installation capacity exceeds 1100 gal; proper support for fuel transfer lines and installation providing adequate flexibility to accommodate tank settlement, thermal or mechanical stress.

#### **Tank Pressure Testing**

Before the vessel is released, the fabricator will have been required to hydraulically test the tank in the presence of the contractor and industrial insuring agency. Nevertheless, hydraulic testing of the tank is usually repeated on site, particular attention being paid to the liquid offtake section. The test is carried out at  $1\frac{1}{2}$  times the maximum working pressure (this is related to the LPG composition and to the maximum anticipated ambient temperature) and should last for at least 30 min with no loss of pressure. Methanol should be added after hydraulic testing and draining, so as to absorb the remaining water into an LPG-soluble medium. A suitable dosage is one gallon per ton of rated LPG capacity.

#### **Leak Testing of Storage Vessel**

The next step is to leak test the pressure vessel after all valves and fittings have been installed. Nitrogen, air or carbon dioxide can be used. For butane vessels, air at 50-90 lb/in<sup>2</sup> gauge delivered from a compressor is suitable. For propane vessels, the required test pressure should be in the range 105-200 lb/in<sup>2</sup> gauge and inert gas supplied from standby pressure cylinders or tanks is required. Leaks are located with soap and water or with sulphur hexafluoride gas using an electron capture detector. Halogenated carbon compounds may also be used.



**Purging of Storage Vessel**

If inert gas was used for leak testing, it is sufficient to vent the vessel and proceed with the LPG filling operation. If air or water was used, then purging with inert gas is required to lower the oxygen content of the vessel atmosphere to less than 10% before admitting the LPG. A 30 ton vessel requires about 2400 ft<sup>3</sup> of inerts delivered at atmospheric pressure.

Purging of air by evacuation is permissible only in the rare circumstance of the tank having been additionally stress rated for full vacuum condition (i.e. for use with n-butane in very cold climates).

**10.3.5 Decommissioning of Storage Vessels**

This can be a hazardous operation which is only required when the LPG vessel is inspected (usually every ten years) for internal corrosion, deposits, cracks, etc. The stages involved include the draining of liquid LPG, the top venting and flaring of residual vapour, purging with inert gas until the vessel atmosphere measures less than some 4-10% of combustibles depending on the composition of the LPG and the type of inert gas used.

The residual oxygen content of a vessel which is being purged into service, or the residual combustibles in one which is being decommissioned, are limits which must be scrupulously observed for safety's sake. (See Tables 10.3 and 10.4)

	<i>Into service</i>		<i>Out of service</i>	
	<i>% required to render mixtures non-inflammable with 20% safety factor</i>		<i>% required to render mixtures non-inflammable when air is added in any amount</i>	
	<i>CO<sub>2</sub></i>	<i>N<sub>2</sub></i>	<i>CO<sub>2</sub></i>	<i>N<sub>2</sub></i>
Propane	43	54	91	95
<i>n</i> -Butane	42	52	93	96
Isobutane	41	52	93	96

**Table 10.3 Inert Gas End Points for Purging into or out of Service using Carbon Dioxide or Nitrogen**

	<i>Into service</i> % of oxygen below which no mixture is inflammable, 20% safety factor		<i>Out of service</i> % of combustibles below which no mixture is flammable when air is added in any amount, 20% safety factor	
	<i>CO<sub>2</sub></i>	<i>N<sub>2</sub></i>	<i>CO<sub>2</sub></i>	<i>N<sub>2</sub></i>
Propane	11.4	9.1	9	5
<i>n</i> -Butane	11.6	9.7	7	4
Isobutane	11.8	9.6	7	4

**Table 10.4 Oxygen and Combustible Gas End Points**

CO<sub>2</sub> is slightly more efficient than N<sub>2</sub> for suppressing flammability, and shows some apparent economy of gas volume. In practice this may not always be the case.

Purging may be carried out by:

1. displacement, or
2. dilution of the gas or air in the vessel by the inert gas

For displacement purging, with no mixing, the inert gas volume will approximate that of the vessel; for dilution purging, with thorough mixing, the volume of inert gas required will be about five times the vessel volume.

One of the ways to inhibit mixing and thereby excessive consumption of purge gas is to ensure that the densities of the purge gas and the gas to be purged are widely different. Thus CO<sub>2</sub> (S.G. 1.52) is useful for removing air (S.G. 1.00) from a vessel, and N<sub>2</sub> (S.G. 0.97) for removing propane (S.G. 1.52) or butane (S.G. 2.01). The heavier gas should always be admitted into or vented from the bottom of the vessel and the lighter gas transferred through top connections.

Purging of an LPG gas-filled tank can also be carried out with water introduced through a bottom connection. Water is cheaper than nitrogen but has the disadvantage that it can dissolve up to about 150 weight parts per million of gas at ambient temperature and pressure. Thus there is a certain hazard in releasing purge water into drains, particularly as dilution with air and a rise in temperature, leading to escape of gas from water into the vapour phases, can give rise to an inflammable condition. Immediate flushing with fresh water minimizes this hazard.

Finally, if the water-purged tank is later to be refilled with LPG, the water should be dosed with methanol at a rate of 0-1 vol. %. This minimizes the possibility of ice formation from the liquid and expanded vapour phases.

Choice of purging medium between water, nitrogen (or carbon dioxide) is ultimately decided on a balance of costs versus safety angles. For LPG operations, nitrogen is usually the preferred inert gas.

In the case of an inert gas-purged storage vessel, further precautions should be taken if one wishes to enter the vessel for inspection and repair purposes. Inspection personnel should be provided with breathing apparatus or, better still, the vessel should finally be air-purged; in that case, the interior atmosphere has to be checked until a breathable atmosphere is obtained, at the same time ensuring that the LPG concentration is below the lower inflammability limit (2.4% propane in air, 1.8% butane).

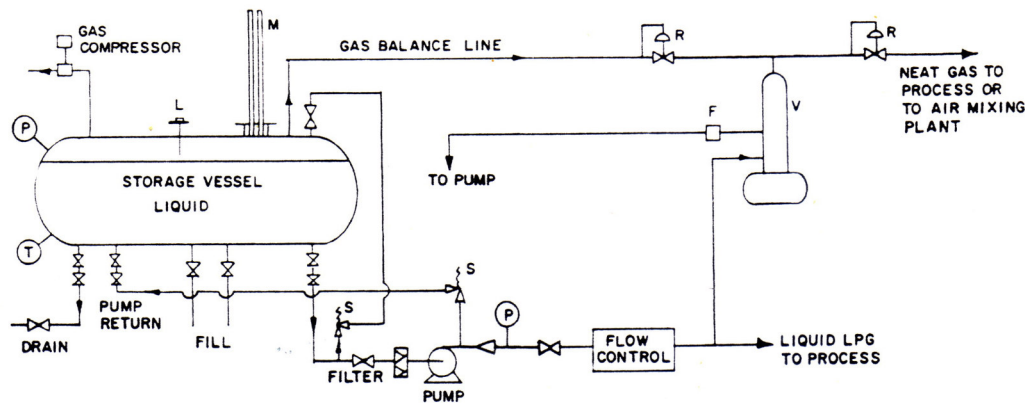
## **10.4 COMPONENTS OF A BULK LPG INSTALLATION, OTHER THAN STORAGE VESSELS**

Additional to the liquid LPG storage vessel, a complete installation for providing fuel gas to a burner-furnace combination will comprise the following items:

- A vaporizer for converting the liquid LPG into the vapour phase
- A pump to transfer the liquid from the tank to the vaporizer (particularly for butane; with or without vapour compressor)
- A gas-air mixing plant to obtain the desired fuel gas combustion characteristics (e.g. Wobbe number to match natural gas)
- Liquid and vapour transfer lines, pressure regulators, valves, gas meter, etc.

Alternatively, combustion equipment can be designed to burn LPG in the liquid state, in which case the vaporizer air mixer and gas lines will be dispensed with.

The multiple components of a typical installation for providing liquid LPG, neat LPG or LP gas-air mix to process are illustrated in Figure 10.5.



M = Multi port pressure relief valve  
 S = Pop relief valve  
 R = Pressure regulator  
 P = Pressure gauge

L = Maximum level gauge  
 T = Temperature gauge  
 F = Float level control  
 V = Liquid vaporiser

**Figure 10.5 Flow Sheet of a Typical LPG Fuel Installation**

### 10.4.1 Vapour Offtake

Some installations which require relatively small gas flow rates for short periods, and which are fed with propane, can rely on vapour withdrawal from the top of the tank. The amount of liquid vaporized depends on the superficial area of wetted liquid surface  $A$ , the temperature difference between outside ambient and internal liquid temperatures  $\Delta T$ , the heat transfer coefficient  $U$  and the latent heat of the LPG liquid  $L$ , thus:

$$\text{Gas offtake rate, } W = \frac{A \times \Delta T \times U}{L}$$

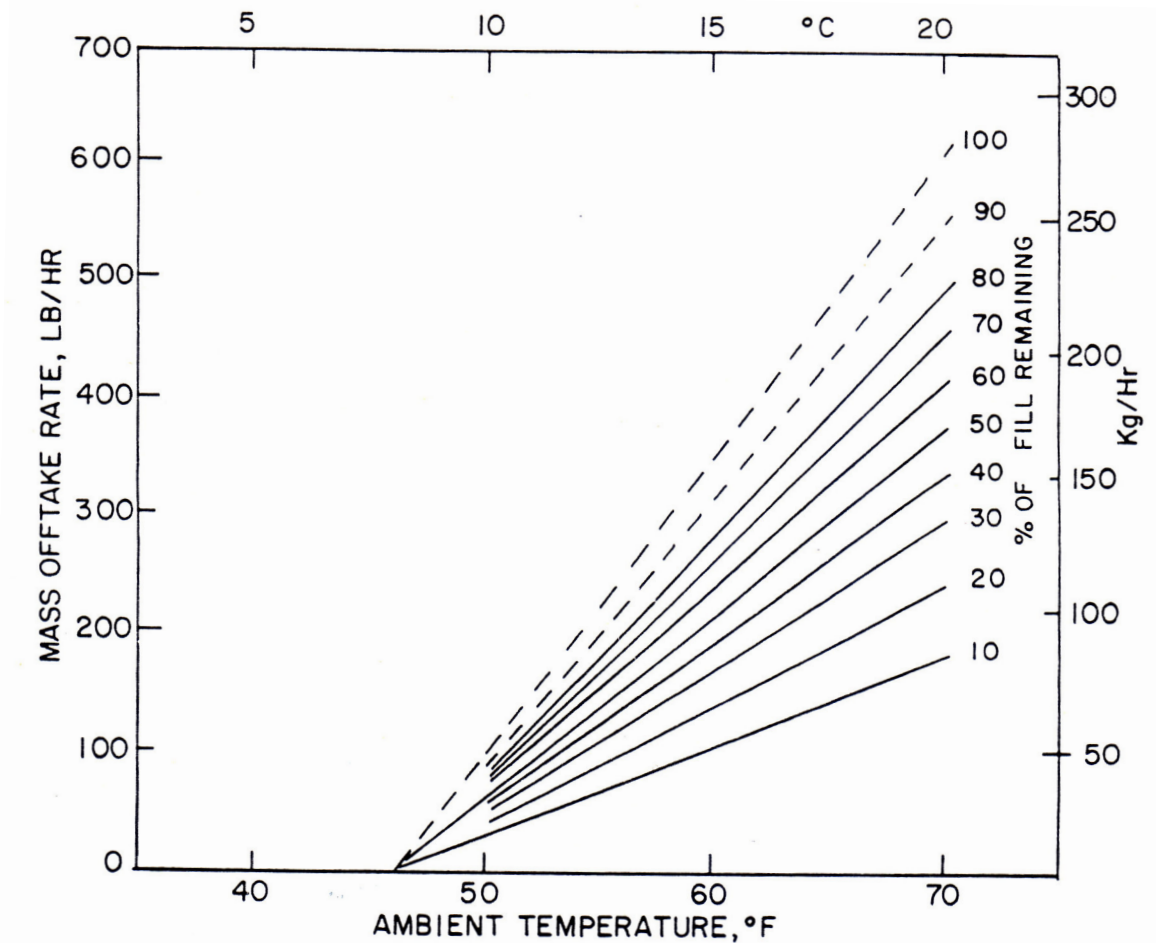
Where:  $U$  can vary from 5 to 15 kcal / m<sup>2</sup> / hr / °C (1 to 3 Btu / ft<sup>2</sup> / hr / °F). The lower value applies to dirt- or frost-covered tanks and the higher one to clean, dull painted vessels. (An average value of 10 kcal, etc. may be assumed.) The value of the internal liquid temperature will depend on the minimum level to which the gas offtake pressure is allowed to fall. This in turn relates to the pressure required downstream at the burner head. Minimum pressures of 0.35 kg/cm<sup>2</sup> (5 lb/in<sup>2</sup>.g) and 0.7 kg/cm<sup>2</sup> (10 lb/in<sup>2</sup>.g) relate to stabilized liquid (propane) temperatures of -34.4°C (-30°F) and -29°C (-20°F), respectively. In such cases, an ambient temperature of -6.7°C (20°F), for example, provides for a temperature difference of 27.7°C and 22.3°C, respectively. The figure to be used for latent heat is that applying at the stabilized liquid temperature, i.e. in the case of propane 100 kcal/kg (179 Btu/lb) and 97 kcal/kg (176 Btu /lb), at - 34.4°C and - 29°C, respectively.

<i>British units</i>						
<i>Natural vaporization rates in lb/hr at a pressure of 5 lb/in<sup>2</sup> gauge for 100 long ton storage tanks for various ambient temperatures (assumed overall heat transfer coefficient = 2 Btu/hr ft<sup>2</sup> °F)</i>						
<i>Per cent capacity</i>	<i>Propane Ambient temperature, °F</i>			<i>Butane Ambient temperature, °F</i>		
	<i>60</i>	<i>50</i>	<i>40</i>	<i>60</i>	<i>50</i>	<i>40</i>
80	1670	1480	1290	424	232	39
70	1560	1380	1200	394	218	36
60	1440	1280	1110	364	198	33
50	1320	1170	1020	333	181	30
40	1200	1060	920	300	164	27
30	1060	940	810	264	144	24
<i>Metric units</i>						
<i>Natural vaporization rates in Kg/hr at a pressure of 0.35 kgf/cm<sup>2</sup> gauge for 106 tonnes storage tanks for various ambient temperatures (assumed overall heat transfer coefficient = 9.75 kcal/hr/m<sup>2</sup>/°C)</i>						
<i>Per cent capacity</i>	<i>Propane Ambient temperature, °C</i>			<i>Butane Ambient temperature, °C</i>		
	<i>15</i>	<i>10</i>	<i>4</i>	<i>15</i>	<i>10</i>	<i>4</i>
80	760	670	585	192	105	19
70	710	625	545	179	99	16
60	650	580	505	165	90	15
50	600	530	460	151	82	14
40	545	480	420	136	74	12
30	480	430	370	120	65	11

**Table 10.5 Vaporization Rates of LPG**

Calculations which have been derived in this fashion for vapour mass offtake rates obtainable from propane when held in a 106 tone (100 ton) storage vessel at varying ambient temperatures and liquid levels, with an assumed U factor of 10 kcal and a minimum tank pressure of 0.35 kgf/cm<sup>2</sup> (5 lb/in<sup>2</sup> gauge) are shown in Table 10.5.

Figure 10.6 indicates the offtake rate for 10 lb/in<sup>2</sup> (0.7 kg cm<sup>2</sup>) of pressure which can be expected from a smaller butane tank (60 ton) under a similar range of conditions. Thus, at 15°C, with the tank half full the rate will be about 220 lb/hr. This will fall to 50 lb/hr with a 20% fill and a drop in ambient temperature to 10°C.



**Figure 10.6 Natural Vaporizations from a 60 Ton Butane Vessel**

A 'rule of thumb' guide for vapour offtake rates obtainable from propane storage vessels has also been provided by the American Society of Mechanical Engineers. This is shown in Table 10.6.



<i>Percentage of container filled</i>	<i>K equals</i>	<i>Propane vaporization capacity at 0°F (Btu/hr)</i>
60	100	$D \times L \times 100$
50	90	$D \times L \times 90$
40	80	$D \times L \times 80$
30	70	$D \times L \times 70$
20	60	$D \times L \times 40$
10	45	$D \times L \times 45$

Where: **D** is the outside diameter in inches,  
**L** is the overall length in inches and  
**K** is the constant for percent volume of liquid in container.

**Table 10.6 'Rule of Thumb' Guide for ASME LPG Storage Containers**

We have found these predictions of gas offtake rate to refer to a minimum tank pressure of 10 lb/in<sup>2</sup> gauge with a U factor of 3. The ambient temperature is to be taken as 0°F as stated but the 'propane vaporization capacity' is the potential heat release obtainable by burning the vaporized propane in air. Hence, to obtain the weight of propane vaporized from the tank, one has to divide by the calorific value (21,650 Btu/lb for propane).

With the usual dimensions pertaining to 100 ton propane tank for example (L = 75 ft: D = 12 ft), some offtake rates predicted by the ASME Guide are as follows:

	<u>W (lb/hr)</u>	
	<u>0°F†</u>	<u>+20°F†</u>
60% liquid fill	600	1200
30% liquid fill	420	840

† Ambient temperature

All these estimates of vaporization rates and capacities obtainable direct from LPG storage vessels should be used for design guidance purposes only, rather than taken as firm predictions.

One disadvantage of natural vaporization in the case of mixed propane-butane feedstock is that propane will concentrate in the earlier fractions and butane in the later ones. This may be important if the factory burners are sensitive to combustion characteristics such as flame length, but in general the slight variations produced in gas composition will be of no consequence. In contrast, an artificially vaporized LPG will have a constant vapour composition whatever the composition of the liquid.

### 10.4.2 Pumps and Vaporizers for Liquid Withdrawal

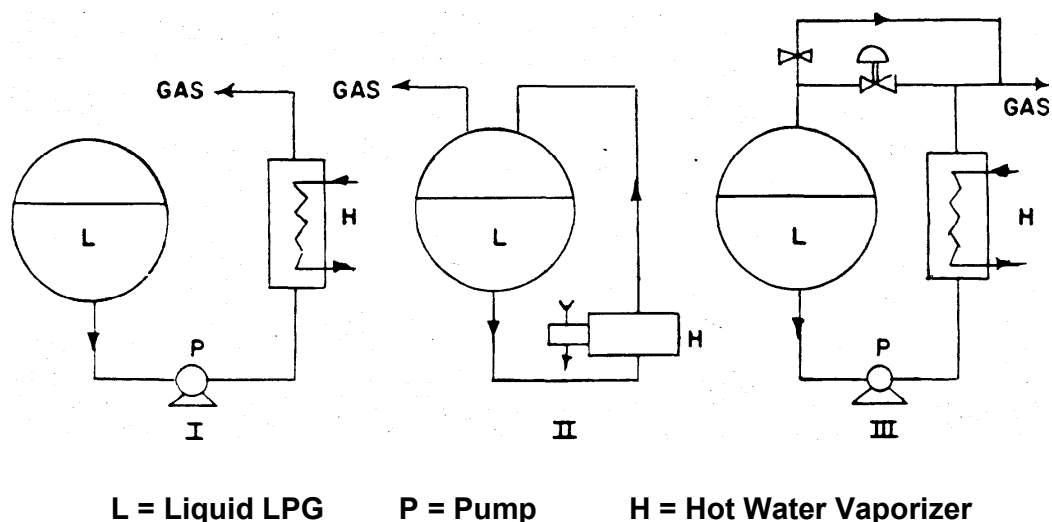
A continuous demand for butane gas usually requires liquid withdrawal via pump and vaporizer. The **pump** will be of the flame proofed centrifugal or positive displacement types situated near (but not directly under) the tank bottom. Any excess pressure developed by the pump is provided for by a spill-back liquid return line to the tank and by the incorporation of a pressure regulator downstream. 'Pop' i.e. pressure relief; valves are also fitted in all liquid LPG lines which have a closing valve fitted at either end. Such 'pop' valves have various pressure settings, e.g. 70, 100, 125, 200 lb/in<sup>2</sup>, etc. and open if line pressure exceeds the predetermined value. Escape gas is vented to the top of the storage vessel (see Figure 10.5).

**Vaporizers** may be direct gas-fired or of the jacketed indirect (steam, hot water or electrically heated) variety. They should be designed for sufficient liquid capacity and thermal input to convert butane at the required flow rate and at 10°C into vapour at least 6°C above the output gas dew point at the design output pressure. In the gas-fired variety, gas to the external burners is supplied from the top of the storage tank and/or from a return line at the vaporizer exit. Gas for cold start-up may be fed from standby propane cylinders. The liquid inlet flow to the vaporizer itself, which is a pressure vessel, is controlled by a float device mounted either inside or externally. As gas demand increases, more liquid vaporizes with a resultant drop in level, and the float opens the inlet valve allowing more liquid to flow into the vaporizer. As gas demand decreases, the liquid level rises in the vaporizer and the float shuts off the inlet valve. Direct fired vaporizers can be supplied in unit sizes up to about 1000 gal/hr. They are particularly useful in remote locations where no services such as steam or electricity are available.

Not every country permits the use of gas-fired vaporizers. They are, however, permitted in the U.K. and U.S.A. for example. The most common vaporizer, though more expensive than the gas-fired type, is the hot-water variety. The liquefied petroleum gas is vaporized by circulating hot water through a heating coil contained in the vaporizer body. Water circulation is effected by means of a fractional horsepower, glandless centrifugal pump located adjacent to the water heater. A water expansion tank is included in the packaged unit. The water temperature is controlled by a thermostat in the water outlet, and by a high-temperature limit thermostat to protect the water heater in the event of pump failure.

Three possible ways of linking the vaporizer with the storage vessel are shown in Figure 10.7.





**Figure 10.7 Practical Arrangements of LPG Vaporizers**

In the first example, gas is supplied from the top of the vaporizer. This is suitable for butane feedstock in moderate climates when the tank pressure never drops below one atmosphere. In the second and third systems, the 'feedback' principle is employed, i.e. vapour is returned from the vaporizer to the tank vapour space. In this way, the tank is protected against a vacuum condition with low vapour pressure butane in a cold environment. In the second system which has been described for propane use, gas is withdrawn from the tank and the vaporizer only cuts in when a certain preset low-pressure limit is reached. The third system differs in that gas is bled into the tank only when the tank pressure approaches atmospheric, gas ordinarily being withdrawn from the vaporizer top. This has the advantages of providing a constant gas composition and collecting any high boiling residues inside the vaporizer whence they can readily be drained.

Strict attention has to be paid to the siting of vaporizers in relation to LPG storage vessels and adjoining property.

Vaporizers other than direct fired and non-flameproof electrical types should be installed at a minimum distance of 5 ft from the nearest storage tank. Direct fired and non-flameproof electrical vaporizers should be installed at minimum safety distances in accordance with Table 10.7.

<i>Water capacity of storage vessel</i>	<i>Minimum distance of vaporizer from storage vessel</i>
<i>U.K. gallons</i>	<i>Feet</i>
Over 250 to 500	10
Over 500 to 2000	25
Over 2000 to 30,000	50
Over 30,000 to 75,000	75
Over 75,000	100
<i>Litres</i>	<i>Metres</i>
Over 1125 to 2250	3
Over 2250 to 9000	7.5
Over 9000 to 135,000	15
Over 135,000 to 377,500	22.5
Over 377,500	30

**Table 10.7 Minimum Safety Distances of Vaporizer from Storage Vessel**

The minimum distance between a vaporizer and the nearest important building or line of adjoining property is set out in Table 10.8.

<i>Capacity of vaporizer</i>	<i>Minimum distance of vaporizer from nearest important building or line of adjoining property</i>
<i>lb/hr</i>	<i>Feet</i>
Up to 80	10
Over 80 to 500	25
Over 500	50
<i>kg/hr</i>	<i>Metres</i>
Up to 36	3
Over 36 to 227	7.5
Over 227	15

**Table 10.8 Minimum Safety Distances of Vaporizers from Nearest Important Building or Line of Adjoining Property**

If a gas pressure higher than that which obtains at the liquid vaporization temperature is needed, a vapour superheater must be added. Other installation features which are necessary or desirable if vaporizers are used include: a liquid level controller, a vapour demister to prevent carry-over of mechanically entrained liquid with the vapour and means of drainage at low level of any heavy products which collect in the liquid LPG section of the system. To provide for continuous gas production and occasional vaporizer inspection and draining, vaporizers are best installed in pairs, each capable of meeting the total gas demand, the manifold having a common float control valve.

Vaporizers, like storage tanks, are pressure vessels and must be designed, fabricated and tested in accordance with a recognized pressure vessel code. Standard sizes up to 5 ton/hr are commercially available.

### 10.4.3 Air Mixing Units

There are various ways in which LPG can be mixed with air. They include the use of positive displacement air blowers and gas boosters, mechanical mixing valves, venturi injectors and carburetors. The energy of mixing is supplied by feeding either or both the gas and the air supply at raised pressures.

All mixing units should be capable of maintaining the gas mixtures at constant calorific value and pressure ( $\pm 10\%$ ) over a wide turn-down range at temperatures ranging from ambient to  $-10^{\circ}\text{C}$ .

Frequently, air mixing plants are used to produce a gas which can be distributed as a replacement for an existing utility gas, generally natural gas. In this case, precautions against failure of gas pressure are incorporated so as to prevent the gas in the mains from entering the flammable range (below 10% LPG). Alternatively, the mixer may be required to produce a gas-air mixture which falls within the flammable range, i.e. for supply to factory premix burners positioned close to the mixer itself. Certain mixing units have a wide degree of flexibility so as to be able to produce gas-air mixtures ranging from partial aeration to stoichiometric conditions. Figure 10.2 shows an LPG-air plant supplying 78,000 ft<sup>3</sup>/hr of simulated natural gas.

The basic element of a gas-air **carburettor** is a special slide valve. The rectangular opening in the valve overlaps the gas and air ports beneath and determines the net size of the openings. The valve moves automatically in response to fuel demands in a crosswise direction, enlarging or reducing both gas and air ports in unison without changing their relative sizes.

The valve is moved by a large diaphragm which responds to the suction caused by the demand for fuel.

An external hand wheel coupled to the valve permits sideways adjustment varying the relative sizes of the air and gas ports so that the gas-air ratio may be changed at will while the plant is operating. Once set, the ratio remains constant over a very wide range of throughputs.

With the venturi mixer, mixing is achieved by passing neat gas through a nozzle into a venturi tube, the gas entraining a controlled quantity of air with it as it enters the tube. A range of various sizes of venturi mixers can be installed in parallel to provide for wide variations in gas output. Variable Venturis are also available. In these the capacity of the unit is varied by moving a tapered needle in the nozzle thereby restricting the orifice and flow of gas.

Factory regulations usually demand that mixing units should not be located within 20 ft (6 m) of tanks containing flammable liquids.

#### **10.4.4 Ancillaries**

Other components of an LPG-air bulk installation plant include a gas holder or surge tank (optional), pipework, valves, liquid and gas pressure regulators, send-out gas meter and gas odorization facilities (if feed LPG is sweet and if send-out gas is required for public utility supplies).

Where **gas holders** are included, protection must be provided against freezing of the water seal (by addition of methanol for example), loss of the water seal due to excessive pressure, and against pressure surges in the distribution system due to the start-stop control system.

**Valves and fittings** should be made of steel, forged brass or from brass produced by extrusion or rolling. Cast iron valves should not be used, but valves of nodular iron made to B.S. 2789 or equivalent standard may be used with the liquid phase. The use of ball valves is strongly recommended.

Regarding **pipework**, liquid lines must be fabricated in steel, gas lines in steel or solid drawn copper. Examples of relevant pipeline manufacturing standards are: liquid B.S. 3601, steel 22 and 27 APSL Grade A; vapour lines below 70 lb/in<sup>2</sup> gauge, B.S. 1357 Class B; vapour lines above 70 lb/in<sup>2</sup> gauge, B.S. 3601. The use of cast-iron pipework is excluded for both liquid and vapour duty. Flexible hoses are not generally permitted for conveying LPG liquid or vapour but plastic pipework is used for distribution of utility gas to housing estates, commercial premises and the like (see Section 10.6).

## 10.5 PIPED LPG SCHEMES FOR UTILITY GAS

Special mention is made in this section of the use of LPG to provide a utility gas for distribution to factory, commercial or household premises. The distributed gas may be neat propane, neat butane or a mixture of LPG with air.

### 10.5.1 LPG-Air

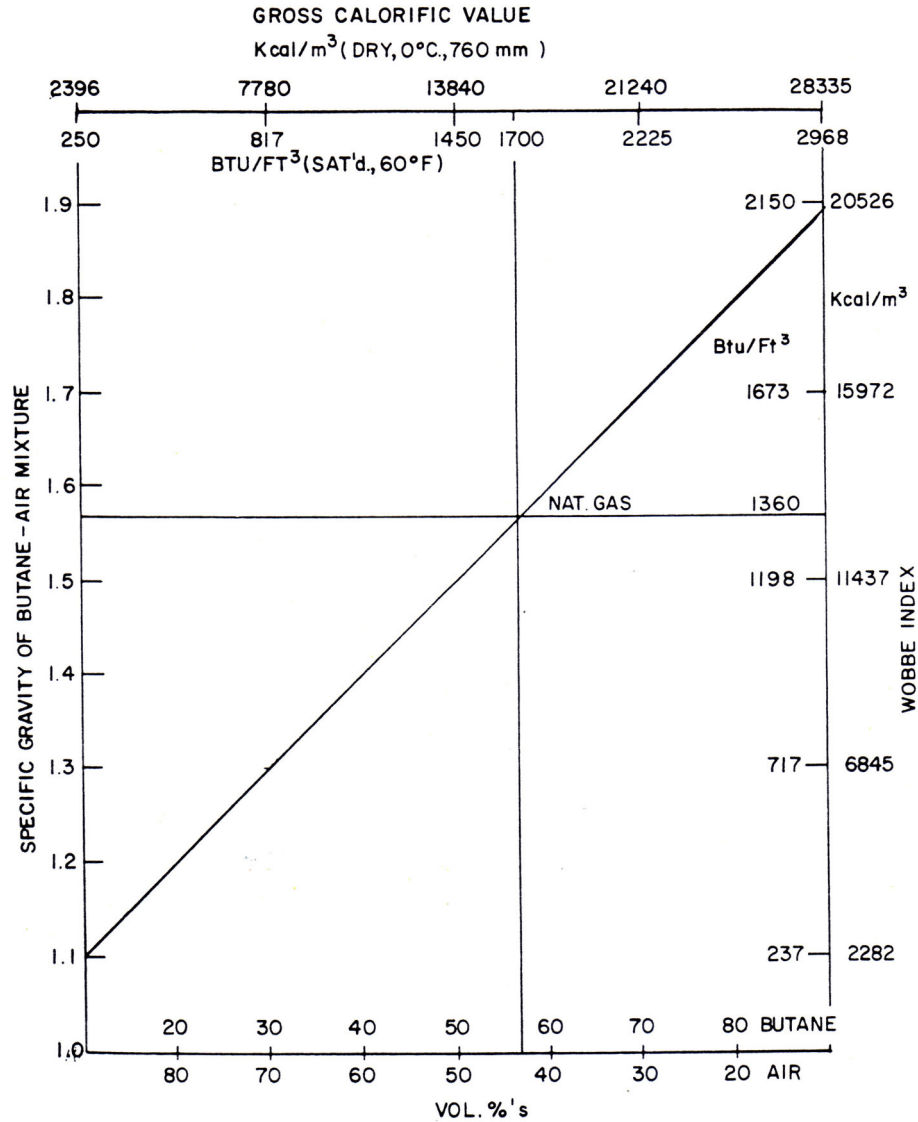
Numerous gas distributing agencies use LPG-air mixtures as a substitute for town or natural gas in country or island areas remote from the main gas transmission lines. In many townships in northern Italy, France, Denmark and Scotland, for example, piped LPG-air schemes have been installed. LPG-air mixtures can also be used for standby or peak shaving purposes within an existing natural or town's gas distribution system. Again, a factory complex may be employing LPG-air mix to fuel a number of separate burners or furnaces.

	<i>Natural gas</i>	<i>57 vol. % butane 43 % vol. % air</i>	<i>Butane</i>
<i>Wobbe Index</i>			
Btu/ft <sup>3</sup>	1360	1360	2390
kcal/m <sup>3</sup>	12,984	12,984	22,817
S.G. (air = 1)	0.589	1.57	2.0
<i>Calorific value</i>			
Btu/ft <sup>3</sup>	1040	1700	3380
kcal/m <sup>3</sup>	9929	16,230	32,269

**Table 10.9 Combustion Characteristics of Simulated Natural Gas**

In all these cases, care will be taken to ensure that the gas within the pipelines is not flammable, the necessary air for combustion being entrained at the entrance to the burner, i.e. at the gas injector.

Consider the case of a housing estate in which the gas appliances have been designed to take natural gas, or a factory where it is desired to feed gas to industrial burners ahead of the arrival of natural gas in the area. For the two types of gas to be interchangeable, the Wobbe Indices must be similar. However, since the specific gravity of natural gas is less than air, and because that of LPG-air mixtures must lie between 1 (air) and 2 (butane), a corresponding match in calorific values cannot be made. The figures in Table 10.9 make this clear.



**Figure 10.8 Combustion Characteristics of Butane-air Mixtures**

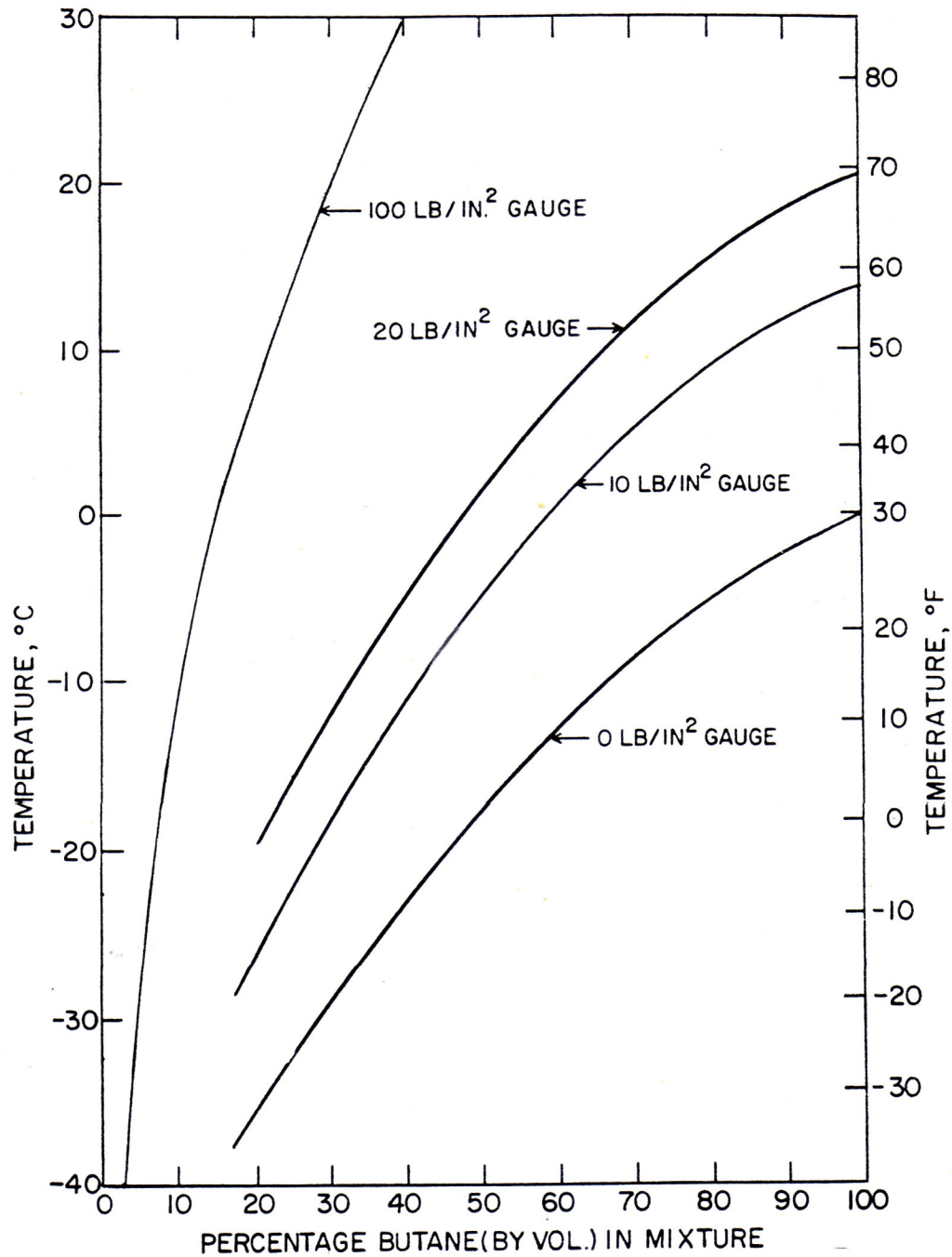
Addition of 43% by volume of air to butane produces a mixture simulating natural gas which has a Wobbe Index of 1360 Btu/ft³. However, the specific gravity of the mixture is 1.57 instead of the 0.59 typical of natural gas. This means that the calorific value of the replacement gas turns out to be 1700 Btu/ft³ whereas that of natural gas is about 1040. Thus the volume flow of LPG-air mixture fed to the burner is less than that which would apply to natural gas itself. The point is of importance only if the calorific value of the send-out system is fixed by statute at a natural gas value with corresponding fixed tariff. At times when LPG-air mixture is substituted (as at peak winter loads), a loss of revenue would occur.

In a permanent LPG-air system with a properly structured therm price and declared calorific value, no such problems arise.

Figure 10.8 enables the composition of any butane-air mixture required to match a given Wobbe Index or calorific value to be calculated. At the same time, the specific gravity of the mixture can be read.

Another effect of incorporating air with LPG is the lowering of the dew point of the send-out gas. This is advantageous where high-pressure butane is distributed at winter temperatures, particularly if no provision for lagging or heat tracing of vapour lines to avoid liquid recondensation is made. Figure 10.9 indicates the dew point of various butane-air mixtures at four different pressures, assuming that the gas consists entirely of n-butane. At 20 lb/in<sup>2</sup> gauge a 50 vol. % mixture of air with n-butane reduces the dew point of the gas from 72°F (22°C) to 34°F (2°C), a 75% air addition to +6°F (-15°C). At atmospheric pressure, the corresponding reductions are from 32°F (0°C) to -4°F (-18°C) and -27°F (-33°C), respectively.

On the subject of gas pressure, air mixing equipment usually provides at the most for 5 lb/in<sup>2</sup> gauge at the outlet. This is sufficient for users on a low-pressure grid, but for long-distance transmission or fuelling of high-pressure burners, a supplementary gas compressor may be required.

**Figure 8.9 Dew Point of n-butane-air Mixtures**



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## 10.6 GENERAL SAFETY PRECAUTIONS

The proper observation of safety procedures which are laid down in existing codes of practice ensures that a highly flammable and explosive gas is handled and used without hazard or incident. That this can be done has been the experience of countless users in all parts of the world over many years.

The design requirements for tanks, vaporizers, etc., their installation and location as have already been defined, provide for safe LPG storage and utilization. Mistakes, however, are sometimes made. Propane may be put into a butane tank with serious consequences. Tanks have been overfilled, gas leaks have been ignored. The lesson is evident. Safe usage starts with user familiarization with the nature of LPG and the rules of operating procedures.

Some guidance on safe practice now follows.

A person concerned with the operation of an LPG plant should be familiar with the following properties of LPG.

1. LPG is stored, normally, as a liquid under pressure
2. Leakage, especially of liquid, may release large volumes of flammable gases
3. A very small proportion of LPG in air can give rise to an explosive mixture
4. LPG vapour is heavier than air and may flow along the ground or through drains and be ignited at a considerable distance from the source of leakage
5. Because of its low boiling temperature, liquid LPG will cause skin burning
6. Ignition of a gas cloud will begin many yards distant downwind of the leakage point
7. The neat gas can cause suffocation

However, LPG is a safer fuel than coke oven gas or manufactured town gas in that the range of flammability of the gas in air is within narrower limits than those of the fuels mentioned (1.8 to 9.5% LPG by volume).

## 10.7 FIRE PRECAUTIONS

Apart from general care which must be taken when handling LPG, the highly flammable nature of the material requires specific precautions:

1. Smoking, welding, cooking or any process which requires heat by use of flame or resistance coils must be eliminated in LPG bulk plant areas and wherever LPG is received or discharged
2. There must be a minimum amount of venting to the atmosphere of gas or air-gas mixtures from cylinders, storage and distribution vessels
3. If venting gas without burning is necessary, ensure that the gas is released at a point away from any flame or other source of ignition
4. Dry vegetation and inflammable material must be permanently removed from areas surrounding fixed tanks and from those areas where portable tanks are stored
5. Leather gloves should be worn when breaking any connections after loading or unloading tank cars, tank trucks, package trucks (used for carrying cylinders), ships and cylinders
6. When repairs are made, the valves on both sides of the section to be repaired must be closed and tight and this section of piping and equipment purged of LPG
7. No one must enter a storage tank for inspection unless all lines leading to it have been disconnected and blanked and the tank thoroughly purged of inflammable gas. If breathing apparatus is not available, the purge gas (nitrogen or carbon dioxide) must be replaced by air, and the oxygen content of the tank checked before entering
8. Tests of any vessels, connections, or piping systems for leaks must not be made with a flame. Soapy water or tracer gas should be used. In case servicing is required by night, only explosion-proof flash-lights shall be used
9. LPG containers must always be filled in accordance with the proper table of filling densities

10. All installations should be earthed to prevent the formation of static electricity. This applies to tank cars, tank trucks and ships as well as permanent installations. However, storage vessels do not require protection against lightning
11. Storage tank safety valves should be inspected and their popping pressures should be checked at least once a year
12. No container shall be filled which does not comply with the safety regulations required by the regulatory body having jurisdiction

To protect and cool down tanks, consideration should be given to the installation of fixed water sprays which can be used when excessive summer temperatures are likely to cause an undue rise in vapour pressure.

An adequate supply of water for use by fire-fighting services must be available on site, as well as hand fire extinguishers of the dry chemical type (e.g. to B.S. 3465) for use by plant operators. Foam extinguishers are not suitable for LPG fires.

Electrical apparatus, instrumentation and telecommunications should comply with authorized codes.

Finally, in order to ensure positive detection of escaping gas by odour, it is laid down by most authorities that all liquefied petroleum gases shall be odorized by an approved agent (ethyl mercaptans, dimethyl sulphide or thiophane, for example). The recommended dosing level is such that the presence of gas down to concentrations in air of one-fifth of the lower limit of flammability is detectable (i.e. a concentration of about 0.4 vol. % gas in air). Addition of a minimum of one pound of ethyl mercaptans to 10,000 gal of liquid LPG usually ensures detection.