Technical Information & Safe Handling Guide for Methanol

October 2002

METHANEX®

A *Responsible Care*® Company

TECHNICAL INFORMATION
& SAFE HANDLING GUIDE
FOR METHANOL

Version 2.0
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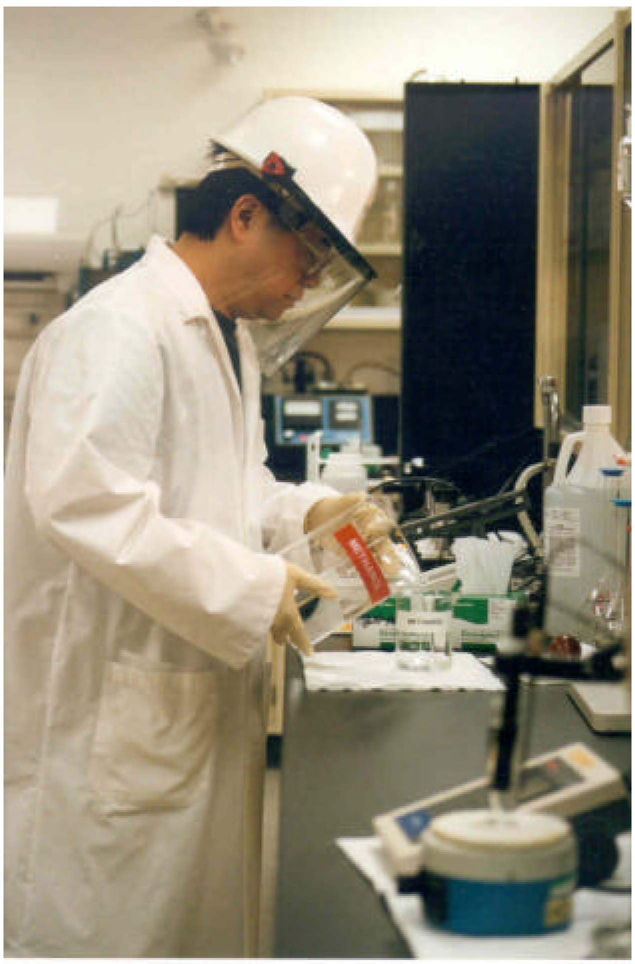
1.0 RESPONSIBLE CARE® AT METHANEX

Responsible Care is a voluntary initiative of the international chemical industry, that is designed to foster continuous improvement in health, safety and environmental performance, as well as sensitivity and responsiveness to public concerns. The ethic ensures the safest possible management of chemical products throughout their life cycle, from the planning of new products through their manufacture, distribution, use, and ultimate disposal.

Methanex Corporation is committed to the responsible management of our products and the processes by which they are created and marketed. We will, in the execution of our responsibilities, make the protection of human health and the environment our first priority. Responsible Care is the means by which this commitment is carried out.



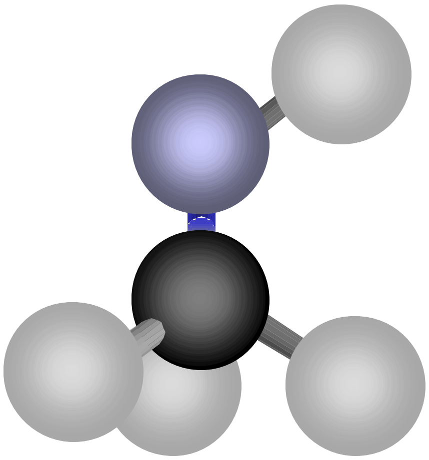
Under the Responsible Care ethic, we are committed to do the right thing and be seen to do the right thing. We are guided towards environmental, societal, and economic sustainability by the following principles:

- We are stewards of our products and services during their life cycles in order to protect people and the environment.
- We are accountable to the public, who have the right to understand the risks and benefits of what we do and to have their input heard.
- We respect all people.
- We work together to improve continuously.
- We work for effective laws and standards, and will meet or exceed them in letter and spirit.
- We inspire others to commit themselves to the principles of Responsible Care.

For further information on Responsible Care and Methanex Corporation's commitment to this important chemical industry initiative, consult the Methanex website (www.methanex.com). For complete information on the Responsible Care ethic, visit the Canadian Chemical Producers' Association's website (www.ccpa.ca).

2.0 INTRODUCTION: METHANOL

Derived from natural gas, methanol is a hydrocarbon, comprised of carbon, hydrogen and oxygen. Its chemical formula is CH_3OH.



Methanol is an alcohol and is a colorless, neutral, polar and flammable liquid. It is miscible with water, alcohols, esters and most other organic solvents. It is only slightly soluble in fats and oils.
Detailed physical and chemical properties of methanol are provided in the following pages.

Methanex produces methanol using a catalytic process with natural gas and steam as the feedstocks. The natural gas is catalytically reformed to carbon oxides and hydrogen. The resulting synthesis gas mixture is circulated under pressure and moderate temperature in the presence of a metallic catalyst and converted to crude methanol. The crude methanol is distilled to yield commercial chemical grade methanol.

Other common names for methanol include methyl alcohol, methyl hydrate, wood spirit, wood alcohol, and methyl hydroxide.

Methanol is used as a building block for many chemicals and products. Other uses include windshield washer antifreeze and fuels. Some specific uses are discussed later in this guide.

3.0 PROPERTIES OF METHANOL

3.1 Physical Properties of Pure Methanol

Molecular Weight	32.04 g mol^{-1}
Critical Temperature	512.5K (239°C; 463°F) [1]
Critical Pressure	8.084MPa (78.5 atm) [5]
Critical Density	0.2715 g cm^{-3} [1]
Critical Compressibility Factor	0.224 [1]
Specific Gravity	
Liquid	
(25°/4°C)	0.7866 [3]
(20°/4°C)	0.7915 [3]
(15°/4°C)	0.7960 [3]
Vapour	1.11 [3]
Vapour Pressure	
20°C (68°F)	12.8 kPa [4] (1.856 psia) (96 mm Hg)
25°C (77°F)	16.96 kPa [4] (2.459 psia) (127.2 mm Hg)
Latent Heat of Vapourization	
25°C (77°F)	37.43 kJ mol^{-1} (279.0 cal g^{-1}) [5]
64.6°C (148.3°F)	35.21 kJ mol^{-1} (262.5 cal g^{-1}) [5]
Heat Capacity at Constant Pressure	
25°C (77°F) (101.3kPa)	
Liquid	81.08 J mol^{-1} K^{-1} [1] (0.604 cal g^{-1} K^{-1}) (0.604 Btu lb^{-1} $°F^{-1}$)
Vapour	44.06 J mol^{-1} K^{-1} [1] (0.328 cal g^{-1} K^{-1}) (0.328 Btu lb^{-1} $°F^{-1}$)
Coefficient of Cubic Thermal Expansion	
20°C	0.00149 per °C [5]
40°C	0.00159 per °C [5]

Boiling Point	
760 mm Hg (101.3 kPa)	64.6°C [5] (148.3°F)
Freezing Point	-97.6°C [5] (-143.7°F)
Reid Vapour Pressure	32 kPa [1]
Flash Point	
Closed vessel (TCC method)	12°C (54°F) [3]
Open vessel (TOC method)	15.6°C (60.1°F) [1]
Auto Ignition Temperature	470°C (878°F) [3]
Viscosity	
Liquid	
-25°C (-13°F)	1.258 mPa s [5]
0°C (32°F)	0.793 mPa s [5]
25°C (77°F)	0.544 mPa s [5]
Vapour	
25°C (77°F)	9.68 µPa s [1]
127°C (261°F)	13.2 µPa s [5]
Surface Tension	
20°C (68°F)	22.6 mN m^{-1} [2]
25°C (77°F)	22.07 mN m^{-1} [5]
Refractive Index	
15°C (59°F)	1.33066 [3]
20°C (68°F)	1.32840 [1]
25°C (77°F)	1.32652 [1]
Thermal Conductivity	
Liquid	
0°C (32°F)	207 mW m^{-1} K^{-1} [5]
25°C (77°F)	200. mW m^{-1} K^{-1} [5]
Vapour	
100°C (212°F)	14.07 mW m^{-1} K^{-1} [5]
127°C (261°F)	26.2 mW m^{-1} K^{-1} [5]
Heat of Combustion	
Higher heating value (HHV) (25°C, 101.325kPa)	726.1 kJ mol^{-1} [5] (22.7 kJ g^{-1})
Lower heating value (LHV) (25°C, 101.325kPa)	638.1 kJ mol^{-1} [calc] (19.9 kJ g^{-1})
Flammable Limits (in air)	Lower 6.0(v/v)% [3] Upper 36.5(v/v)% [3]

A copy of the MSDS for methanol can be obtained from the Methanex Corporation web site:

www.methanex.com/methanol/techsafetydata.htm

3.2 Regulatory and Health & Safety Information for Methanol

Hazardous Material Information:	
EINECS No. (EU)	200-659-6
UN Number	UN 1230
Dangerous Goods Classification	
Primary Classification	3
Subsidiary Classification	6.1
Packing Group	PG II
ADR Classification (transport by road)	
Class	3
Packing	II
Danger Label Tanks	3+6.1
Danger Label Packages	3+6.1
RID Classification (transport by rail)	
Class	3
Packing	II
Danger Label Tanks	3+6.1
Danger Label Packages	3+6.1
ADNR Classification (transport by inland waterways)	
Class	3
Packing	II
Danger Label Tanks	3+6.1
Danger Label Packages	3+6.1
IMDG Classification (maritime transport)	
Class	3
Sub Risks	6.1
Packing	II
MFAG	19
ICAO Classification (air transport)	
Class	3
Sub Risks	6.1
Packing	II

Health & Safety Information:	
Exposure Limits*	
TLV-TWA	262 mg m^{-3} [5] (200 ppm)
TLV-STEL	328 mg m^{-3} [5] (250 ppm)
OES-LTEL	266 mg m^{-3} (200 ppm)
OES-STEL	333 mg m^{-3} (250 ppm)
MAK	270 mg m^{-3} (200 ppm)
MAC-TGG 8 h	260 mg m^{-3}
VME-8 h	260 mg m^{-3} (200 ppm)
VLE-15 min.	1300 mg m^{-3} (1000 ppm)
GWBB-8 h	266 mg m^{-3} (200 ppm)
GWK-15 min.	333 mg m^{-3} (250 ppm)
EC	260 mg m^{-3} (200 ppm)
NFPA Classification	1B Flammable Liquid
NFPA Hazard Rating	
Health	1
Flammability	3
Reactivity	0

** Additional exposure data and guidelines can be found in the US EPA Proposed Acute Exposure Guideline [6].*

TLV - Threshold Limit Value (ACGIH US 2000)
MAK - Maximale Arbeitsplatzkonzentrationen (Germany 2001)
VME - Valeurs limites de Moyenne d'Exposition (France 1999)
GWBB - Grenswaarde beroepsmatige blootstelling (Belgium 1998)
EC - Indicative occupational exposure limit values (EU directive 2000/39/EC)
OES - Occupational Exposure Standards (United Kingdom 2001)
MAC - Maximale aanvaarde concentratie (the Netherlands 2002)
VLE - Valeurs limites d'Exposition à court terme (France 1999)
GWK - Grenswaarde kortstondige blootstelling (Belgium 1998)

3.3 Some Binary Azeotropes of Methanol

The following table shows the proportion of methanol in some binary mixtures.

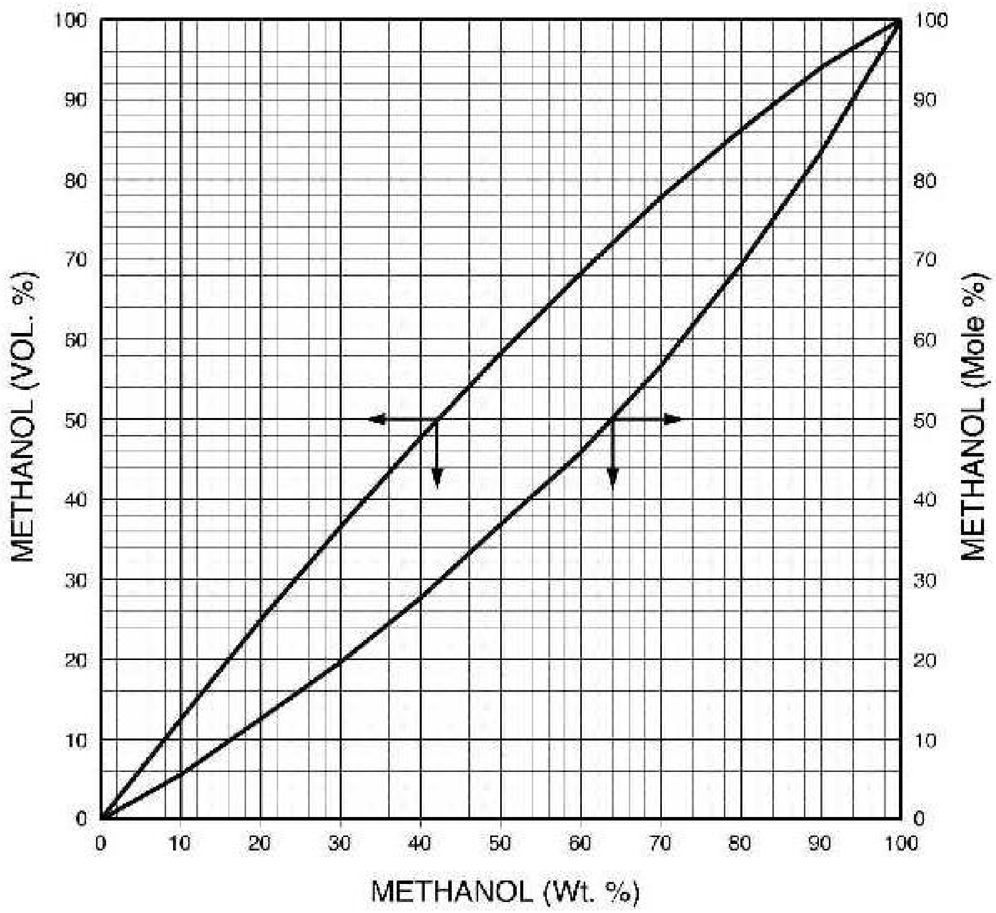
(Constant Boiling Mixtures)

Component	**Pure boiling point of component** (°C @ 760 mm Hg)	**Constant boiling point of mixture** (°C @ 760 mm Hg)	**Methanol content of azeotrope** (wt%)
Acetonitrile [1]	81.6	63.45	19
Acrylonitrile [1]	77.3	61.4	61.3
Acetone [1]	56.15	55.5	12
Benzene [1]	80.1	57.50	39.1
Butyl Methyl Ether [7]	71.0	56.3	35.4
2-Butanone [1]	79.6	64.5	70
Carbon Tetrachloride [4]	76.8	55.7	20.7
Chloroform [7]	61.2	53.5	12.5
Cyclohexane [1]	80	54	38
Cyclohexene [1]	82.75	55.9	40
Cyclopentane [1]	49.4	38.8	14
Dichloromethane [7]	41.5	39.2	8
Ethyl acetate [1]	77.1	62.25	44
Ethyl formate[1]	54.15	50.95	16
Ethylene Dichloride [7]	83.5	59.5	35
Furan [1]	31.7	<30.5	<7
n-Hexane [7]	68	50	21.5
Methyl acetate [1]	57.1	53.9	17.7
Methyl acrylate [1]	80	62.5	54
Methyl methacrylate [1]	99.5	64.2	82
Methyl propionate [1]	79.8	62.45	47.5
n-Octane [7]	125.6	63	72
n-Pentane [1]	36.15	30.85	7
Tetrahydrofuran [1]	66	60.7	31.0
Thiophene [1]	84	<59.55	<55
Toluene [1]	110.6	63.5	72.5
Trichloroethylene [4]	87	59.4	38.0

Some Non-Azeotropes [7]	Acetaldehyde	Ethane	Propyl acetate
	Acetone (@ <100 mm Hg)	Ethanol	Pyridine
	Chloroethane	Diethyl ether	Triethylamine
	Cumene	Ethylene Oxide	Water
	Diethylamine	Isopropanol	M/O/P-Xylenes

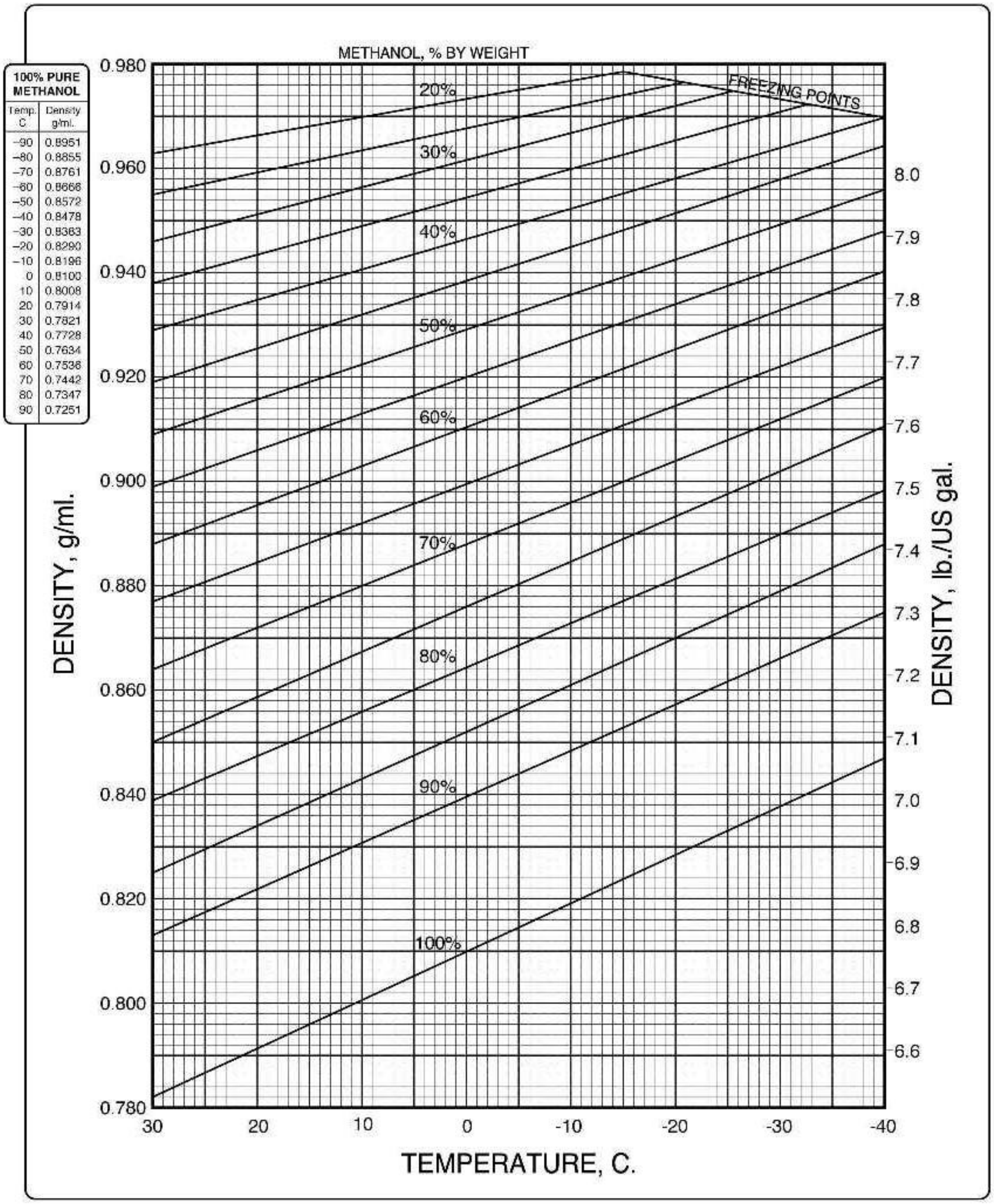
3.4 Volume - Weight - Mole% Conversions

GRAPH 1:
VOLUME – WEIGHT – MOLE % CONVERSIONS
FOR METHANOL WATER SOLUTIONS AT 20C (68F)



3.5 Densities of Methanol - Water Solutions

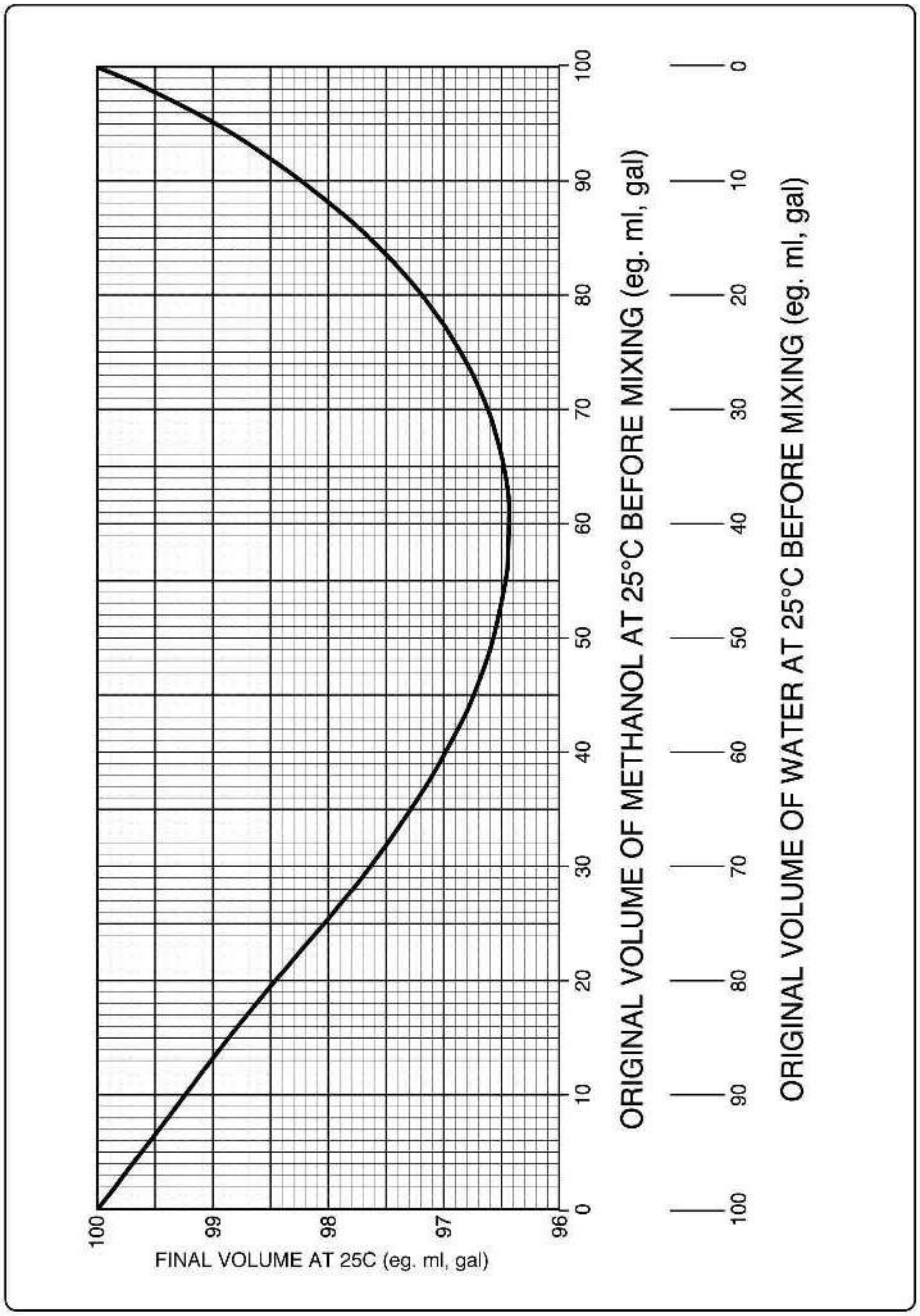
GRAPH 2: DENSITIES OF METHANOL – WATER SOLUTIONS



Temp. C	Density g/ml.
−90	0.8951
−80	0.8855
−70	0.8761
−60	0.8666
−50	0.8572
−40	0.8478
−30	0.8363
−20	0.8290
−10	0.8196
0	0.8100
10	0.8008
20	0.7914
30	0.7821
40	0.7728
50	0.7634
60	0.7536
70	0.7442
80	0.7347
90	0.7251

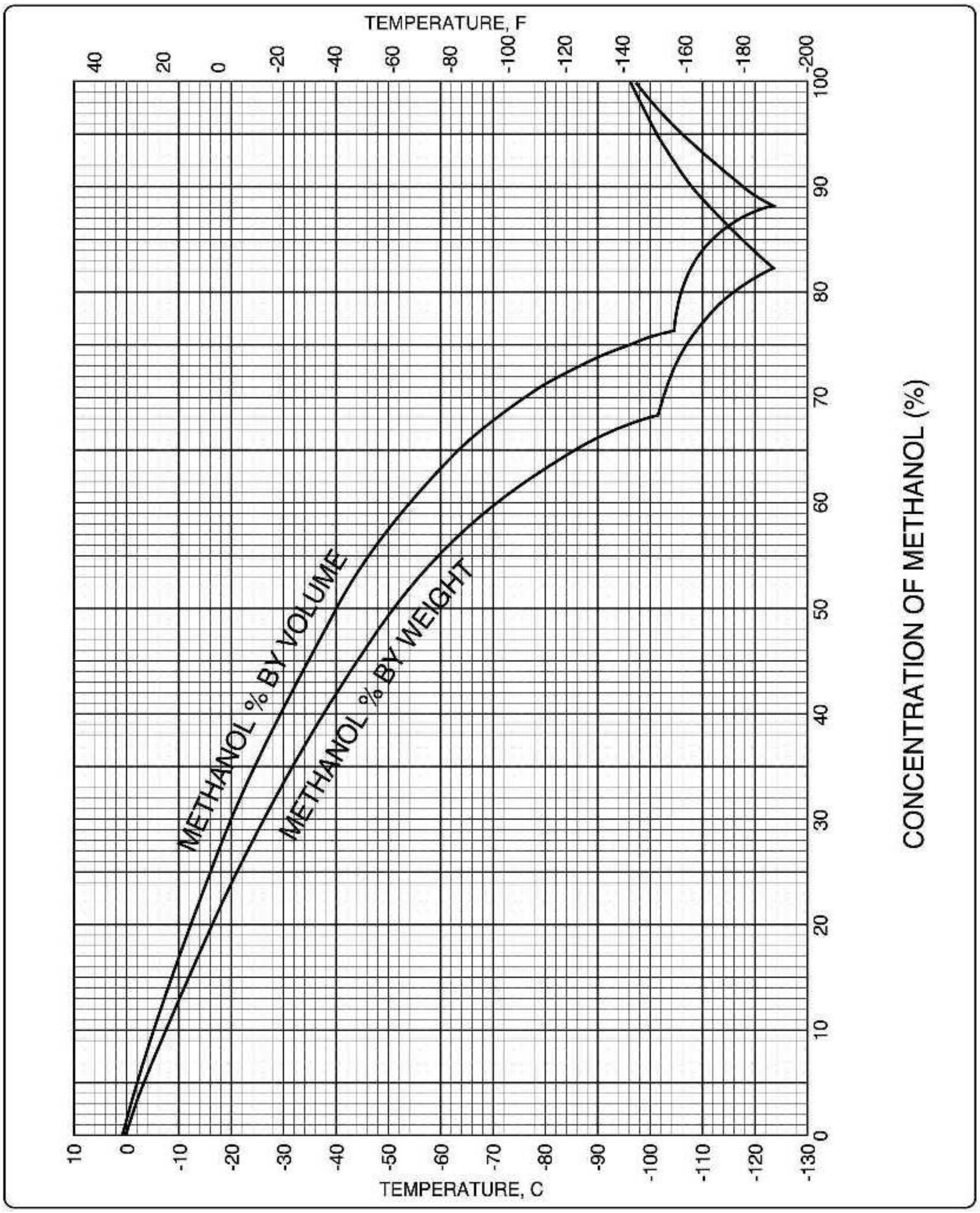
3.6 Final Volume when Methanol and Water are Mixed

GRAPH 3:
FINAL VOLUME WHEN METHANOL AND WATER ARE MIXED



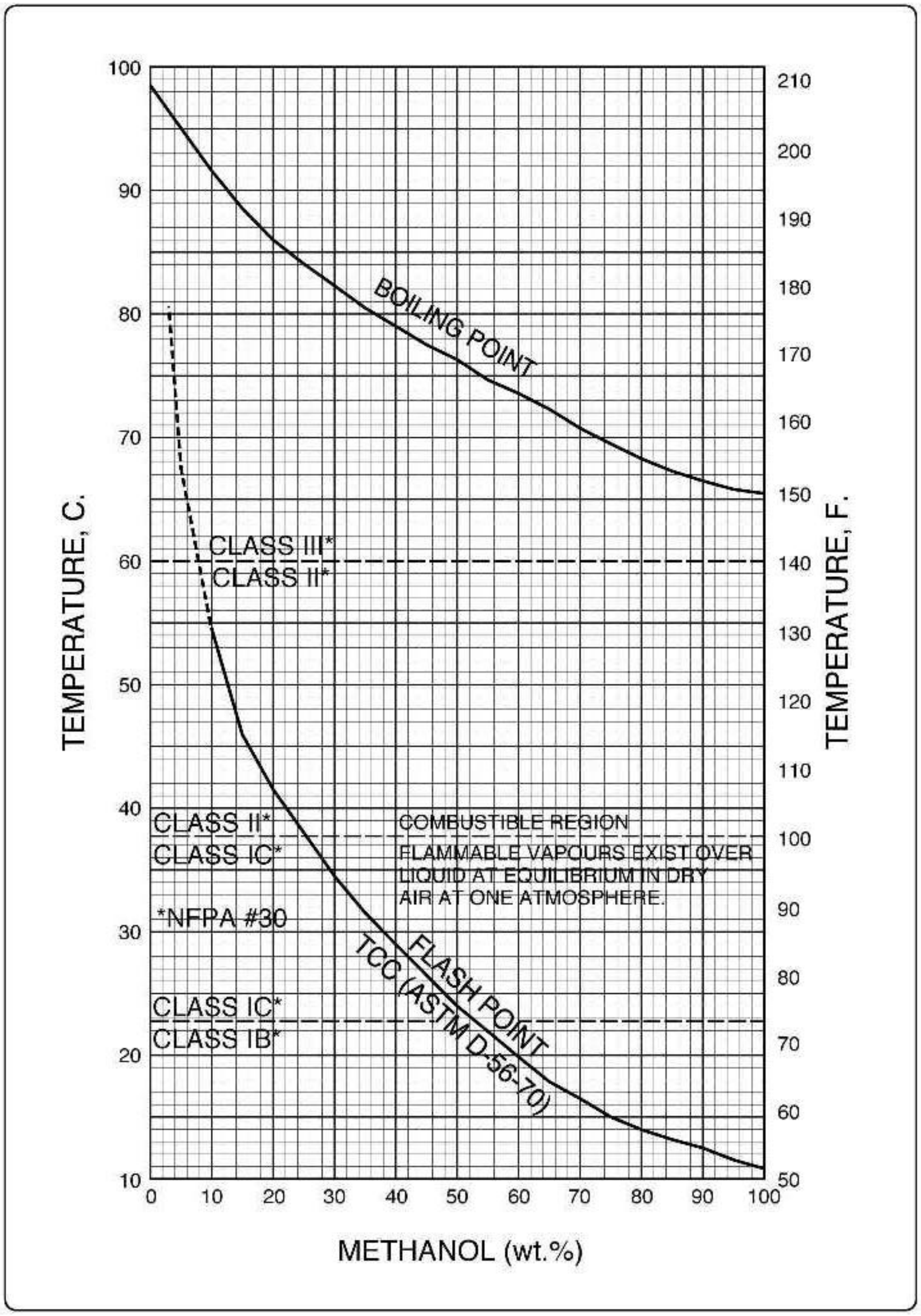
3.7 Freezing Points of Methanol - Water Solutions

GRAPH 4:
FREEZING POINTS OF METHANOL
–WATER SOLUTIONS, % BY WEIGHT AND % BY VOLUME



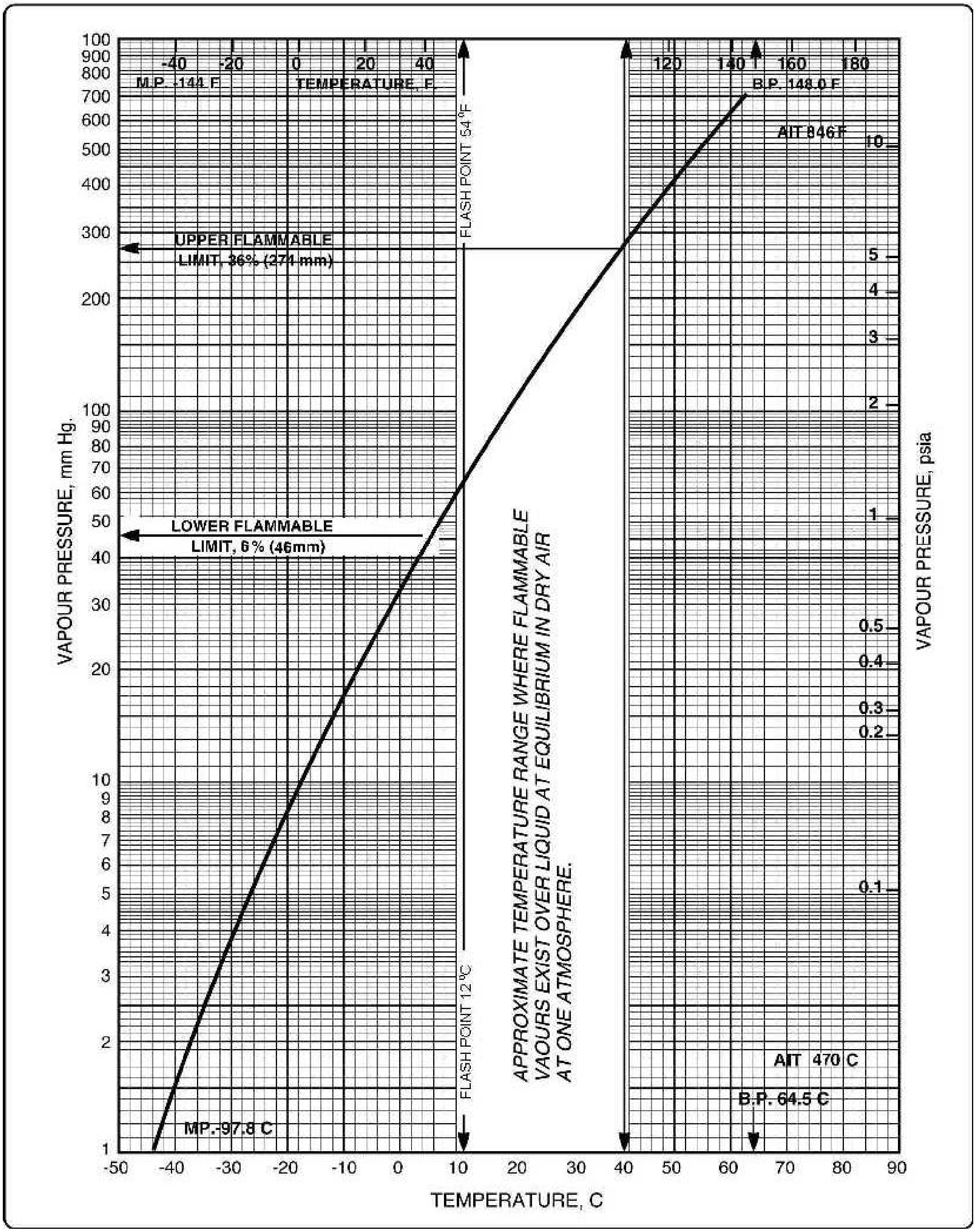
3.8 Boiling and Flash Points of Methanol - Water Solutions

GRAPH 5:
BOILING AND FLASH POINTS OF METHANOL – WATER SOLUTIONS



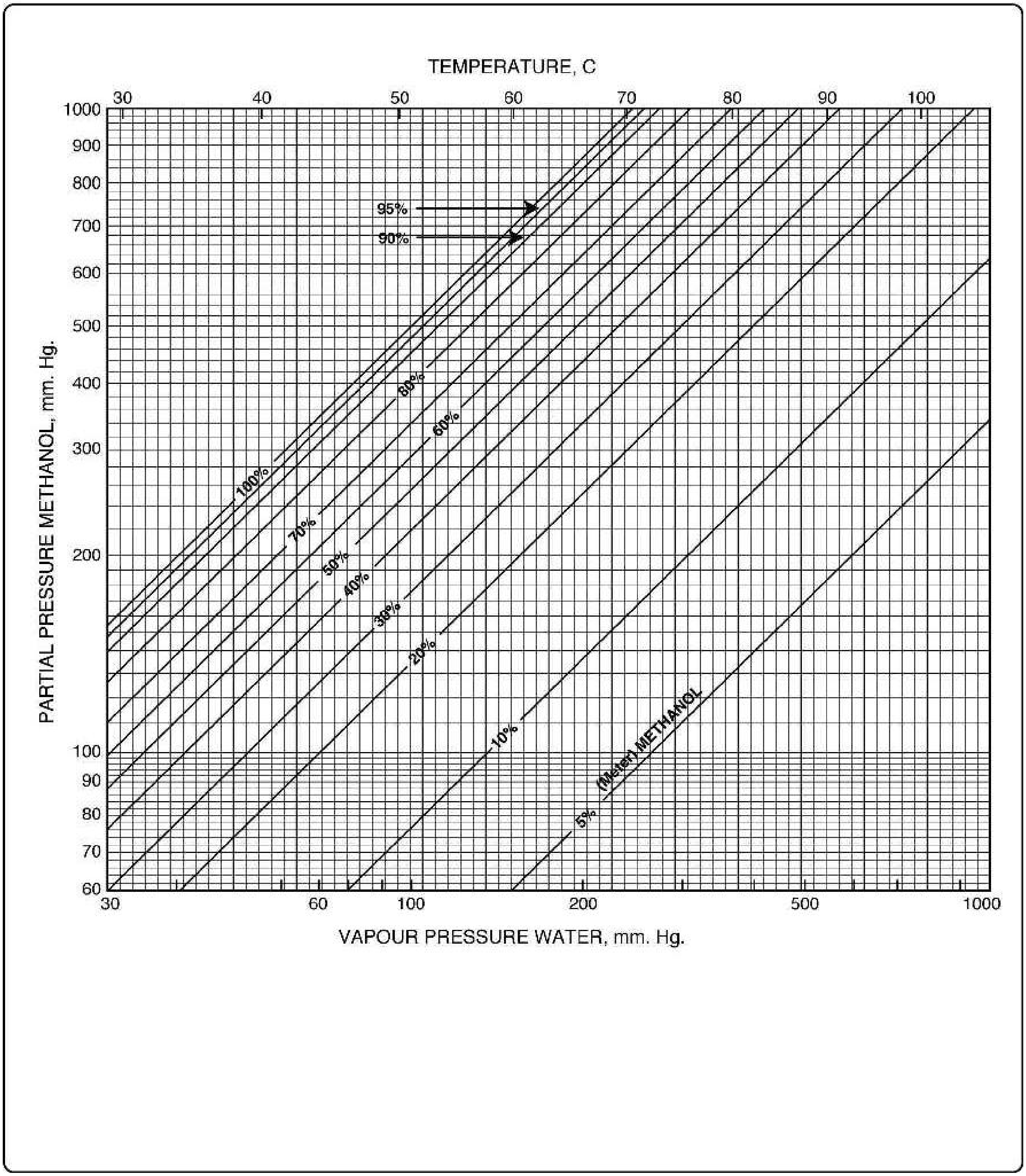
3.9 Vapour Pressure versus Temperature with Flammable Limits

GRAPH 6: VAPOUR PRESSURE VERSUS TEMPERATURE WITH FLAMMABLE LIMITS FOR METHANOL



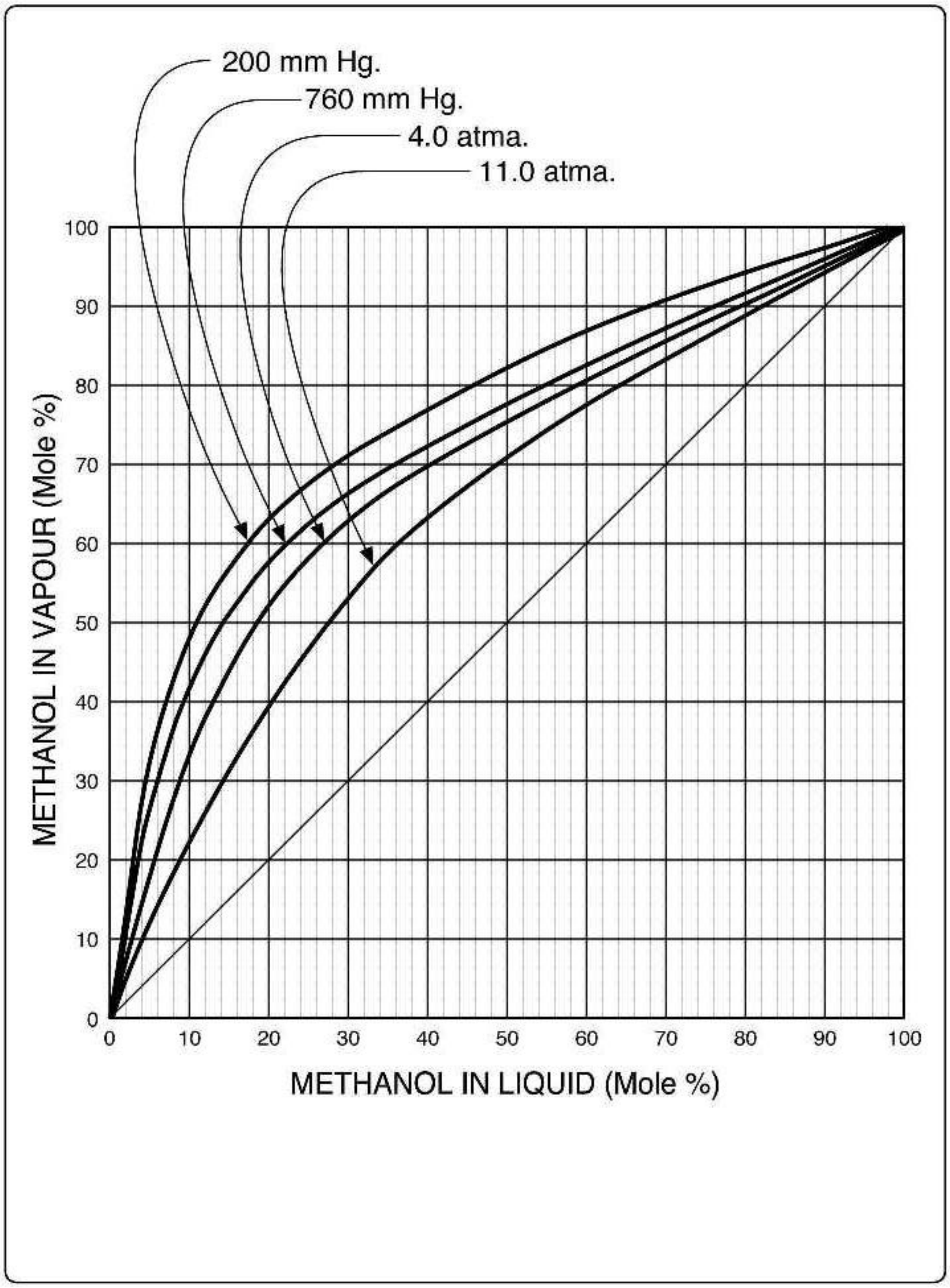
3.10 Partial Pressures versus Temperature of Methanol - Water Solutions

GRAPH 7: PARTIAL PRESSURES OF METHANOL – WATER SOLUTIONS AT VARIOUS TEMPERATURES



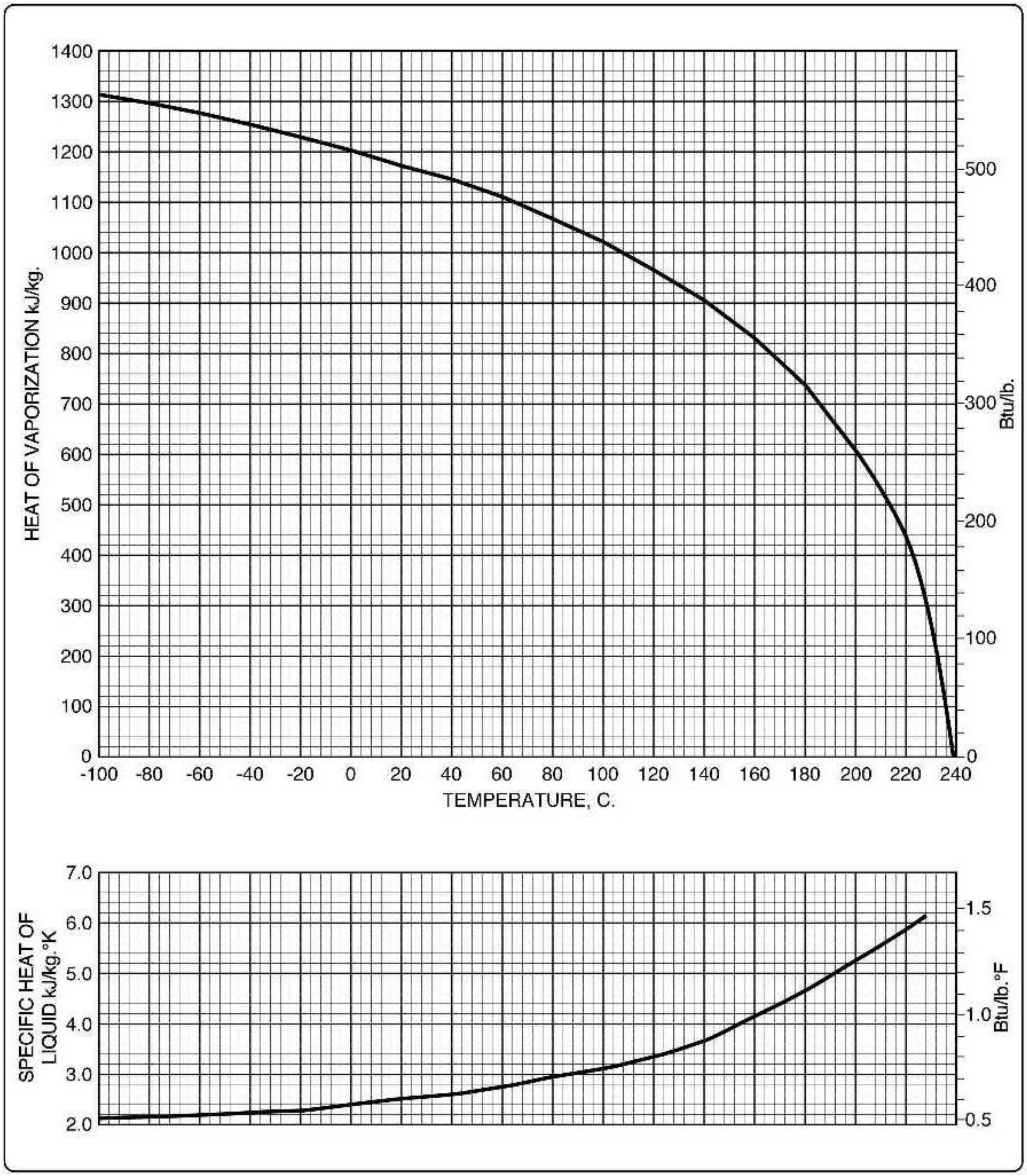
3.11 Vapour - Liquid Equilibrium Data for Methanol - Water Solutions

**GRAPH 8:
VAPOUR – LIQUID
EQUILIBRIUM DATA FOR METHANOL
– WATER SOLUTIONS** (at pressures shown)



3.12 Latent Heat of Vaporization and Specific Heat of Liquid Methanol

GRAPH 9: LATENT HEAT OF VAPORIZATION AND SPECIFIC HEAT OF LIQUID METHANOL



4.0 USES OF METHANOL

4.1 Methanol as a Chemical Intermediate & Fuel

The primary uses for methanol are the production of chemical products and use as a fuel.

Roughly three-quarters of all methanol is used in the production of formaldehyde, acetic acid and a variety of other chemical intermediates which form the foundation of a large number of secondary derivatives. These secondary derivatives are used in the manufacture of a wide range of products including plywood, particleboard, foams, resins and plastics.

The remainder of methanol demand is in the fuel sector, principally in the production of MTBE, which is blended with gasoline to reduce the amount of harmful exhaust emissions from motor vehicles. Methanol is also being used on a small scale as a direct fuel and it is actively being considered as a preferred fuel for fuel cells.

4.2 Methanol as a Fuel for Fuel Cell Applications

Over the longer term, methanol has potential to power fuel cells, an alternative means of generating electrical energy in an environmentally friendly manner that does not use traditional combustion.

Methanol is widely considered to be one of the most promising fuels for fuel cell applications. Several distinct attributes of methanol make it an ideal hydrogen carrier for hydrogen based fuel cell system.

Efficient and Versatile

With its low energy chemical bonds, methanol can be converted to hydrogen at relatively low temperatures (250°C to 300°C). Other hydrocarbon fuels require temperatures of 800°C to 900°C. Methanol's lower reforming temperatures ensure faster start-up, improved system efficiency, lower fuel processor costs, and a longer life for the fuel cell system.

In addition, because of methanol's low-energy chemical bonds, methanol is one of the only chemicals that can be converted directly to electricity in a Direct Methanol Fuel Cell (DMFC). DMFC systems are currently being developed as battery replacements for the portable power market.

High Quality, Readily Available

Methanol is widely distributed both globally and regionally as a commercial product. And because methanol is a liquid at normal conditions, it can be handled much the same way as conventional fuels like gasoline or diesel.

Furthermore, methanol is an inherently pure product, which greatly simplifies the reforming process, reduces the capital, operating and maintenance costs of the fuel cell system, and greatly reduces the risk of fuel cell catalyst contamination.

Environmentally Friendly

Methanol fuel cell systems convert chemical energy directly into electricity with greater efficiency than combustion-based power systems, thereby reducing associated greenhouse gas and urban smog forming emissions. Methanol is more environmentally benign than conventional liquid fuels. It has fewer potential environmental impacts and offers a greater degree of environmental protection.

4.3 Miscellaneous Uses of Methanol

Methanol is also used in the following applications:

- Crystallization, precipitation and washing of alkali metal halide salts
- Precipitation of polystyrene and chloroprene resins
- Washing and drying of powdered coal fractions
- Paint stripping
- Metal surface washing
- Cleaning of ion exchange resins
- Moisture and resin removal from lumber
- Extraction agent in the oil, chemical and food industries
- Fondue fuel
- Fuel for picnic stoves and soldering torches
- De-icer and windshield washer fluid for automobiles
- Antifreeze for pipeline dehydration.

5.0 TRANSPORTATION & DISTRIBUTION

At all stages of transport and distribution, methanol must be stored securely and handled responsibly. This minimizes risk to people and the environment, and preserves product quality.

The most common modes of bulk transportation of methanol worldwide are ship, barge, rail, truck, and pipeline.

5.1 Storage & Handling

Comprehensive product handling procedures and systems must be in place at all storage and transfer points.

Contamination Avoidance

When transferring or storing methanol, dedicated systems are preferable. Non-dedicated systems should be cleaned, flushed and sampled before being used, in order to ensure product integrity.

Equipment should be clearly labeled to indicate that it is for methanol service only. When not in use, the equipment must be protected from contamination.

Materials of Construction

Materials and methods of construction must be compatible with methanol service.

Methanol is non-corrosive to most metals at ambient temperatures; exceptions include lead, magnesium and platinum. Mild steel is usually selected as the construction material.

Tanks built with copper alloys, zinc (including galvanized steel), aluminium or plastics are not suitable for methanol-water solutions. While plastics can be used for short-term storage, they are generally not recommended for long-term storage due to deterioration effects and the subsequent risk of contamination.

Furthermore, coatings of copper (or copper alloys), zinc (including galvanized steel) or aluminium are attacked slowly.

Many resins, nylons and rubbers, particularly nitrile (Buna-N), ethylene propylene rubber (EPDM), teflon and neoprene are used satisfactorily as components of equipment in methanol service.

Methods of Construction

Storage containers and transfer systems must be designed according to appropriate engineering standards, and comply with all legislative requirements.

Storage tanks of welded construction are normally satisfactory. They should have secondary containment such as dikes or bunds to reduce fire risks and prevent large spills. Large tanks and containers must have control devices such as level gauges, conservation vents and pressure vacuum relief valves, as well as grounding. In some locations, vapour recovery may be required.

In confined areas or buildings, ventilation systems may be necessary in order to keep airborne concentrations of methanol below permissible exposure limits.

Storage areas must be secure from unauthorized access.

Grounding

Carbide tipped clamps (to ensure good contact through paint) and dip tube filling are generally used to guard against ignition from static electricity.

Loading Conversion Factors for Methanol

The following table [7] may be used to calculate the volume of methanol in gallons from weigh scale weights, or to determine weigh scale equivalent weights from gallons.

The tabulated conversions are derived from true mass densities that have been modified to account for the effect of air buoyancy that occurs in weigh scale measurements.

Temperature	Lb/Impgal	Lb/USgal
-20°F(-28.9°C)	8.3780	6.9762
-19°F(-28.3°C)	8.3728	6.9719
-18°F(-27.8°C)	8.3676	6.9675
-17°F(-27.2°C)	8.6324	6.9632
-16°F(-26.7°C)	8.3572	6.9589
-15°F(-26.1°C)	8.3520	6.9546
-14°F(-25.6°C)	8.3468	6.9502
-13°F(-25.0°C)	8.3416	6.9549
-12°F(-24.4°C)	8.3364	6.9416
-11°F(-23.9°C)	8.3312	6.9372
-10°F(-23.3°C)	8.3260	6.9329
-9°F(-22.8°C)	8.3208	6.9286
-8°F(-22.2°C)	8.3156	6.9242
-7°F(-21.7°C)	8.3104	6.9199
-6°F(-21.1°C)	8.3052	6.9156
-5°F(-20.6°C)	8.3000	6.9113
-4°F(-20.0°C)	8.2948	6.9069
-3°F(-19.4°C)	8.2896	6.9026
-2°F(-18.9°C)	8.2844	6.8983
-1°F(-18.3°C)	8.2792	6.8963
0°F(-17.8°C)	8.2740	6.8896
1°F(-17.2°C)	8.2688	6.8853

Temperature	Lb/Impgal	Lb/USgal
2°F(-16.7°C)	8.2636	6.8809
3°F(-16.1°C)	8.2584	6.8766
4°F(-15.6°C)	8.2532	6.8723
5°F(-15.0°C)	8.2480	6.8680
6°F(-14.4°C)	8.2428	6.8636
7°F(-13.9°C)	8.2376	6.8593
8°F(-13.3°C)	8.2324	6.8550
9°F(-12.8°C)	8.2272	6.8506
10°F(-12.2°C)	8.2220	6.8463
11°F(-11.7°C)	8.2168	6.8420
12°F(-11.1°C)	8.2116	6.8376
13°F(-10.6°C)	8.2064	6.8333
14°F(-10.0°C)	8.2012	6.8290
15°F(-9.4°C)	8.1960	6.8247
16°F(-8.9°C)	8.1908	6.8203
17°F(-8.3°C)	8.1856	6.8160
18°F(-7.8°C)	8.1804	6.8117
19°F(-7.2°C)	8.1752	6.8073
20°F(-6.7°C)	8.1700	6.8030
21°F(-6.1°C)	8.1684	6.7987
22°F(-5.6°C)	8.1596	6.7943
23°F(-5.0°C)	8.1544	6.7900

Temperature	Lb/Impgal	Lb/USgal
24°F(-4.4°C)	8.1492	6.7857
25°F(-3.9°C)	8.1440	6.7814
26°F(-3.3°C)	8.1388	6.7770
27°F(-2.8°C)	8.1336	6.7727
28°F(-2.2°C)	8.1284	6.7850
29°F(-1.7°C)	8.1232	6.7640
30°F(-1.1°C)	8.1180	6.7597
31°F(-0.6°C)	8.1128	6.7554
32°F(0.0°C)	8.1076	6.7510
33°F(0.6°C)	8.1024	6.7467
34°F(1.1°C)	8.0972	6.7426
35°F(1.7°C)	8.0920	6.7381
36°F(2.2°C)	8.0868	6.7337
37°F(2.8°C)	8.0816	6.7294
38°F(3.3°C)	8.0761	6.7251
39°F(3.9°C)	8.0712	6.7207
40°F(4.4°C)	8.0660	6.7164
41°F(5.0°C)	8.0608	6.7121
42°F(5.6°C)	8.0556	6.7077
43°F(6.1°C)	8.0504	6.7034
44°F(6.7°C)	8.0452	6.6991
45°F(7.2°C)	8.0400	6.6948
46°F(7.8°C)	8.0348	6.6904
47°F(8.3°C)	8.0296	6.6861
48°F(8.9°C)	8.0244	6.6818
49°F(9.4°C)	8.0192	6.6774
50°F(10.0°C)	8.0140	6.6731
51°F(10.6°C)	8.0088	6.6688
52°F(11.1°C)	8.0036	6.6644
53°F(11.7°C)	7.9984	6.6601
55°F(12.8°C)	7.9880	6.6515
56°F(13.3°C)	7.9828	6.6471
57°F(13.9°C)	7.9776	6.6428
58°F(14.4°C)	7.9724	6.6385
59°F(15.0°C)	7.9672	6.6341
60°F(15.6°C)	7.9620	6.6300
61°F(16.1°C)	7.9568	6.6255
62°F(16.7°C)	7.9516	6.6211
63°F(17.2°C)	7.9464	6.6168
64°F(17.8°C)	7.9412	6.6125
65°F(18.3°C)	7.9360	6.6082
66°F(18.9°C)	7.9308	6.6038
67°F(19.4°C)	7.9256	6.5995
68°F(20.0°C)	7.9204	6.5952
69°F(20.6°C)	7.9152	6.5908
70°F(21.1°C)	7.9100	6.5865
71°F(21.7°C)	7.9048	6.5822
72°F(22.2°C)	7.8996	6.5778
73°F(22.8°C)	7.8944	6.5735

Temperature	Lb/Impgal	Lb/USgal
74°F(23.8°C)	7.8892	6.5692
75°F(23.9°C)	7.8840	6.5649
76°F(24.4°C)	7.8788	6.5605
77°F(25.0°C)	7.8736	6.5562
78°F(25.6°C)	7.8684	6.5519
79°F(26.1°C)	7.8632	6.5475
80°F(26.7°C)	7.8580	6.5432
81°F(27.2°C)	7.8528	6.5389
82°F(27.8°C)	7.8476	6.5345
83°F(28.3°C)	7.8424	6.5302
85°F(29.4°C)	7.8320	6.5216
86°F(30.0°C)	7.8268	6.5172
87°F(30.6°C)	7.8216	6.5129
88°F(31.1°C)	7.8164	6.5086
89°F(32.27°C)	7.8112	6.5084
90°F(32.2°C)	7.8060	6.4999
91°F(32.8°C)	7.8008	6.4959
92°F(33.3°C)	7.7956	6.4912
93°F(33.9°C)	7.7904	6.4869
94°F(34.4°C)	7.7852	6.4826
95°F(35.0°C)	7.7800	6.4783
96°F(35.6°C)	7.7748	6.4739
97°F(36.1°C)	7.7696	6.4696
98°F(36.7°C)	7.7644	6.4653
99°F(37.2°C)	7.7592	6.4609
100°F(37.8°C)	7.7540	6.4566
101°F(38.3°C)	7.7488	6.4523
102°F(38.9°C)	7.7436	6.4479
103°F(39.4°C)	7.7384	6.4436
104°F(40.0°C)	7.7332	6.4393
105°F(40.6°C)	7.7280	6.4350
106°F(41.1°C)	7.7228	6.4306
107°F(41.7°C)	7.7176	6.4263
108°F(42.2°C)	7.7124	6.4220
109°F(42.8°C)	7.7072	6.4176
110°F(43.3°C)	7.7020	6.4133
111°F(43.9°C)	7.6968	6.4090
112°F(44.4°C)	7.6916	6.4049
113°F(45.0°C)	7.6864	6.4003
114°F(45.6°C)	7.6812	6.3960
115°F(46.1°C)	7.6760	6.3917
116°F(46.7°C)	7.6708	6.3873
117°F(47.2°C)	7.6656	6.3830
118°F(47.8°C)	7.6604	6.3787
119°F(48.3°C)	7.6552	6.3743
120°F(48.9°C)	7.6500	6.3700
121°F(49.4°C)	7.6448	6.3657
122°F(50.0°C)	7.6396	6.3614

Pipes & Hoses

Industry best practices make use of mild steel piping with welded flanges and methanol compatible gaskets. Generally, screwed connections are not used.

In most loading and unloading situations, the possibility of spark generation due to the accumulation of static electricity is minimal, as the electrical conductivity of methanol is relatively high. Velocity limits should be considered with regard to high pressure drop, hydraulic impacts, and erosion or corrosion concerns.

Non-ferrous materials should not be used for the construction of permanent pipework.

Rubber hoses should have an internal wire coil for strength and electrical continuity, and should only be used for temporary connections. The hose material must be compatible with methanol (Refer to the section 'Materials of Construction').

All hoses should be clearly labeled for methanol service only. The ends must be capped, or otherwise protected from contamination, when the hose is not in use.

Prior to putting any new pipework or hose into methanol service, it should be thoroughly washed with water and then with methanol to ensure that all contaminants are removed.

Motors and Pumps

Motors and associated electrical equipment used in methanol service should conform to local or national electrical codes.

Motors and pumps must be grounded. Pumps should be dedicated to methanol service, and flushed with methanol prior to first use.

Vapour Controls

Internal or external floating roofs can be used to control methanol vapour emissions from storage tanks.

Inert gas blanketing can be used to prevent the formation of explosive atmospheres in vapour spaces inside tanks. Dry nitrogen is the preferred inert gas and should be essentially free of carbon dioxide (CO_2). The presence of CO_2 may impact the methanol quality by increasing its acidity.

Pressure vacuum relief valves are normally used to control tank pressures.

Venting

Methanol can vent to atmosphere through pressure vacuum relief valves, flame arresters or vacuum breakers.

Overflow pipes are not recommended due to condensed methanol dripping from the pipes when the ambient temperature is below the storage temperature. This could create a fire and environmental hazard.

Reduced vapour losses will result from painting tanks white or other reflective colours.

5.2 Cleaning & Maintenance

For all forms of transportation, methanol vessels should be inspected for cleanliness and mechanical soundness prior to loading. Mechanical or contamination concerns should be resolved promptly.

Procedures for entry into methanol vessels and storage tanks in preparation for cleaning and maintenance are prescribed by local regulations. The following suggestions are made for general guidance only:

- Partially fill and flush 3-4 times with water.
- Open top and bottom manways for natural ventilation. On large tanks, install air moving devices.
- Tank or vessel must test "gas free". Before entry, check for safe oxygen and combustible levels.
- When unattended, manways should be blocked to prevent entry by unauthorized personnel.
- No one should enter any confined space without a safety watch in place.
- At least two escape routes should be provided from all storage and handling areas.

6.0 PERSONAL PROTECTION

6.1 Sources of Exposure to Methanol

Human exposure to methanol can occur via inhalation, ingestion or absorption.

Inhalation

Inhalation of methanol vapours is the most frequent type of exposure. The methanol threshold limit value (TLV) for a time weighted average (TWA) is 200 ppm. This is the maximum average concentration a worker should be exposed to over a continuous eight hour period.

The short term exposure limit (STEL) of methanol is 250 ppm. The STEL sets limits on excursions for periods of up to 15 minutes, four times per day with at least 60 minutes between exposure periods, so long as individuals are suffering no irritation or discomfort.

It is important to note that the odour threshold of methanol is several times higher than the TLV-TWA.

Ingestion

Methanol taken by mouth may pose a serious threat to life. One to four ounces of methanol have been known to cause fatalities. Ingestion produces similar effects to that of inhalation of vapors, but severity and speed of appearance of symptoms are increased.

Absorption

No serious adverse effects result from skin contact so long as repeated and excessive exposures are avoided.

6.2 Symptoms & Effects of Exposure

Methanol can cause poisoning, systemic acidosis, optic nerve damage and central nervous system (CNS) effects. Methanol can degrease the skin, which may cause dermatitis.

Symptoms of methanol poisoning do not depend on the uptake route and develop in three stages:

1. An initial narcotic effect; followed by
2. a symptom-free interval lasting 10-48 hours; and
3. nonspecific symptoms such as abdominal pain, nausea, headache, vomiting, and lassitude, followed by characteristic symptoms such as blurred vision, opthalmalgia, photophobia and possibly xanthopsia.

For instance [7]:

- 1,000 ppm will produce symptoms such as irritation of the eyes and mucous membranes.
- 5,000 ppm will result in a stupor or sleepiness.
- 50,000 ppm will result in narcosis (deep unconsciousness) in one or two hours, probably resulting in death.

Because the compound and its harmful metabolites are eliminated slowly, methanol is regarded as a cumulative poison.

6.3 First Aid Measures

In case of methanol **contact with the skin**, remove contaminated clothing. Wash with soap and water for 15 minutes. Seek medical attention if irritation occurs.

In case of methanol **contact with the eyes**, flush immediately with gently running water for a minimum of 15 minutes, ensuring all surfaces and crevices are flushed by lifting lower and upper lids. Obtain medical attention.

In case of **inhalation** of methanol vapours, remove the individual to fresh air. Asphyxiation from vapours may require artificial respiration. Due to the possibility of delayed onset of more serious illness, it is important to obtain medical attention.

Ingestion of methanol is life threatening. Onset of symptoms may be delayed for 18 to 24 hours after ingestion. Do not induce vomiting. Transport to medical attention. The individual should remain under close medical care and observation for several days.

6.4 Safety Precautions

All personnel must be aware of the hazardous properties of methanol, and exercise caution to avoid contact with it. At all times, avoid prolonged or repeated breathing of methanol vapours.

Proper ventilation is required to ensure safe working conditions. The type of ventilation will depend upon such factors as dead air spaces, temperature, convection currents and wind direction and must be considered when determining equipment location, type and capacity. If mechanical ventilation is used, spark-proof fans should be implemented.

Methanol should always be kept within closed systems or approved containers and never left open to the atmosphere. Containers should be labeled in accordance with local regulations and site requirements.

Eye wash fountains or bottles should be strategically placed within the work place. When large quantities of methanol are handled, safety showers with quick opening valve systems should be suitably located and protected from freezing. Breathing apparatus and resuscitation kits should be available.

6.5 Personal Protective Equipment

The level of risk of exposure to methanol will dictate the appropriate level of personal protective equipment (PPE) required.

At a minimum, we recommend wearing side shielded safety spectacles and task appropriate gloves. Depending upon the situation, PPE may also include appropriate footwear, face shields, respiratory protection, fire-resistant clothing, or chemical suits.

7.0 FIRE SAFETY

7.1 Flammability

Methanol is defined by the National Fire Protection Association (NFPA) and the Occupational Safety and Health Administration (OSHA) in the USA as a Class 1B flammable liquid.

Solutions of methanol containing up to 74% water are classified by NFPA as flammable (Refer to graph 5).

Flash Point

Flash point is defined as the minimum temperature at which the vapour pressure of a liquid is sufficient to form an ignitable mixture with air near the surface of the liquid [5]. Pure methanol has a flash point of 12°C (54°F) (TCC method).

When ambient temperature is less than the methanol flash point, the fire hazard is reduced. However, local hot spots can exceed the flash point and methanol can be ignited. Warmer ambient conditions increase the overall fire hazard.

Lower and Upper Explosive Limits

The lower explosive limit (LEL) of a flammable liquid is defined as the minimum concentration of the vapour in air for which a flame can propagate. The methanol LEL is 6% by volume.

The LEL and the flash point are closely related, as shown on the methanol vapour pressure curve (Refer Graph 6).

The upper explosive limit (UEL) of a flammable liquid is defined as the maximum concentration of the vapour in air for which a flame can propagate. The methanol UEL is 36% by volume. The UEL corresponds to a methanol temperature of 41°C (106°F).

Within the approximate temperature range of 12°C to 41°C, methanol will produce a concentration of vapour that is explosive upon contact with an ignition source.

Auto Ignition Temperature

The auto ignition temperature of a substance is the minimum temperature required for self-sustained combustion in the absence of an external ignition source. Methanol has an auto ignition temperature of 470°C (878°F).

7.2 Safety Precautions

The low flash point and wide explosive range require facilities to exercise caution when handling methanol.

The following is a general safety checklist that is provided for guidance only. Specific situations may require additional precautions as determined through a formal risk assessment process.

- Smoking must be prohibited.
- Vehicle access should be strictly controlled.
- Ventilation must be sufficient to cope with the maximum expected vapour levels in buildings.
- Positive pressure may be required for methanol-free areas such as control, switch and smoking rooms.
- Storage tank vents to atmosphere should be sized for fire-heated emergency vapour release.
- Electrical equipment must be explosion-proof to meet with national electrical code requirements.
- Grounding is required for all equipment, including tanks, pipe racks, pumps, vessels, filters, etc.
- Aqueous Film Forming Foam of the alcohol-resistant type (AR-AFFF) with 6% foam

proportioning (with water) equipment is advised for use on methanol fires.

- Dry chemical extinguishers should be accessible for small fires. An adequate supply of hand-held and wheeled types should be available.
- Hydrants should be strategically placed with adequate hoses.
- Small spills should be remediated with sand, earth or other non-combustible absorbent material, and the area then flushed with water. Larger spills should be diluted with water and diked for later disposal.
- Lighting should be grounded. Tall vessels and structures should be fitted with lightning conductors that are securely grounded.

7.3 Fire Fighting Techniques

Methanol flames are almost invisible in daylight, producing no soot or smoke. They may be detected by the heat generated, a heat haze, or burning of materials in the affected area.

Dry chemical powder, carbon dioxide (CO_2) and alcohol-resistant foam extinguish methanol fires by oxygen deprivation. Water will remove heat and dilute the liquid methanol. Fog or fine sprays will absorb methanol vapours, quench heat and provide a curtain shield for upwind advancement to a fire source.

Small fires can be extinguished using powder, CO_2, or foam in the early stages. Be aware that the methanol may re-ignite spontaneously, due to surrounding high temperatures that may exceed the auto ignition temperature.

In addition to its cooling effect, water can be effective by diluting methanol to the point where it is no longer flammable. The amount of water required will be three to four times the volume of methanol.

Permanent sprinkler/drench systems are very effective in controlling potentially large fires at an early stage. Water cannons are generally installed in storage tank farms to cool adjacent structures and neighboring tanks in the event of fire.
Use of Alcohol-Resistant Aqueous Film Forming Foam (AR-AFFF) is effective for large-scale fires. Protein-based alcohol-resistant foams are also suitable.

7.4 Fire Fighting Personal Protective Equipment

Due consideration must be given to hazards from chemical and heat exposure. Protective fire-fighting structural clothing is not effective protection from methanol.

In addition to methanol vapours, fire-fighters may be exposed to combustion products, such as formaldehyde and carbon monoxide which may form under conditions of depleted oxygen. Therefore, fire-fighters should wear full-face, positive pressure, self-contained breathing apparatus or an air line.

Chemical protection may be provided with impervious clothing, gloves and footwear. Suitable materials include polyvinyl plastic, neoprene or rubber.

8.0 ENVIRONMENTAL PROTECTION

8.1 Biodegradation / Aquatic Toxicity

Methanol biodegrades easily in water and soil. Methanol in high concentrations (>1%) in fresh or salt water can have short-term harmful effects on aquatic life within the immediate spill area.

8.2 Spill Response

If a spill occurs, stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition. Avoid skin contact and inhalation. Do not walk through spilled product. Stay upwind; keep out of low-lying areas. Prevent spilled methanol from entering sewers, confined spaces, drains, or waterways. Maximize methanol recovery for recycling or reuse.

Leaking containers should be removed to the outdoors or to an isolated, well-ventilated area, and the contents transferred to a suitable container. Foam may be used for vapour suppression. Vapours can be knocked down using a water spray.

Whenever possible, contain land spills by forming mechanical or chemical barriers. Remove spilled product with explosion proof pumps or vacuum equipment. Treat the surface with sorbent materials, such as vermiculite or activated carbon, to remove the remaining methanol. Remove the sorbents after use. Soil contaminated with methanol should be removed and remediated.

Spills into large natural bodies of water, such as rivers and oceans, cannot be recovered. Whenever possible, contain spills to small surface waters using natural or mechanical barriers. Then remove the contained material with explosion proof pumps or vacuum equipment. Sorbents such as zeolite and activated carbon should also be considered for in situ clean up.

8.3 Treatment & Disposal

Possible treatment processes for spill countermeasures include biological degradation, reverse osmosis, carbon adsorption, steam stripping and air stripping.

Large quantities of waste methanol can either be disposed of at a licensed waste solvent company or reclaimed by filtration and distillation.

Waste methanol, or water contaminated with methanol, must never be discharged directly into sewers or surface waters.

8.4 Spill Prevention

An effective spill prevention program will include engineering controls, training and procedures, and spill response planning.

Effective engineering controls include overfill alarms, secondary containment for tanks, such as dikes or bunds to contain large spills, and hydrocarbon detectors within dikes.

Workers must be trained to handle methanol in a safe manner. Systems and procedures that protect the employees, the plant and the environment should be implemented.

To be prepared in the event of a spill, the facility should develop and implement spill response plans. Regular exercises of the plan will ensure that workers know how to respond safely and effectively to a release.

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