3

Production Methods, Properties, and Main Applications

3.1 DEFINITIONS AND SOLVENT CLASSIFICATION

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Several definitions are needed to classify solvents. These are included in Table 3.1.1

Table 3.1.1 Definitions

Term	Definition
Solvent	A substance that dissolves other material(s) to form solution. Common solvents are liquid at room temperature but can be solid (ionic solvents) or gas (carbon dioxide). Solvents are differentiated from plasticizers by limiting their boiling point to a maximum of 250^{o}C. To differentiate solvents from monomers and other reactive materials - a solvent is considered to be non-reactive.
Polarity	Polarity is the ability to form two opposite centers in the molecule. The concept is used in solvents to describe their dissolving capabilities or the interactive forces between solvent and solute. Because it depends on dipole moment, hydrogen bonding, entropy, and enthalpy, it is a composite property without a physical definition. The dipole moment has the greatest influence on polar properties of solvents. Highly symmetrical molecules (e.g. benzene) and aliphatic hydrocarbons (e.g. hexane) have no dipole moment and are considered non-polar. Dimethyl sulfoxide, ketones, esters, alcohol are examples of compounds having dipole moments (from high to medium, sequentially) and they are polar, medium polar, and dipolar liquids.
Polarizability	The molecules of some solvents are electrically neutral but dipoles can be induced by external electromagnetic field.
Normal	A normal solvent does not undergo chemical associations (e.g. the formation of complexes between its molecules).

Term	Definition
Aprotic/Protic	Aprotic solvents (also commonly called inert) have very little affinity for protons and are incapable to dissociating to give protons. Aprotic solvents are also called indifferent, non-dissociating, or non-ionizing. Protic solvents contain proton-donating groups.
Protogenic	An acidic solvent capable of donating protons.
Protophilic	A basic solvent able to combine with hydrogen ion or to act as a proton acceptor.
Acidic/Basic	Lewis acidity/basicity determines the solvent's ability to donate or accept a pair of electrons to form a coordinate bond with solute and/or between solvent molecules. A scale for this acid/base property was proposed by Gutman (DN and AN - donor and acceptor number, respectively) based on calorimetric determination. The complete proton transfer reaction with formation of protonated ions is determined by proton affinity, gas phase acidity, acid or base dissociation constants. Both concepts differ in terms of net chemical reaction.
Hydrogen-bonding	A bond involving a hydrogen atom, which is bound covalently with another atom, is referred to as hydrogen bonding. Two groups are involved: hydrogen donor (e.g., hydroxyl group) and hydrogen acceptor (e.g., carbonyl group).
Solvatochromism	Shift of UV/Vis absorption wavelength and intensity in the presence of solvents. A hypsochromic (blue) shift increases as solvent polarity increases. The shift in the red direction is called bathochromic.
Dielectric constant	A simple measure of solvent polarity (the electrostatic factor is a product of dielectric constant and dipole moment). The electrical conductivity of solvent indicates if there is a need to earth (or ground) the equipment which handles solvent to prevent static spark ignition. Admixtures affect solvent conductivity. These are most important in electronics industry.
Miscible	Solvents are usually miscible when their solubility parameters do not differ by more than 5 units. This general rule does not apply if one solvent is strongly polar.
Good solvent	Substances readily dissolve if the solubility parameters of solvent and solute are close (less than 6 units apart). This rule has some exceptions (for example, PVC is not soluble in toluene even though the difference of their solubility parameters is 2.5).
Θ solvent	The term relates to the temperature of any polymer/solvent pair at which chain expansion is exactly balanced by chain contraction. At this temperature, called Θ temperature chain dimensions are unperturbed by long-range interactions.
Reactivity	Solvent, according to this definition, should be a non-reactive medium but in some processes solvent will be consumed in the reaction to prevent its evaporation (and pollution). Solvents affect reactivity in two major ways: viscosity reduction and decreasing the barrier of Gibbs activation energy.
Hygroscopicity	Some solvents such as alcohols and glycols are hygroscopic and, as such, are unsuitable for certain applications which require a moisture-free environment or a predetermined freezing point. Solvents which are not hygroscopic may still contain moisture from dissolved water.

Term	Definition
Solvent strength	Solvent strength is used to establish required solvent concentration to form a clear solution and to estimate the diluting capabilities of pre-designed system. Two determined quantities are used for the purpose: Kauri butanol value and aniline point.
Solvent partition	Solvent partition is determined for three purposes: to estimate the potential for solvent removal from dilute solution by carbon black adsorption, to evaluate the partition of solute between water and solvent for the purpose of studying biological effects of solvents and solutes, and to design system for solvent extraction.
Volatility	Solvent volatility helps in estimation of the solvent evaporation rate at temperatures below its boiling point. The Knudsen, Henry, Cox, Antoine, and Clausius-Clapeyron equations are used to estimate the vapor pressure of a solvent over a liquid, its evaporation rate, and the composition of the atmosphere over the solvent. The boiling point of a solvent gives an indication of its evaporation rate but it is insufficient for its accurate estimation because of the influence of the molar enthalpy of evaporation.
Residue	This may refer to either the non-volatile residue or the potential for residual solvent left after processing. The former can be estimated from the solvent specification, the later is determined by system and technology design.
Carcinogenic	Solvents may belong to a group of carcinogenic substances. Several groups of solvents have representatives in this category (see listings in Section 3.3)
Mutagenic	Mutagenic substance causes genetic alterations, such as genetic mutation or a change to the structure and number of chromosomes (mutagens listed in Section 3.3).
Impairing reproduction	Several solvents in the glycols and formamides groups are considered to impair fertility.
Toxicity	LD50 and LC50 give toxicity in mg per kg of body weight or ppm, respectively. Threshold limit values place a limit on permissible concentration of solvent vapors in the work place. Also “immediate-danger-to-life” and “short-term-exposure-limits” are specified for solvents. Odor threshold values have limited use in evaluating the potential danger to solvent exposure.
Flammable	Several data are used to evaluate the dangers of solvent explosion and flammability. Flash point and autoignition temperature are used to determine a solvent’s flammability and its potential for ignition. The flash points for hydrocarbons correlate with their initial boiling points. Lower and upper explosive limits determine the safe ranges of solvent concentration.
Combustible	The net heat of combustion and the calorific value help to estimate the potential energy which can be recovered from burning used solvents. In addition, the composition of the combustion products is considered to evaluate potential corrosiveness and the effect on the environment.
Ozone depleter	Ozone depletion potential is the value relative to that of CFC-11. It represents the amount of ozone destroyed by the emission of gas over its entire atmospheric life-time. Photochemical ozone creation potential is a relative value to that of ethene to form ozone in an urban environment. Numerous solvents belong to both groups.

Term	Definition
Biodegradability	Several methods are used to express biodegradability. These include biodegradation half-life, biological oxygen demand, chemical and theoretical oxygen demand.
Cost	Cost of solvent is a key factor in solvent selection.

The above list of terms and parameters is not exhaustive. These and related subjects are discussed at length in various parts of the book. The table is presented to assist in an understanding solvent classification.

A review of the selected definitions suggests that there are many important determinants of solvent quality for specific application. Some solvent parameters are conflicting, some not well quantified, and each solvent application requires a unique set of solvent performance criteria. It can be thus anticipated, prior to any analysis, that the chemical structure can be used as the best means of solvent classification for any application. Such a classification is used in this book because of its broad application. Chemical names used are the common names because they are generally understood by all solvents users.

Other means of classification are briefly analyzed below because they are useful in some applications. For a classification to be useful, it must be based on a model and a method which permits its quantification.

In organic synthesis, the solvent's polarity plays an important role. Dimroth and Reichardt[1] developed a classification based on the normalized empirical parameter of solvent polarity, E_T^N, given by the following equation:

$$E_T^N = \frac{E_T(solvent) - E_T(TMS)}{E_T(water) - E_T(TMS)} = \frac{E_T(solvent) - 30.7}{32.4} \qquad [3.1.1]$$

where:

E_T excitation energy
TMS tetramethylsilane

The values of E_T are known for several hundred solvents based on measurements of solvent-induced shifts with betaine dye used as the solvatochromic indicator. Based on such data, solvents can be divided into 3 groups: protic (E_T^N from 0.5 to 1), dipolar non-hydrogen donating (E_T^N from 0.3 to 0.5) and apolar (E_T^N from 0 to 0.3). The E_T^N values have a good linear correlation with light absorption, reaction rates, and chemical equilibria. In addition, the E_T^N values have a very good correlation with the Kosower's polarity parameter, Z, for which there is also large amount of data available. Both sets of data can be converted using the following equation:

$$E_T = 0.752Z - 7.87 \qquad [3.1.2]$$

Gutman[2,3] chose the reaction enthalpy of solvent with the reference acceptor (antimony pentachloride) to quantify Lewis-donor properties. The donor number, DN, is a dimensionless parameter obtained from negative values of reaction enthalpy. The data obtained from electrochemical and NMR studies were combined into one scale in which data are available for several hundred solvents. These data have a linear correlation with E_T^N according to the following equation:[4]

$$AN = -59.9 + 1850E_T \qquad [3.1.3]$$

The donor number is frequently used in various fields of polymer chemistry (see Chapter 10). Another classification based on acidity/basicity of solvents allows the division of solvents into six groups containing protic-neutral; protogenic; protophilic; aprotic-protophilic; aprotic-protophobic; and aprotic-inert.[4]

Snyder[5,6] developed classification of solvents for chromatography which arranges solvents according to their chromatographic strength. It is classification based on the solvent's ability to engage in hydrogen bonding or dipole interaction using the experimentally determined partition coefficients by Rohrschneider.[7] Eight groups of solvents were defined based on cluster analysis. In addition to the usefulness of this classification in chromatography, it was found recently that it is also useful in the design of coatings which do not affect undercoated paints.[8]

Numerous other classifications and sets of data are available, such as those included in various databases on solvent toxicity, their environmental fate, combustion properties, explosive limits, etc.

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3.2 OVERVIEW OF METHODS OF SOLVENT MANUFACTURE

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Crude oil is the major raw material source for solvents. Aliphatic and aromatic hydrocarbons are produced by physical processes used in petrochemical industry. Other solvents are synthetic but their starting raw materials are usually products of the petrochemical industry. Figure 3.2.1 shows the main groups of materials produced by petrochemical industry from crude oil.

Two observations are pertinent: the main goal of petrochemical industry is to convert crude oil to fuels. Solvents are only a small fraction of materials produced. Figure 3.2.2 shows that solvents are not only used directly as solvents but are also the building blocks in the manufacture of a large number of materials produced by organic chemistry plants.

Desalting of crude oil is the first step in crude oil processing. It is designed to remove corrosive salts which may cause catalyst deactivation. After desalting, crude oil is subjected to atomospheric distillation. Figure 3.2.3 shows a schematic diagram of the crude oil distillation process. The raw material is heated to 400ºC and separated into fractions on 30-50 fraction trays in distillation column. The diagram in Figure 3.2.3 shows the main fractions obtained from this distillation. The heavier fraction cannot be distilled under atmospheric

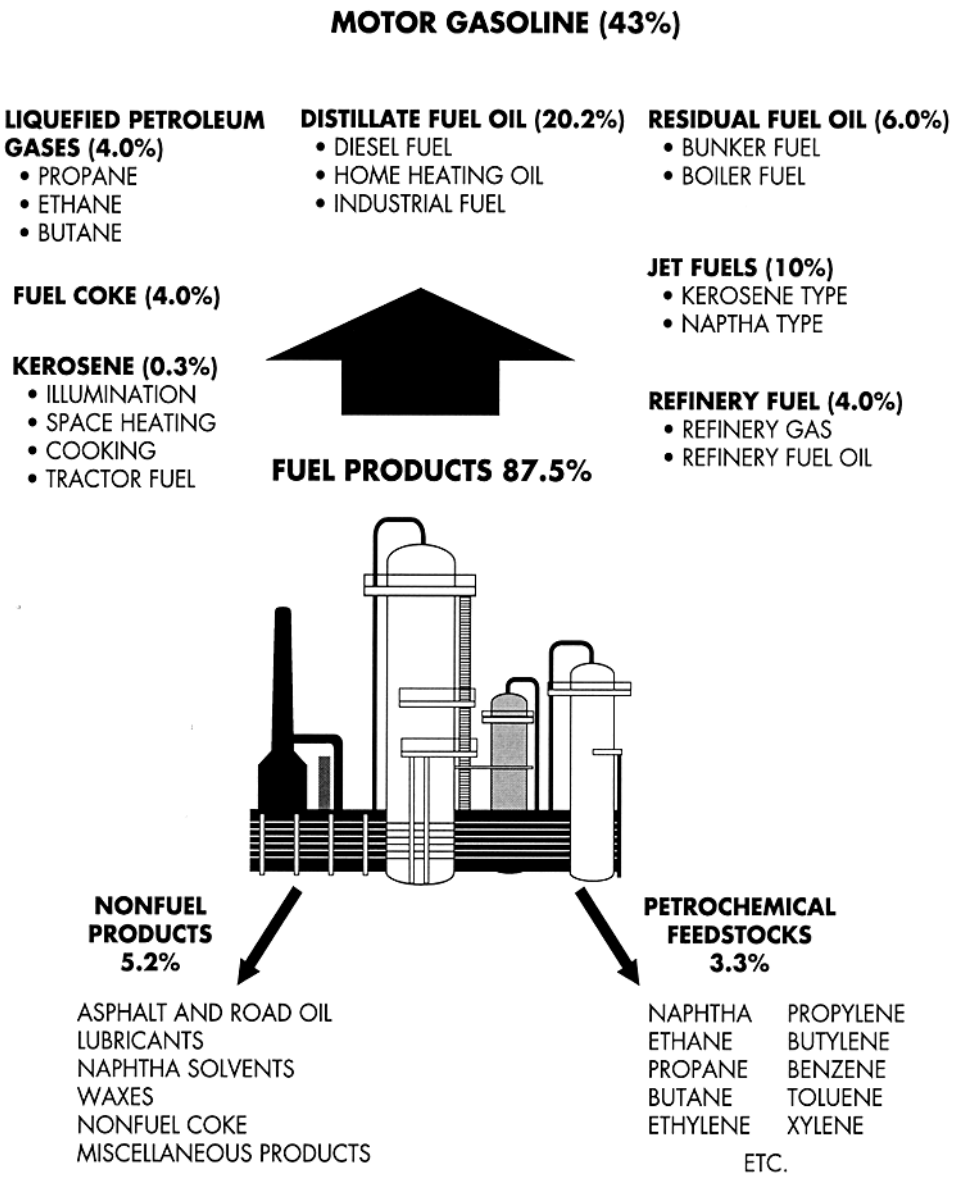

Figure 3.2.1. Schematic diagram of petroleum industry products and yields. [Reproduced from reference 1]

pressure therefore in the next step vacuum is applied to increase volatilization and separation.

Certain fractions from the distillation of crude oil are further refined in thermal cracking (visbreaking), coking, catalytic cracking, catalytic hydrocracking, alkylation,

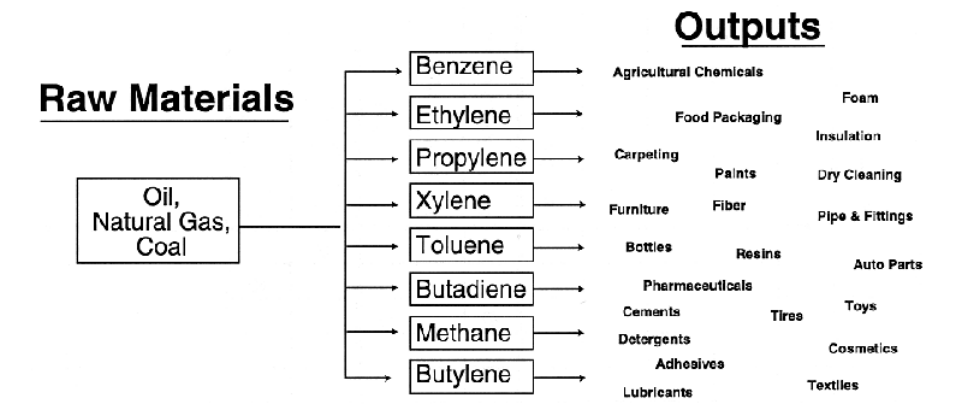

Figure 3.2.2. Organic chemicals and building block flow diagram. [Reproduced from reference 2]

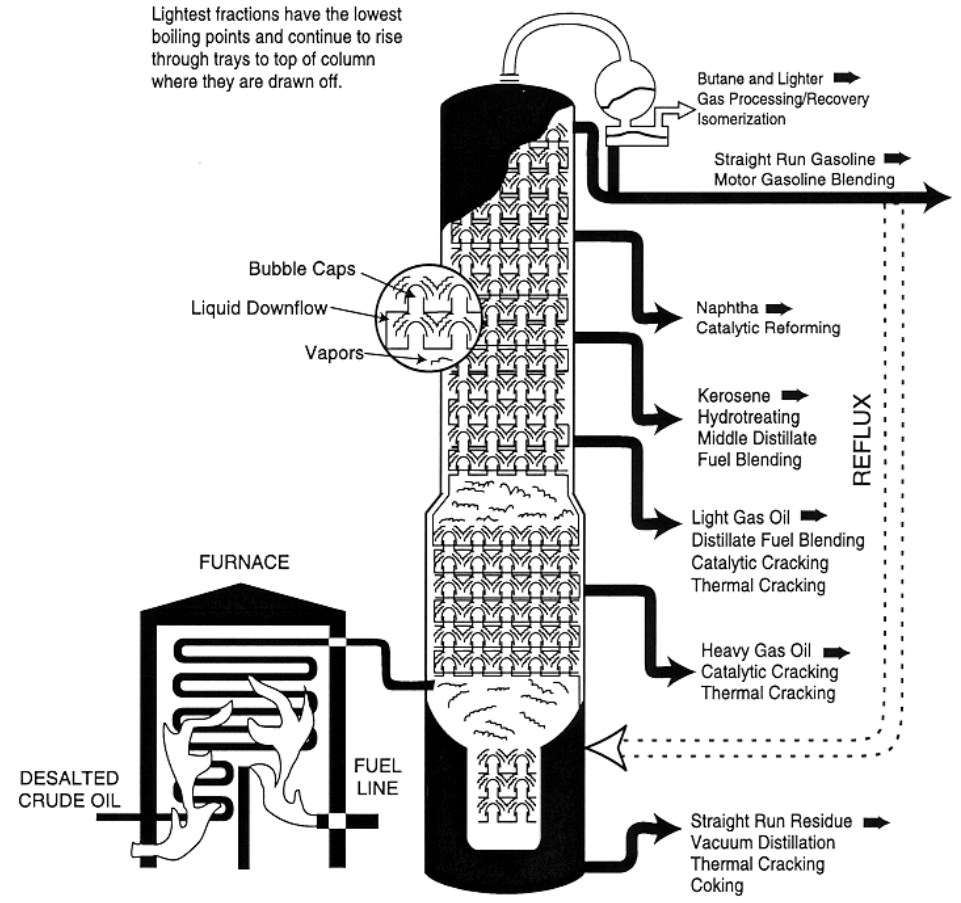

Figure 3.3.3. Crude oil distillation. [Reproduced from reference 1]

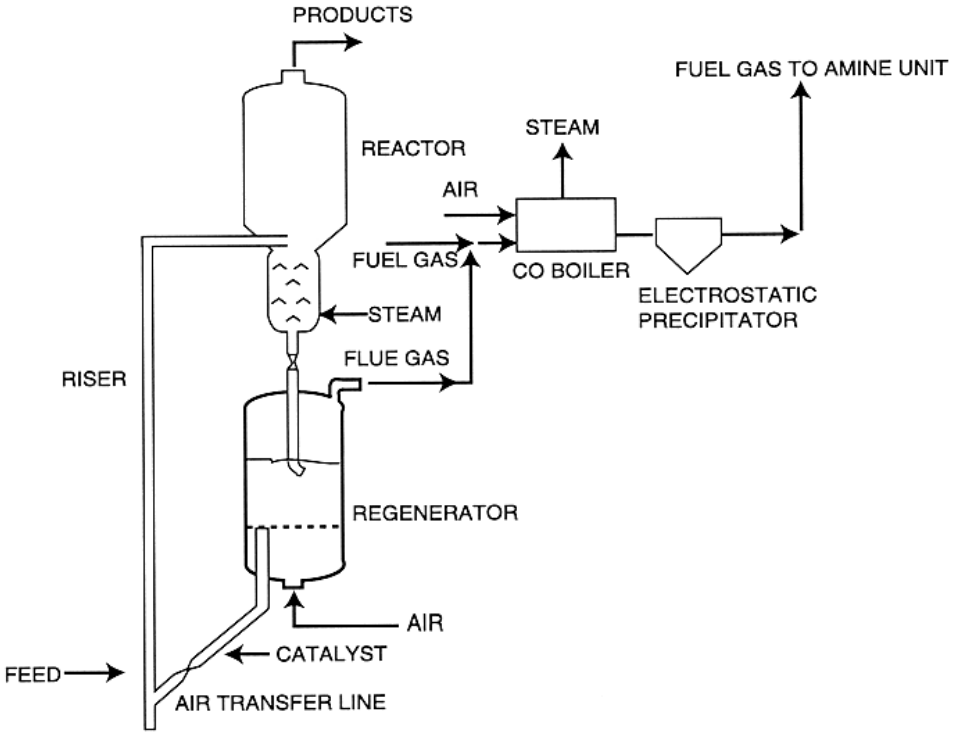

Figure 3.3.4. Simplified catalytic cracking flow diagram. [Reproduced from reference 1]

isomerization, polymerization, catalytic reforming, solvent extraction, and other operations.

Thermal cracking (visbreaking), uses heat and pressure to break large hydrocarbon molecules into lower molecular weight products. Most refineries do not use this process but use instead its replacement – catalytic cracking which gives a better yield of gasoline. Feedstock includes light and heavy oils from the crude oil distillation process. The cracking process occurs at a temperature of 550°C and under increased pressure. The cracking reaction is discontinued by mixing with cooler recycle stream. The mixture is stripped of lighter fractions which are then subjected to fractional distillation. Figure 3.2.4 is a schematic flow diagram of catalytic cracking. Hydrocracking is a somewhat different process which occurs under higher pressure and in the presence of hydrogen. It is used to convert fractions which are difficult to crack, such as middle distillates, cycle oils, residual fuel oils, and reduced crudes. Alkylation is used to produce compounds from olefins and isoparaffins in a catalyzed process. Isomerization converts paraffins to isoparaffins. Polymerization converts propene and butene to high octane gasoline. The application of these three processes has increased output and performance of gasoline.

Catalytic reforming processes gasolines and naphthas from the distillation unit into aromatics. Four major reactions occur: dehydrogenation of naphthenes to aromatics, dehydrocyclization of paraffins to aromatics, isomerization, and hydrocracking.

In some cases mixtures of solvents are required to meet a particular requirement. For example, linear paraffins have a very low viscosity. Branched paraffins have high viscosity but very good low temperature properties and low odor. A combination of the two carried out in the conversion process (not by mixing) results in a solvent which has the desirable properties of both solvents: low viscosity and good low temperature properties.[3]

The recovery of pure aromatics from hydrocarbon mixtures is not possible using distillation process because the boiling points of many non-aromatics are very close to benzene, toluene, etc. Also, azeotropes are formed between aromatics and aliphatics. Three principle methods are used for separation: azeotropic distillation, liquid-liquid extraction, and extractive distillation. Three major commercial processes have been developed for separation: Udex, Sulpholane, and Arosolvan. Over 90% plants now use one of these processes. Each use an addition of solvent such as a mixture of glycols, tetramethylene sulfone, or N-methyl-2-pyrrolidone to aid in the extraction of aromatics. This occurs with high precision and efficiency. Pure benzene, toluene, and xylene are produced by these processes.

These three are used for synthesis of several other important solvents. Benzene is used in the production of ethyl benzene (alkylation), cyclohexanone, cyclohexanol, cyclohexane, aniline (hydrogenation), acetone, nitrobenzene, and chlorobenzene. Toluene is used in the production of cresol and benzene. Xylene is the raw material for the production of ethyl benzene and the fractionation of the xylene mixture to isomers.

Lower boiling fractions from the primary distillation are also used in the production of solvents. Ethylene is used to produce ethylene dichloride, ethylene glycol, ethanol, and ethyl benzene. Propylene is used to produce isopropyl alcohol. Halogenation, hydrohalogenation, alkylation, and hydrolysis reactions are used in these conversions.

With different feedstock and methods of processing it is inevitable that there will be some differences between products coming from different feedstock sources and manufacturers. Over the years processes have been refined. Long practice, globalization of technology has occurred and restrictions have been imposed. Today, these differences are small but in some technological processes even these very small differences in solvent quality may require compensating actions.

There are many other unitary operations which are used by organic chemistry plants to manufacture synthetic solvents. These include: alkoxylation (ethylene glycol), halogenation (1,1,1-trichloethane), catalytic cracking (hexane), pyrolysis (acetone and xylene), hydrodealkylation (xylene), nitration (nitrobenzene), hydrogenation (n-butanol, 1,6-hexanediol), oxidation (1,6-hexanediol), esterification (1,6-hexanediol), and many more.

In the manufacture of oxygenated solvents, the typical chemical reactions are hydration, dehydration, hydrogenation, dehydrogenation, dimerization and esterification. For example methyl ethyl ketone is manufactured from 1-butene in a two step reaction. First, 1-butene is hydrated to 2-butanol then a dehydrogenation step converts it to methyl ethyl ketone. The production of methyl isobutyl ketone requires several steps. First acetone is dimerized producing diacetone alcohol which, after dehydration, gives mesityl oxide subjected in the next step to hydrogenation to result in the final product. Ethylene glycol is a product of the addition (ethylene oxide and ethanol) followed by esterification with acetic acid. 18% of all phenol production is converted to cyclohexanone.[4] Some solvents are obtained by fermentation processes (e.g., ethanol, methanol).

Synthetic routes are usually quite complex. For example, the manufacture of N-methyl-2-pyrrolidone involves the reaction of acetylene with formaldehyde. The resulting but-2-ine-1,4-diol is hydrated to butane-1,4-diol and then dehydrated to γ-butyrolactone then reacted with monomethyl amine to give the final product. Strict process control is essential to obtain very high purity.

New processes have been developed to produce solvents which are based on non-conventional materials (e.g., lactide and drying oil). The resultant solvent is non-volatile and useful in production of coatings, paints and inks.[5] These new technological processes are driven by the need to reduce VOCs.

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3.3 SOLVENT PROPERTIES

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The purpose of this section is to provide analysis of properties of major groups of solvents. The data on individual solvents are included in a separate publication on CD-ROM as a searchable database containing 1145 the most common solvents. The information on properties of solvents is included in 110 fields containing chemical identification of solvent, physical chemical properties, health and safety data, and its environmental fate. Here, the analysis of this data is provided in a form of tables to show the range of properties for different groups of solvents and their strengths and weaknesses. For each group of solvents a separate table is given below. No additional discussion is provided since data are self-explanatory. The data are analyzed in the final table to highlight the best performance of various groups of solvents in different properties.

By their nature, these data have a general meaning and for the exact information on particular solvent full data on CD-ROM should be consulted. For example, in the list of target organs, there are included all organs involved on exposure to solvents included in the group which does not necessary apply to a particular solvent. The data are given to highlight overall performance of entire group which may contain very diverse chemical materials.

One very obvious method of use of this information is to review the list of carcinogens and mutagens to and relate them to actually used in particular application. These solvents should be restricted from use and possibly eliminated or equipment engineered to prevent exposure of workers and release to environment. The comparative tables also provide suggestions as to where to look for suitable substitutes based on physical chemical characteristics and potential health and environmental problems.

Other application of this data is in selection of solvents for new products. The bulk of the data allows to analyze potential requirements critical for application and select group or groups which contain solvents having these properties. Further, based on their health and environmental characteristics suitable candidates can be selected.

The bulk data are also very useful in constructing set of requirements for specification. Many specifications for industrial solvents are very simplistic, which is partially caused by the lack of data provided by manufacturers of these solvents. This may cause potential fear of future problems with such solvents since solvent replacement in formulated product is not always a trivial substitution. It is also possible that solvents for which inadequate data exist at the present moment will be more studied in future for their environmental and health impacts and will then require to be replaced. Also, incomplete specification means that solvents may contain undesirable admixtures and contaminations and were used on premisses that manufacturer considered its application for a particular purpose which was, in fact, never intended by solvent manufacturer for this particular application. These details should be obtained from manufacturers and relevant parameters included in the specification. It is known from experience of creation of the database of solvents that there are still large gaps in information which should be eliminated by future efforts. The practice of buying solvents based on their boiling point and specific gravity does not serve the purpose of selecting reliable range of raw materials.

These and other aspects of created reference tables should be continuously updated in future to provide a reliable base of data which will be broadly used by industry. Application of full information allows to decrease quantity of solvents required for task and eliminate questionable materials and wastes due to solvent evaporation too rapid to make an impact on product properties at the time of its application. Also many sources of the problems with formulated products are due to various manifestations of incompatibility which can be eliminated (or predicted) based on solvent's characteristics.

3.3.1 HYDROCARBONS

3.3.1.1 Aliphatic hydrocarbons

Property	Value		
	minimum	maximum	median
boiling temperature, ^{o}C	-11.7	285	124
freezing temperature, ^{o}C	-189	18	-75
flash point, ^{o}C	-104	129	46
autoignition temperature, ^{o}C	202	640	287
refractive index	1.29	1.46	1.41
specific gravity, g/cm^3	0.51	0.84	0.74
vapor density (air=1)	1	5.90	4.5
vapor pressure, kPa	0.00	1976	4.42
viscosity, mPa.s	0.21	1.58	0.46
surface tension, mN/m	15	40	21

Property	Value		
	minimum	maximum	median
donor number, DN, kcal/mol	0	0	0
acceptor number, AN	0	1.6	0
polarity parameter, $E_T(30)$, kcal/mol	30.9	31.1	31
coefficient of cubic expansion, $10^{-4}/^oC$	8	10	9
specific heat, cal/K mol	41.24	93.41	60.33
heat of vaporization, cal/g	6.32	8.47	7.54
heat of combustion, MJ/kg	4.35	49.58	46.52
dielectric constant	1.8	2.15	2
Kauri-butanol number	22	56	32
aniline point, ^oC	21	165	81
Hildebrand solubility parameter, $cal^{1/2}\ cm^{-3/2}$	6.8	8.2	7.4
Henry's Law constant, atm/m^3 mol	2.59E-4	4.56E-4	3.43E-4
evaporation rate (butyl acetate = 1)	0.006	17.5	0.45
threshold limiting value - 8h average, ppm	0.1	1000	300
maximum concentration (15 min exp), ppm	375	1000	500
LD50 oral, mg/kg	218	29820	2140
route of entry	absorption, contact. ingestion, inhalation		
target organs	blood, bone marrow, central nervous system, eye, gastrointestinal tract, heart, kidney, lymphatic system, liver, lung, nervous system, peripheral nervous system, respiratory system, skin, spleen, stomach, testes, thyroid		
carcinogenicity	-		
mutagenic properties	n-hexane		
theoretical oxygen demand, g/g	3.46	3.56	3.53
biodegradation probability	days-weeks		
octanol/water partition coefficient	2.3	5.98	
urban ozone formation	0.11	0.13	0.12

3.3.1.2 Aromatic hydrocarbons

Property	Value		
	minimum	maximum	median
boiling temperature, ^oC	74	288	168

Property	Value		
	minimum	maximum	median
freezing temperature, °C	-96	5.5	-31
flash point, °C	-11	144	52
autoignition temperature, °C	204	550	480
refractive index	1.43	1.61	1.5
specific gravity, g/cm^3	0.71	1.02	0.87
vapor density (air=1)	2.8	4.8	4.1
vapor pressure, kPa	0.00	21.3	0.43
viscosity, mPa.s	0.58	6.3	1.04
surface tension, mN/m	24.3	36.8	28
donor number, DN, kcal/mol	0.1	10	5
acceptor number, AN	6.8	8.2	7.3
polarity parameter, $E_T(30)$, kcal/mol	32.9	34.8	34.7
coefficient of cubic expansion, 10^{-4}/°C	8	10.7	8
specific heat, cal/K mol	32.44	63.48	52.41
heat of vaporization, cal/g	8.09	10.38	10.13
heat of combustion, MJ/kg	41.03	43.5	41.49
dielectric constant	2.04	2.6	2.3
Kauri-butanol number	33	112	86
aniline point, °C	7	85	26
Hildebrand solubility parameter, cal$^{1/2}$ cm$^{-3/2}$	7.9	9.3	8.8
Henry's Law constant, atm/m^3 mol	5.19E-3	3.8E-1	7.6E-3
evaporation rate (butyl acetate = 1)	0.006	5.1	0.16
threshold limiting value - 8h average, ppm	0.3	100	50
maximum concentration (15 min exp), ppm	6	150	125
LD50 oral, mg/kg	636	6989	4300
LD50 dermal, mg/kg	4400	17800	12400
route of entry	absorption, contact. ingestion, inhalation		
target organs	blood, bone marrow, central nervous system, eye, gastrointestinal tract, kidney, liver, lung, respiratory system, skin		
carcinogenicity	benzene, styrene		
mutagenic properties	benzene, ethylbenzene, xylene		

Property	Value		
	minimum	maximum	median
biological oxygen demand, 5-day test, g/g	0.92	2.53	1.65
chemical oxygen demand, g/g	2.15	2.91	2.56
theoretical oxygen demand, g/g	2.41	3.29	3.17
biodegradation probability	days-to weeks, weeks		
octanol/water partition coefficient	2.13	4.83	
urban ozone formation	0.03	1.13	0.90

3.3.2 HALOGENATED HYDROCARBONS

Property	Value		
	minimum	maximum	median
boiling temperature, ^oC	-40.6	253	87
freezing temperature, ^oC	-189	17	-36
flash point, ^oC	-50	350	45
autoignition temperature, ^oC	240	648	557
refractive index	1.20	1.63	1.43
specific gravity, g/cm^3	0.9	3	1.6
vapor density (air=1)	1.8	33.4	6.5
vapor pressure, kPa	0.01	4000	10.2
viscosity, mPa.s	0.02	5.14	1.1
surface tension, mN/m	0.03	33.4	15.2
pH	4	8	7
donor number, DN, kcal/mol	0	4	3
acceptor number, AN	8.6	23.1	16.2
polarity parameter, $E_T(30)$, kcal/mol	32.1	41.3	36.7
specific heat, cal/K mol	12.32	205	41.5
heat of vaporization, cal/g	3.76	81.2	11.54
heat of combustion, MJ/kg	6.27	29.14	15.73
dielectric constant	1.0	8.93	2.32
Kauri-butanol number	31	500	90
Hildebrand solubility parameter, $cal^{1/2}\ cm^{-3/2}$	5.9	10.75	8.3
Henry's Law constant, $atm/m^3\ mol$	3.6E-4	8.5E0	3E-2
evaporation rate (butyl acetate = 1)	0.9	14.5	1

Property	Value		
	minimum	maximum	median
threshold limiting value - 8h average, ppm	0.5	1000	100
maximum concentration (15 min exp), ppm	20	1250	250
maximum concentration any time, ppm	5	500	400
LD50 oral, mg/kg	214	13000	1210
LD50 dermal, mg/kg	500	20000	8750
route of entry	absorption, contact. ingestion, inhalation		
target organs	central nervous system, eye, gastrointestinal tract, heart, kidney, liver, lung, respiratory system, skin		
carcinogenicity	benzotrichloride, carbon tetrachloride,chloroform, 1,2-dibromomethane, 1,4-dichlorobenzene, 1,2-dichloroethane, Dowper, 1,1,2,2-tetrachlroethylene		
mutagenic properties	benzotrichloride, carbon tetrachloride, chloroform, chloromethane, chlorodifluoromethane, dichloromethane, 1,2-dibromomethane, Freon MS-117 TE, Freon MS-178 TES, 1,1,2,2-tetrachloroethylene, 1,1,1-trichloroethane, 1,1,2-trichloroethylene, trifluoromethane		
theoretical oxygen demand, g/g	0	0.19	0.09
biodegradation probability	weeks		
octanol/water partition coefficient	0.64	4.02	
ozone depletion potential	0.00	1.1	0.8
global warming potential	0.25	11700	4600
urban ozone formation	0.00	0.09	0.01

3.3.3 NITROGEN-CONTAINING COMPOUNDS (NITRATES, NITRILES)

Property	Value		
	minimum	maximum	median
boiling temperature, ^{o}C	77	234	134
freezing temperature, ^{o}C	-112	6	-50
flash point, ^{o}C	2	101	36
autoignition temperature, ^{o}C	414	550	481
refractive index	1.34	1.55	1.39
specific gravity, g/cm^3	0.78	1.21	0.87
vapor density (air=1)	1.4	4.2	3.1

Property	Value		
	minimum	maximum	median
vapor pressure, kPa	0.01	11.0	2.62
viscosity, mPa.s	0.34	1.96	0.77
dissociation constant, pKa	7.67	10.21	8.98
donor number, DN, kcal/mol	4.4	16.6	11.0
acceptor number, AN	14.8	20.5	17.7
polarity parameter, $E_T(30)$, kcal/mol	41.5	46.7	43.6
heat of combustion, MJ/kg	22.46	30.38	27.25
Hildebrand solubility parameter, $cal^{1/2}\ cm^{-3/2}$	9.5	12.3	10.5
evaporation rate (butyl acetate = 1)	1.15	2.3	2.1
threshold limiting value - 8h average, ppm	1	100	25
LD50 oral, mg/kg	39	3800	510
route of entry	absorption, contact. ingestion, inhalation		
target organs	blood, central nervous system, eye, kidney, liver, respiratory system, skin		
carcinogenicity	acrylonitrile, 2-nitropropane		
mutagenic properties	acrylonitrile, 2-nitropropane		
biodegradation probability	days-weeks		
octanol/water partition coefficient	-0.3	1.86	

3.3.4 ORGANIC SULFUR COMPOUNDS

Property	Value		
	minimum	maximum	median
boiling temperature, ^oC	37	287	142
freezing temperature, ^oC	-116	32	-38
flash point, ^oC	-38	177	43
autoignition temperature, ^oC	206	470	395
refractive index	1.38	1.62	1.47
specific gravity, g/cm^3	0.80	1.43	1.00
vapor density (air=1)	2.14	4.35	3.05
vapor pressure, kPa	0.00	19.00	1.05
viscosity, mPa.s	0.28	10.29	0.97
surface tension, mN/m	35.5	42.98	39.00

Property	Value		
	minimum	maximum	median
dissociation constant, pKa	-1.54	15.3	13.6
donor number, DN, kcal/mol	2	41	29.8
acceptor number, AN	7.5	19.3	19.2
polarity parameter, $E_T(30)$, kcal/mol	26.8	54.4	38.4
specific heat, cal/K mol	36.61	43	40.1
dielectric constant	43.26	46.45	44.30
Hildebrand solubility parameter, $cal^{1/2}\ cm^{-3/2}$	8.2	12.6	9.8
Henry's Law constant, atm/m^3 mol	4.96E-8	4.85E-6	1.25E-6
evaporation rate (butyl acetate = 1)	0.005	0.026	0.013
threshold limiting value - 8h average, ppm	0.1	10	0.5
LD50 oral, mg/kg	505	14500	1941
LD50 dermal, mg/kg	380	40000	20000
route of entry	absorption, contact. ingestion, inhalation		
target organs	central nervous system, eye, liver, lung		
carcinogenicity	diethyl sulfate, dimethyl sulfate		
mutagenic properties	diethyl sulfate, dimethyl sulfoxide, sulfolane		
theoretical oxygen demand, g/g	1.73	1.84	1.75
biodegradation probability	days-weeks		
octanol/water partition coefficient	-1.35	2.28	
urban ozone formation	0.07	0.23	0.15

3.3.5 MONOHYDRIC ALCOHOLS

Property	Value		
	minimum	maximum	median
boiling temperature, °C	64.55	259	155
freezing temperature, °C	-129	71	-38.6
flash point, °C	11	156	67
autoignition temperature, °C	231	470	295
refractive index	1.277	1.539	1.42
specific gravity, g/cm^3	0.79	1.51	0.81
vapor density (air=1)	1.10	5.50	3.0
vapor pressure, kPa	0.00	21.20	0.4

Property	Value		
	minimum	maximum	median
viscosity, mPa.s	0.59	41.1	4.4
surface tension, mN/m	21.99	40.0	26.2
dissociation constant, pKa	9.3	19.0	15.4
donor number, DN, kcal/mol	5	44	30
acceptor number, AN	22.2	66.7	37.1
polarity parameter, $E_T(30)$, kcal/mol	41	65.3	48.8
coefficient of cubic expansion, 10^{-4}/°C	9	12.2	10.3
specific heat, cal/K mol	19.47	78.03	43.03
heat of vaporization, cal/g	8.95	15.40	12.32
heat of combustion, MJ/kg	22.66	38.83	34.56
dielectric constant	8.17	32.66	17.51
Hildebrand solubility parameter, $cal^{1/2}$ $cm^{-3/2}$	9.26	23	11.5
Henry's Law constant, atm/m^3 mol	4.1E-9	3.44E+1	3.1E-5
evaporation rate (butyl acetate = 1)	0.005	2.9	0.39
threshold limiting value - 8h average, ppm	1	1000	100
maximum concentration (15 min exp), ppm	4	500	125
LD50 oral, mg/kg	275	50000	2300
LD50 dermal, mg/kg	400	20000	3540
route of entry	absorption, contact. ingestion, inhalation		
target organs	central nervous system, eye, kidney, liver, lung, lymphatic system, respiratory system, skin		
carcinogenicity	-		
mutagenic properties	1-butanol, 2-butanol, ethanol, 1-octanol, 1-pentanol, 1-propanol		
biological oxygen demand, 5-day test, g/g	0.41	2.37	1.5
chemical oxygen demand, g/g	1.5	2.97	2.46
theoretical oxygen demand, g/g	1.5	2.9	2.59
biodegradation probability	days-weeks		
octanol/water partition coefficient	-1.57	2.97	
urban ozone formation	0.04	0.45	0.16

3.3.6 POLYHYDRIC ALCOHOLS

Property	Value		
	minimum	maximum	median
boiling temperature, °C	171	327.3	214
freezing temperature, °C	-114	60	-4
flash point, °C	85	274	152
autoignition temperature, °C	224	490	371
refractive index	1.43	1.48	1.44
specific gravity, g/cm^3	0.92	1.22	1.12
vapor density (air=1)	2.14	6.70	3.10
vapor pressure, kPa	0.00	0.32	0.01
viscosity, mPa.s	21	114.6	54.65
surface tension, mN/m	33.1	48.49	44.13
dissociation constant, pKa	14.1	15.1	14.5
donor number, DN, kcal/mol	19	20	19
acceptor number, AN	34.5	46.6	36.2
polarity parameter, $E_T(30)$, kcal/mol	51.8	56.3	54.1
specific heat, cal/K mol	36.1	294	77.6
heat of vaporization, cal/g	13.0	18.7	16.2
heat of combustion, MJ/kg	19.16	29.86	23.69
dielectric constant	7.7	35.0	28.8
Hildebrand solubility parameter, cal$^{1/2}$ cm$^{-3/2}$	10.7	16.18	12.81
Henry's Law constant, atm/m^3 mol	4.91E-13	2.3E-7	6E-8
evaporation rate (butyl acetate = 1)	0.001	0.01	0.01
threshold limiting value - 8h average, ppm	1	25	10
maximum concentration any time, ppm	25	50	
LD50 oral, mg/kg	105	50000	16000
LD50 dermal, mg/kg	2000	225000	20000
route of entry	absorption, contact. ingestion, inhalation		
target organs	blood, eye, gastrointestinal tract, kidney, lymphatic system, liver, lung, respiratory system, skin, spleen		
carcinogenicity	-		

Property	Value		
	minimum	maximum	median
mutagenic properties	tetraethylene glycol, triethylene glycol, trimethylene glycol		
biological oxygen demand, 5-day test, g/g	0.03	1.08	0.18
chemical oxygen demand, g/g	1.29	1.64	1.57
theoretical oxygen demand, g/g	1.07	1.68	1.60
biodegradation probability	days-weeks		
octanol/water partition coefficient	-0.92	-2.02	
urban ozone formation	0.16	0.47	0.38

3.3.7 PHENOLS

Property	Value		
	minimum	maximum	median
boiling temperature, ^oC	182	245	202
freezing temperature, ^oC	-18	105	25
flash point, ^oC	43	127	95
autoignition temperature, ^oC	558	715	599
refractive index	1.52	1.60	1.54
specific gravity, g/cm^3	0.93	1.34	1.02
vapor density (air=1)	3.2	4.4	3.7
vapor pressure, kPa	0.00	0.23	0.02
viscosity, mPa.s	3.5	11.55	9.4
dissociation constant, pKa	9.1	10.85	10.3
donor number, DN, kcal/mol	11		
acceptor number, AN	44.8	50.4	
polarity parameter, $E_T(30)$, kcal/mol	50.3	60.8	53.3
Hildebrand solubility parameter, $cal^{1/2}\ cm^{-3/2}$	8.7	12.1	10.6
Henry's Law constant, $atm/m^3\ mol$	3.84E-11	3.14E-9	
threshold limiting value - 8h average, ppm	5	5	5
LD50 oral, mg/kg	40	320000	810
LD50 dermal, mg/kg	950	1040	
route of entry	absorption, contact. ingestion, inhalation		

Property	Value		
	minimum	maximum	median
target organs	central nervous system, eye, respiratory system, skin		
carcinogenicity	3-chlorophenol, o-chlorophenol		
mutagenic properties	3-chlorophenol, o-chlorophenol		
octanol/water partition coefficient	0.59	2.47	

3.3.8 ALDEHYDES

Property	Value		
	minimum	maximum	median
boiling temperature, ^oC	-21	253	162
freezing temperature, ^oC	-123	12.4	-86
flash point, ^oC	-39	102	13
autoignition temperature, ^oC	180	424	196
refractive index	1.33	1.62	1.44
specific gravity, g/cm^3	0.70	1.25	0.85
vapor density (air=1)	1	4.5	2.5
vapor pressure, kPa	0.00	438	2.30
viscosity, mPa.s	0.32	5.4	1.32
surface tension, mN/m	23.14	41.1	32.00
donor number, DN, kcal/mol			16
acceptor number, AN			12.8
heat of vaporization, cal/g	5.53	10.33	6.77
Hildebrand solubility parameter, $cal^{1/2}\ cm^{-3/2}$	8.33	11.7	10.85
evaporation rate (butyl acetate = 1)			7.8
threshold limiting value - 8h average, ppm	0.1	100	2
maximum concentration (15 min exp), ppm	0.3	150	
maximum concentration any time, ppm	0.2	0.3	
LD50 oral, mg/kg	46	3078	100
LD50 dermal, mg/kg	270	16000	582
route of entry	absorption, contact. ingestion, inhalation		
target organs	eye, heart, liver, respiratory system, skin		
carcinogenicity	acetaldehyde, formaldehyde, furfural		

Property	Value		
	minimum	maximum	median
mutagenic properties	acrolein, formaldehyde, furfural		
biological oxygen demand, 5-day test, g/g	0.00	0.77	0.74
chemical oxygen demand, g/g	1.72		
theoretical oxygen demand, g/g	1.07	2.00	1.67
biodegradation probability	days-weeks		
octanol/water partition coefficient	0.35	1.48	
urban ozone formation	0.94	1.55	1.23

3.3.9 ETHERS

Property	Value		
	minimum	maximum	median
boiling temperature, ^oC	34.4	289	104
freezing temperature, ^oC	-137	64	-58
flash point, ^oC	-46	135	25
autoignition temperature, ^oC	189	618	429
refractive index	1.35	1.57	1.42
specific gravity, g/cm^3	0.71	1.21	0.89
vapor density (air=1)	1.5	6.4	4.0
vapor pressure, kPa	0.00	174.7	1.33
viscosity, mPa.s	0.24	1.1	0.42
surface tension, mN/m	17.4	38.8	24.8
dissociation constant, pKa	-5.4	-2.08	-2.92
donor number, DN, kcal/mol	6	24	19
acceptor number, AN	3.3	10.8	8
polarity parameter, $E_T(30)$, kcal/mol	16	43.1	36
specific heat, cal/K mol	28.77	60.22	45.86
heat of vaporization, cal/g	5.99	13.1	10.57
heat of combustion, MJ/kg	34.69	38.07	36.58
dielectric constant	2.2	13.0	4.5
Hildebrand solubility parameter, $cal^{1/2}\ cm^{-3/2}$	7	10.5	9.2
Henry's Law constant, atm/m^3 mol	54E-9	8.32E0	3.19E-4
evaporation rate (butyl acetate = 1)	0.004	11.88	8.14

Property	Value		
	minimum	maximum	median
threshold limiting value - 8h average, ppm	1	1000	200
maximum concentration (15 min exp), ppm	2	500	250
LD50 oral, mg/kg	72	30900	4570
LD50 dermal, mg/kg	250	2000	7600
route of entry	absorption, contact. ingestion, inhalation		
target organs	blood, central nervous system, eye, kidney, liver, respiratory system, skin		
carcinogenicity	bis(chloromethyl) ether, chloromethyl methyl ether, 1,4-dioxane, epichlorohydrin, ethylene oxide, propylene oxide		
mutagenic properties	diethyl ether, 1,4-dioxane, ethylene oxide, propylene oxide		
biological oxygen demand, 5-day test, g/g	0.06	0.48	0.19
chemical oxygen demand, g/g	1.74	1.75	1.75
theoretical oxygen demand, g/g	1.07	2.95	2.21
biodegradation probability	days-weeks		
octanol/water partition coefficient	-0.56	5.10	
urban ozone formation	0.02	0.49	0.31

3.3.10 GLYCOL ETHERS

Property	Value		
	minimum	maximum	median
boiling temperature, ^oC	117	265	191
freezing temperature, ^oC	-148	14	-83
flash point, ^oC	27	143	85
autoignition temperature, ^oC	174	406	255
refractive index	1.39	1.53	1.43
specific gravity, g/cm^3	0.83	1.11	0.95
vapor density (air=1)	3.00	8.01	5.25
vapor pressure, kPa	0.00	1.33	0.12
viscosity, mPa.s	0.7	20.34	3.3
surface tension, mN/m	25.6	42.0	28.5
acceptor number, AN	9	36.1	

Property	Value		
	minimum	maximum	median
polarity parameter, $E_T(30)$, kcal/mol	38.6	52	51
coefficient of cubic expansion, $10^{-4}/^oC$	9.7	11.5	11.2
specific heat, cal/K mol	24.85	108	65.27
heat of vaporization, cal/g	10.33	14.3	13.3
heat of combustion, MJ/kg	24.3	30.54	28.75
dielectric constant	5.1	29.6	10.5
Hildebrand solubility parameter, $cal^{1/2}\ cm^{-3/2}$	8.2	12.2	8.8
Henry's Law constant, atm/m^3 mol	6.5E-10	7.3E-5	7.3E-8
evaporation rate (butyl acetate = 1)	0.001	1.05	0.37
threshold limiting value - 8h average, ppm	5	100	25
maximum concentration (15 min exp), ppm	150		150
LD50 oral, mg/kg	470	16500	6500
route of entry	absorption, contact. ingestion, inhalation		
target organs	blood, brain, central nervous system, eye, kidney, lymphatic system, liver, lung, respiratory system, skin, spleen, testes		
carcinogenicity	-		
mutagenic properties	diethylene glycol monobutyl ether, diethylene glycol dimethyl ether, 2-ethoxyethanol, ethylene glycol diethyl ether, ethylene glycol monophenyl ether, triethylene glycol dimethyl ether		
biological oxygen demand, 5-day test, g/g	0.12	1.18	0.71
chemical oxygen demand, g/g	1.69	2.20	1.85
theoretical oxygen demand, g/g	1.07	3.03	2.17
biodegradation probability	days-weeks		
octanol/water partition coefficient	-1.57	3.12	
urban ozone formation	0.27	0.58	0.44

3.3.11 KETONES

Property	Value		
	minimum	maximum	median
boiling temperature, ^oC	56.1	306	147
freezing temperature, ^oC	-92	28	-55

Property	Value		
	minimum	maximum	median
flash point, °C	-18	143	44
autoignition temperature, °C	393	620	465
refractive index	1.35	1.55	1.41
specific gravity, g/cm^3	0.74	1.19	0.82
vapor density (air=1)	2	4.9	3.5
vapor pressure, kPa	0.00	30.8	1.1
viscosity, mPa.s	0.30	2.63	0.68
surface tension, mN/m	22.68	35.05	25.50
dissociation constant, pKa	-8.3	24.2	20.5
donor number, DN, kcal/mol	11	18	17
acceptor number, AN			12.5
polarity parameter, $E_T(30)$, kcal/mol	36.3	42.2	39.8
coefficient of cubic expansion, 10^{-4}/°C	9.7	13	13
specific heat, cal/K mol	29.85	58.22	51.0
heat of vaporization, cal/g	7.48	12.17	9.94
heat of combustion, MJ/kg	26.82	40.11	36.35
dielectric constant	11.98	20.56	16.1
Hildebrand solubility parameter, cal$^{1/2}$ cm$^{-3/2}$	7.54	11.0	9.2
Henry's Law constant, atm/m^3 mol	4.4E-8	2.7E-4	8.7E-5
evaporation rate (butyl acetate = 1)	0.02	6.6	0.83
threshold limiting value - 8h average, ppm	5	750	50
maximum concentration (15 min exp), ppm	75	1000	300
maximum concentration any time, ppm	5		
LD50 oral, mg/kg	148	5800	2590
LD50 dermal, mg/kg	200	20000	6500
route of entry	absorption, contact. ingestion, inhalation		
target organs	central nervous system, eye, kidney, liver, lung, peripheral nervous system, respiratory system, skin, stomach, testes		
carcinogenicity	-		
mutagenic properties	diacetone alcohol, methyl isopropyl ketone		
biological oxygen demand, 5-day test, g/g	0.68	2.03	1.37

Property	Value		
	minimum	maximum	median
chemical oxygen demand, g/g	1.92	2.88	2.31
theoretical oxygen demand, g/g	1.67	2.93	2.44
biodegradation probability		days-weeks	
octanol/water partition coefficient	-1.34	2.65	
urban ozone formation	0.01	0.65	0.15

3.3.11 ACIDS

Property	Value		
	minimum	maximum	median
boiling temperature, ^oC	20	337	164
freezing temperature, ^oC	-83	137	-3
flash point, ^oC	37	140	100
autoignition temperature, ^oC	298	539	380
refractive index	1.285	1.551	1.421
specific gravity, g/cm^3	0.9	1.83	1.08
vapor density (air=1)	0.7	5.0	3.3
vapor pressure, kPa	0.00	410	0.08
viscosity, mPa.s	0.25	23.55	2.82
surface tension, mN/m	27.4	37.6	33
dissociation constant, pKa	0.23	4.88	4.25
donor number, DN, kcal/mol	2.3	20	10.5
acceptor number, AN	18.5	105	52.9
polarity parameter, $E_T(30)$, kcal/mol	43.9	57.7	54.4
specific heat, cal/K mol	2367	29.42	2.612
heat of vaporization, cal/g	4.8	5.58	4.80
dielectric constant	6.17	58.5	40.5
Hildebrand solubility parameter, $cal^{1/2}\ cm^{-3/2}$	9.79	15.84	12.29
Henry's Law constant, atm/m^3 mol	1.26E-8	4.4E-5	1.67E-7
evaporation rate (butyl acetate = 1)	0.00	1.34	0.3
threshold limiting value - 8h average, ppm	1	10	4
maximum concentration (15 min exp), ppm	10	15	10
LD50 oral, mg/kg	200	74000	3310

Property	Value		
	minimum	maximum	median
route of entry	absorption, contact. ingestion, inhalation		
target organs	eye, kidney, liver, respiratory system, skin		
carcinogenicity	-		
mutagenic properties	formic acid		
biological oxygen demand, 5-day test, g/g	0.2	0.65	
chemical oxygen demand, g/g	0.36	1.09	
theoretical oxygen demand, g/g	0.35	1.07	0.67
biodegradation probability	days-weeks		
octanol/water partition coefficient	-0.17	+1.88	
urban ozone formation	0-0.09		

3.3.12 AMINES

Property	Value		
	minimum	maximum	median
boiling temperature, ^oC	-33	372	152
freezing temperature, ^oC	-115	142	-6
flash point, ^oC	-37	198	55
autoignition temperature, ^oC	210	685	410
refractive index	1.32	1.62	1.48
specific gravity, g/cm^3	0.7	1.66	1.02
vapor density (air=1)	0.54	10.09	3.2
vapor pressure, kPa	0.00	1.013	0.13
viscosity, mPa.s	0.13	4000	3.15
surface tension, mN/m	19.11	48.89	32.43
dissociation constant, pKa	8.96	11.07	10.78
pH	7.2	12.1	11
donor number, DN, kcal/mol	24	61	33.1
acceptor number, AN	1.4	39.8	18.8
polarity parameter, $E_T(30)$, kcal/mol	32.1	55.8	42.2
specific heat, cal/K mol	30.4	74.1	53.4
heat of vaporization, cal/g	5.65	16.13	8.26
heat of combustion, MJ/kg			30.22

Property	Value		
	minimum	maximum	median
dielectric constant	2.42	37.78	29.36
Hildebrand solubility parameter, $cal^{1/2}\ cm^{-3/2}$	7.4	15.5	10.5
Henry's Law constant, $atm/m^3\ mol$	1.7E-23	3.38E+1	1.56E-8
evaporation rate (butyl acetate = 1)	0.001	3.59	0.06
threshold limiting value - 8h average, ppm	0.1	100	5
maximum concentration (15 min exp), ppm	6	35	15
maximum concentration any time, ppm	5		
LD50 oral, mg/kg	100	12760	470
LD50 dermal, mg/kg	64	8000	660
route of entry	absorption, contact. ingestion, inhalation		
target organs	eye, kidney, lymphatic system, liver, lung, respiratory system, skin, testes		
carcinogenicity	acetamide, p-chloroaniline, N,N-dimethylformamide, hydrazine, N-nitrosodimethylamine, o-toluidyne		
mutagenic properties	dimethylamine, ethylene diamine tetracetic acid, methylamine, N-methylpyrrolidone, N-nitrosomethyl amine, tetraethylene pentamine		
biological oxygen demand, 5-day test, g/g	0.01	2.24	0.84
chemical oxygen demand, g/g	1.28	1.9	1.53
theoretical oxygen demand, g/g	0.65	2.85	1.8
biodegradation probability	days-weeks		
octanol/water partition coefficient	-1.66	1.92	
urban ozone formation	0.00	0.51	0.21

3.3.13 ESTERS

Property	Value		
	minimum	maximum	median
boiling temperature, ^oC	32	343	165
freezing temperature, ^oC	-148	27.5	-54
flash point, ^oC	-19	240	64
autoignition temperature, ^oC	252	505	400
refractive index	1.34	1.56	1.44
specific gravity, g/cm^3	0.81	1.38	0.92

Property	Value		
	minimum	maximum	median
vapor density (air=1)	2.5	9.60	5.2
vapor pressure, kPa	0.00	64.0	0.27
viscosity, mPa.s	0.42	32.7	1.07
surface tension, mN/m	23.75	41.39	28.6
dissociation constant, pKa	10.68	13.3	12.0
pH	5	7	7
donor number, DN, kcal/mol	11	23.7	16.3
acceptor number, AN	6.7	18.3	16.3
polarity parameter, $E_T(30)$, kcal/mol	36.7	48.6	40.9
coefficient of cubic expansion, 10^{-4}/°C	8.76	10.3	
specific heat, cal/K mol	31.54	119	46.9
heat of vaporization, cal/g	7.72	21.8	10.04
heat of combustion, MJ/kg	18.5	36.35	28.19
dielectric constant	4.75	64.9	64.0
Kauri-butanol number	62	1000	1000
Hildebrand solubility parameter, $cal^{1/2}\ cm^{-3/2}$	7.34	12.6	8.8
Henry's Law constant, atm/m^3 mol	9.9E-8	1.9E-2	3.6E-4
evaporation rate (butyl acetate = 1)	0.001	11.8	0.22
threshold limiting value - 8h average, ppm	0.2	400	100
maximum concentration (15 min exp), ppm	2	310	150
LD50 oral, mg/kg	500	42000	5600
LD50 dermal, mg/kg	500	20000	5000
route of entry	absorption, contact. ingestion, inhalation		
target organs	blood, brain, central nervous system, eye, gastrointestinal tract, lung, respiratory system, skin, spleen		
carcinogenicity	ethyl acrylate, vinyl acetate		
mutagenic properties	methyl ester of butyric acid, γ-butyrlactone, dibutyl phthalate, 2-ethoxyethyl acetate, ethyl acetate, ethyl propionate, ethylene glycol methyl ether acetate, methyl propionate, n-propyl acetate		
biological oxygen demand, 5-day test, g/g	0.25	1.26	0.6
chemical oxygen demand, g/g	1.11	2.32	1.67
theoretical oxygen demand, g/g	1.09	2.44	1.67

Property	Value		
	minimum	maximum	median
biodegradation probability	days-weeks		
octanol/water partition coefficient	-0.56	+3.97	
urban ozone formation	0.02	0.42	0.08

3.3.14 COMPARATIVE ANALYSIS OF ALL SOLVENTS

Property	Value		
	minimum	maximum	range
boiling temperature, ^oC	CFCs	PHA	-40.6-372
freezing temperature, ^oC	CFCs	amines	-189-142
flash point, ^oC	aliphatic HC	CFCs (none)	-104-350
autoignition temperature, ^oC	glycol ethers	phenols	174-715
refractive index	CFCs	halogenated	1.20-1.63
specific gravity, g/cm^3	aliphatic HC	CFCs	0.51-3
vapor density (air=1)	aldehydes	CFCs	1-33.4
vapor pressure, kPa	many	CFCs	0.00-4000
viscosity, mPa.s	CFCs	PHA	0.02-114.6
surface tension, mN/m	CFCs	PHA	0.03-48.49
dissociation constant, pKa	ethers	alcohols	-8.3-19.00
pH	acids	amines	1-14
donor number, DN, kcal/mol	hydrocarbons	amines	0-61
acceptor number, AN	hydrocarbons	acids	0-105
polarity parameter, $E_T(30)$, kcal/mol	ethers	alcohols	16-65.3
coefficient of cubic expansion, $10^{-4}/^oC$	alcohols	ethers	7-14.5
specific heat, cal/K mol	CFCs	PHA	12.32-294
heat of vaporization, cal/g	CFCs	halogenated	3.76-81.2
heat of combustion, MJ/kg	CFCs	aliphatic HC	6.57-44.58
dielectric constant	CFCs	esters	1.0-64.9
Kauri-butanol number	aliphatic HC	esters	22-1000
aniline point, ^oC	aromatic HC	aliphatic HC	7-165
Hildebrand solubility parameter, $cal^{1/2}\ cm^{-3/2}$	CFCs	alcohols	5.9-23
Henry's Law constant, atm/m^3 mol	amines	alcohols	1.7E-23-34.4
evaporation rate (butyl acetate = 1)	many	aliphatic HC	0-17.5

Property	Value		
	minimum	maximum	range
threshold limiting value - 8h average, ppm	several	several	0.1-1000
maximum concentration (15 min exp), ppm	aldehydes	CFCs	0.3-1250
LD50 oral, mg/kg	aldehydes	phenols	46-320000
LD50 dermal, mg/kg	amines	alcohols	64-225000
route of entry	absorption, contact. ingestion, inhalation		
target organs	blood, brain, bone marrow, central nervous system, eye, gastrointestinal tract, heart, kidney, lymphatic system, liver, lung, peripheral nervous system, respiratory system, skin, spleen, stomach, testes, thyroid		
carcinogenicity	some in the following groups: aromatic hydrocarbons, halogenated hydrocarbons, nitrogen-containing compounds, organic sulfur compounds, phenols, aldehydes, ethers, amines, esters		
mutagenic properties	each group contains some species		
theoretical oxygen demand, g/g	CFCs	aliphatic HC	0-3.56
biodegradation probability	days-weeks in the most cases		
ozone depletion potential	CFCs		
global warming potential	CFCs		
urban ozone formation	CFCs	aldehydes	0-1.55

HC - hydrocarbons, PHA - polyhydric alcohols

The comparative chart allocates for each group the highest and the lowest position in relationship to their respective values of particular parameters. The chart allows to show that the fact of having many good solvent properties does not warrant that solvent is suitable for use. For example, CFCs have many characteristics of good solvents but they are still eliminated from use because they cause ozone depletion and are considered to be a reason for global warming. On the other hand, esters do not appear on this chart frequently but they are very common solvents.

The chart also shows that solvents offer very broad choice of properties, which can be selected to satisfy any practical application.

3.4 TERPENES

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3.4.1 DEFINITIONS AND NOMENCLATURE

Terpenes are natural products. Terpenoids enlarge this division to include natural or synthetic derivatives.

The structures of terpenes or terpenoids varies widely and are classified according to various aspects, e.g. number of isoprene units (C_{10} monoterpenes, C_{15} sesquiterpenes, C_{20} diterpenes, C_{25} sesterterpenes, C_{30} triterpenes, C_{40} tetraterpenes) or division in acyclic, mono-, bi-, tri-, tetra-, pentacyclic terpenes.[1,2] Often terpenes are named by their trivial names, e.g. d-limonene.

3.4.2 OCCURRENCE

The occurrence of terpenes is ubiquitous. Natural terpenes are found in plants and animals in minute amounts. Especially in higher plants, terpenes characterize the type of plant (chemotaxonomy): mono- and sesquiterpenes in essential oils, sesqui-, di-, triterpenes in balsams and resins, tetraterpenes in pigments and polyterpenes in latexes.[1,3,4,5] Therefore, terpenes are often emitted from natural products such as citrus fruits or trees, e.g. conifers.

Terpenes are components of various products: e.g. tobacco smoke, wax pastes (furniture and floor polishes etc.), liquid waxes (floor polishes etc.), cleansers (detergents etc.), polishes, dyes and varnishes, synthetic resins, so-called “natural” building products, deodorants, perfumes, softeners, air fresheners, foods, beverages, pharmaceutical products (e.g. camomile oil, eucalyptus oil).[1,3,4,5] In these products terpene compounds such as geraniol, myrcene (beta-myrcene), ocimene, menthol, alpha-pinene, beta-pinene, d-limonene, 3-carene, cineole, camphene or caryophyllene can be detected.[1,3,4,5]

Often terpenes may be included as additives, e.g. food additives licensed by the FDA. Terpenes detected in indoor air are mainly the monoterpenes alpha-, beta- pinenes, 3-carene and d-limonene which occur primarily in conifer products.[5] Some of the monoterpenes may be converted into well-known epoxides and peroxides with high allergic potential.[5]

Several products containing terpenes are more highly refined which influences quality and quantities of terpenes in these products: e.g. in oil of turpentine or in resin components. The quantity of monoterpenes is essentially influenced by the composition of the raw materials, e.g. d-limonene dominates in agrumen oils as citrus oil products.[5]

Terpene products are often associated with “natural positive” properties, e.g. attributes such as “biological, positive health effects and good biodegradability” which are often neither substantiated nor proven.

Indoor concentrations of some terpenes, e.g., d-limonene and pinene, are highest in the group of VOCs.[6]

3.4.3 GENERAL

Terpenes are synthesized in chloroplasts, mitochondria and microsomes of plants or in the liver of animals. Typical biosynthesis pathways of terpenes are well-known, e.g. via

decarboxylation, isomerization and acetyl-CoA-processes.[1] Degradation of terpenes is possible by microorganisms, e.g. Pseudomonas and Aspergillus sp., in plants and in animals.[1]

In terpene products, terpenes exist as two enantiomers in different mixture ratios. Enantiomers are associated with characteristic odour (e.g. d-limonene in orange-oil).[5] Odors of terpenes are essential criteria in the classification of terpenes. Some terpenes can be smelt in extremely low concentrations.[5]

Threshold limit values are in the range of $\mu g/m^3$ in indoor air.[5] This applies primarily to monoterpenes pinenes, d-limonene, carenes and sesquiterpenes longifolenes and caryophyllenes.

3.4.4 TOXICOLOGY

Most terpenes show low acute oral toxicity and low dermal toxicity. Contact dermatitis is the most common symptom described as a result of exposure to terpenes. Other allergic reactions occur more rarely: e.g. allergic rhinitis or allergic bronchial asthma. The most common products with an allergic potential (contact dermatitis) are oils of turpentine.[5] Older turpentine products show higher allergic potential than freshly distilled products. Turpentines have now been replaced by other less toxic petrochemical products.

Many terpenes or metabolites are well-known contact allergens causing allergic dermatitis, e.g. d-limonene or oxygenated monocyclic terpenes which are produced by autoxidation of d-limonene.[7] Normally the highest allergic potential is associated with photo-oxidants (e.g. peroxides, epoxides) which are formed from terpenes. The symptoms of allergic dermatitis disappear if dermal contact to the causative terpene allergens is removed.

Exposure to the monoterpenes (alpha-pinene, beta-pinene and 3-carene) showed no major changes in lung function, but showed chronic reaction in the airways (reduced lung function values which persist between shifts) in workers of joinery shops.[8] In studies of dwellings, bronchial hyper-responsiveness could be related to indoor air concentrations of d-limonene.[9] Other studies did not find significant changes in the respiratory tract.[10,11] Nevertheless, these studies postulate effects of metabolites of terpenes (e.g. pinenes) as relevant causative agents. It is suggested in some cases that “Multiple Chemical Sensitivity” (MCS) may be attributed to increased values of terpenes and aromatic hydrocarbons.[12]

Often mixtures of terpene products or so-called “natural products” show allergic effects, e.g. fragrant mixtures containing d-limonene,[7] tea tree oil,[13] oilseed rape.[14] Consumer products such as deodorants or perfumes also contain terpenes with allergic potential.[15,16]

3.4.5 THRESHOLD LIMIT VALUES

Relevant threshold limit values for terpenes are rare because of a lack of basic information about specific terpene products and by-products on the one hand, and occupational and environmental exposures on the other hand.[5] The threshold limit values which have been documented the best concern oil of turpentine. A MAK-value of 100 ppm is defined in German regulations and noted to be dermally sensitive.[17] For other terpenes, such as d-limonene which is also classified as dermally sensitive, it has not yet been possible to establish a MAK-value because of a lack of information of their effects on animals or humans. With terpenes, as is often the case, aggregate concentration parameters are used as limit values such as the minimum level goals recommended by the former German Federal Health Authority.[18] These suggested minimum values bear in mind actual levels detected in indoor areas.

Although Mohr[5] quotes values of 30 µg/m³ for terpene aggregate and 15 µg/m³ for a single terpene compound from a scheme of Seifert, he considers values of 60 µg/m³ for terpene aggregate to be more appropriate according to his experience. He also discusses aggregate values of 200 µg/m³ (these exceed the olfactory threshold level) as posing possible health hazards in individual cases. These concentration limits only concern monoterpenes (pinenes, d-limonene, 3-carene) not other terpene products (e.g. sesquiterpenes).[5]

Table 3.4.1 Selected examples of terpenes

Substance group	Examples	Common occurrence	Selected properties
Acyclic monoterpenes	geraniol	in essential oils, perfume products and luxury foods, production from other terpene products, e.g. beta-pinene	acyclic, double unsaturated alcohol, several possible reactions, occurrence as esters, typical rose odor
	myrcene	naturally occurring in plant oils and organisms, industrial production	very reactive, pleasant odor, part of many synthetic reactions (synthesis of other terpenes)
	ocimene	in essential oils and perfume products	pleasant odor, sensitive to oxidation
Monocyclic monoterpenes	p-menthane	in essential oils, e.g. eucalyptus fruits	typical odor (fennel)
	p-cimene	perfume and soap products (musk perfumes), in various production processes, e.g., sulfite leaching of wood	typical odor (aromatic hydrocarbons), inflammable
Bicyclic monoterpenes	pinenes	in essential oils and conifer products, industrial production and use, e.g. in fragrance and flavor industry	typical odor (turpentine), softening agent
Acyclic sesquiterpenes	farnesol	in essential oils, in perfume and soap products	typical odor, sensitive to oxidation, heat and light
Monocyclic sesquiterpenes	bisabolenes	in various oils, e.g. myrrh and limete oil, in perfume and fragrance products	balsamic odor
Bicyclic sesquiterpenes	caryophyllenes	in essential oils, as perfume and fragrance products, chewing gum, synthesis of other perfumes	typical odor (clove)
Tricyclic sesquiterpenes	longifolene	in essential oils, e.g. turpentine, solvent additive, production of perfumes	colorless, oily liquid

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