Flotation Frothers: Review of Their Classifications, Properties and Preparation

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Abstract: The importance of frothers in flotation is widely acknowledged, particularly in terms of their role with respect to bubble size, and the stability and mobility of the froth phase. These factors play a significant role in the kinetic viability of the process, and the overall recovery and the grade that can be achieved from a flotation cell or circuit. About 60 years ago, Wrobel [1] presented a comprehensive review of flotation frothers, their action, properties and structures. However, during recent six decades flotation reagent technology has undergone considerable evolutions and innovations. The aim of the present review is to provide an updated, comprehensive database comprising recent developments in flotation frother technology as well as some historical aspects. Different types of flotation frothers are discussed regarding to their classifications, properties, and preparation methods. New classification schemes have been suggested in parallel with introducing new characterization criteria. New classes of frothers are actually conventional frothers modified by incorporating certain functional "group" or "atoms" into their molecular structure. Like particle surface modifiers, frothers are also influenced by biotechnology, leading to introducing a new class of frothers named as "biofrothers".

Keywords: Flotation frother, Classification, Properties, Preparation.

1. INTRODUCTION

When two bubbles come in contact with each other, the liquid film between them thins and breaks, causing bubbles to coalesce. When coalescence of bubbles formed in a liquid (or released into it) does not take place in fractions of seconds, the bubbles rise to the surface and aggregate, forming a foam or a froth [2]. Two definitions can be derived from the literature to distinguish between foam and froth, as follow:

- The imperfectly drained liquid-bubble systems, generally unstable, are called foam, while the more persistent, better drained bubble systems are referred to as froths [2]. In a review on foaming, Kitchener and Cooper [3] provided a sequence of photographs showing a gradual transition of structure from that of non-drained "foam" with spherical bubbles to a relatively well-drained "froth" with polyhedral bubbles, separated by very thin lamellae. Fig. (**1**) shows this structural transition from foam to froth. This description is frequently used in colloidal sciences.

- Foam comprises a two-phase system of air and liquid, whereas froth contains dispersed solid particles, so that the structure consists of three phases of air, liquid and solid and when broken down gives a two-phase system (aqueous solution and finely divided particles) [4]. Such a distinction is commonly used in coal and mineral flotation.

Foams and froths are of considerable practical importance not only in froth flotation of minerals or in adsorptive bubble-separation techniques applied to wastewater treatment, deinking of paper in paper recycling and processing of oil sands but also in the food industry [2, 5].

Despite the area of application, there is one known fact that pure liquids of low viscosity do not foam or froth and neither do the solutions containing hydrophilic solutes. Here is the area where a group of surface-active agents come into account which is so called "frothers", supporting the requirements in regard to forming foams and froths. After over a century from the appearance of froth flotation, the technology of flotation reagents has undergone significant mutations as well as other physical and mechanical aspects of this process. In parallel, several investigators have always tried to present comprehensive reviews to provide updated databases of such developments. Since 1953s when Wrobel [1] presented a comprehensive review of flotation frothers, their action, properties and structures, a large body of literature on frother studies has risen by different workers. In this regard, the present review has been prepared to provide an updated database including recent advances in flotation frother technology in terms of their classifications, characteristics, and preparation methods.

2. FROTHERS

Without reagents there would be no flotation, and without flotation the mining industry, as we know it today, would not exist. Flotation is the only processing method in which three phases of air, liquid, and solid are involved, simultaneously. Therefore, the reagent schemes are those resulting in reliable conditions of mentioned phases. In this regard, flotation reagents include collectors and surface modifiers, frothers, and pH-regulators controlling physical and chemical conditions of solid, air, and liquid phases, respectively. The

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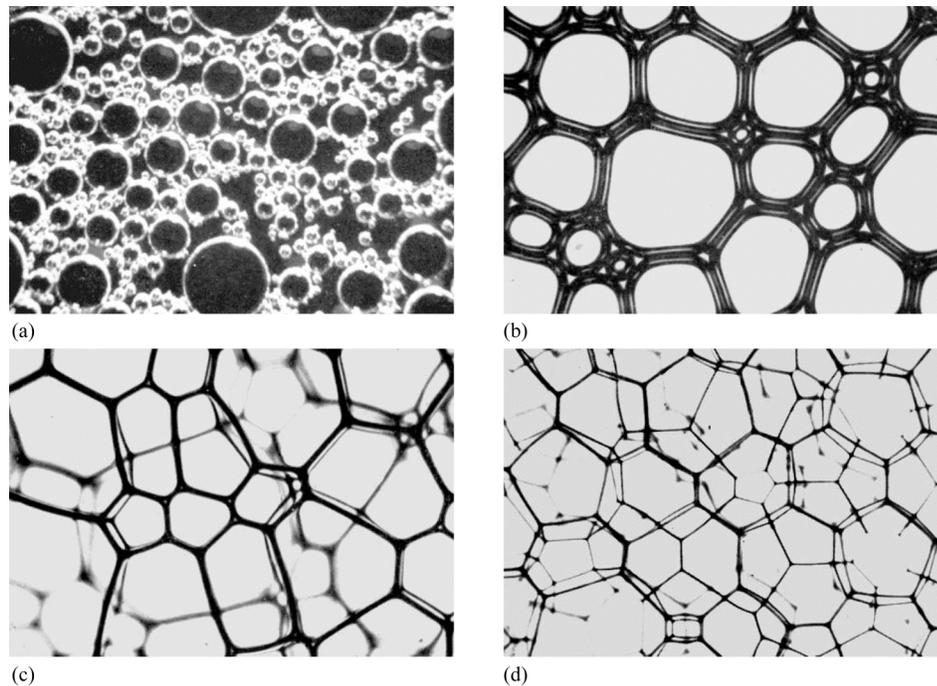
Fig. (1). Photomicrographs showing foam to froth transition: (**a**) a non-drained spherical bubble "foam"; (**b**) a partially-drained foam, showing distortion of bubbles; (**c**) after further drainage, the lamellae and Plateau borders continue to thin; and (**d**) a well-drained froth, showing polyhedral cells and very thin Plateau borders [3].

importance of frothers in flotation is widely acknowledged, particularly in terms of their role with respect to bubble size, and the stability and mobility of the froth phase. These factors play a significant role in the kinetic viability of the process, and the overall recovery and the grade that can be achieved from a flotation cell or circuit [6].

Frothers are heteropolar surface-active compounds containing a polar group and a hydrocarbon radical, capable of adsorbing in the air-water interface. As shown in Fig. (**2**), the frother molecules are arranged at the air-water interface such that the hydrophilic or polar groups are oriented into the water phase and the hydrophobic or non-polar hydrocarbon chain in the air phase. In fact, the frother creates conditions for froth formation. As fallowed, the flotation froth is a three-phase system. The frother concentrates at the interface of water and air bubbles, forming an envelope around the bubbles, which prevents them from colliding or touching. Frothers also lower the surface tension of the water. The forces created around the air bubble in the presence of a frother prevent the bubbles from collapsing [7]. Two edited books frothing in flotation volume I and II give a comprehensive information on frother mechanisms and frothing practices [8, 9].
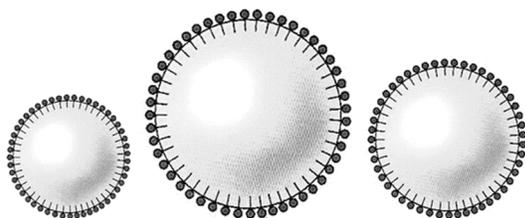

Fig. (2). Orientation of the frother molecules in the surface of bubbles [10].

3. CLASSIFICATION OF FROTHERS

In the literature, there are several different classifications of frothers depending on their properties and behaviors in solution and pulp. Four classification methods commonly used are based on pH-sensitivity, solubility, frothing/collecting ability, and selectivity/frothing-power relationship. The other classifications are tentative because some of the compounds used as frother have been or still are proprietary products and their structures are seldom disclosed, e.g. F# and T# frothers.

3.1. pH-Sensitivity Based Classification

Dudenkov and Galikov [11] have classified the frothers depending on the frother behavior at different pH values. This classification is shown in Table **1**.

Table 1.   Classification of Frothers Based on Their pH-Sensitivity

Acidic	Neutral	Basic
Phenols Alkyl sulfonates	Aliphatic alcohols Cyclic alcohols and Natural oils Alkoxy paraffins Polypropylene glycol ethers Polyglycol ethers Polyglycol glycerol ethers	Pyridine base

3.1.1. Acidic Frothers

These frothers perform well only in acidic pHs. In an alkaline medium, their frothing properties are reduced. The

acidic frothers have been used extensively until the 1960s. Their application has been diminishing because of environmental considerations. The two following groups of these frothers have been used in mineral processing plants: phenols and alkyl sulfonates [7].

A) Phenols

Phenols are also known as aromatic alcohols. The general formulas of the main members of these frothers are shown in Fig. (**3**). These frothers are obtained as a byproduct during gasification of coal tar and/or distillation of crude oil. The main problem associated with the use of phenol as a frother is its variable composition, which depends on the source from which the frother is derived. For example, phenol can be made from the partial oxidation of benzene, the reduction of benzoic acid, by the cumene process, or by the Raschig-Hooker process. It can also be found as a product of coal oxidation [12]. Naphthalene (naphthalin) is the most abundant single component of coal tar. From the 1960s to the 1990s, significant amounts of naphthalene were also produced from heavy petroleum fractions during petroleum refining, but today petroleum-derived naphthalene represents only a minor component of naphthalene production. Although the composition of coal tar varies with the coal from which it is produced, typical coal tar is about 10 percent naphthalene by weight. In industrial practice, distillation of coal tar yields oil containing about 50 percent naphthalene, along with a variety of other aromatic compounds. This oil, after being washed with aqueous sodium hydroxide to remove acidic components, undergoes fractional distillation to isolate naphthalene. The crude naphthalene resulting from this process is 95 percent naphthalene by weight, often referred to as 78°C (melting point). The chief impurities are the sulfur-containing aromatic compound benzothiophene (< 2 percent), indane (0.2 percent), indene (< 2 percent), and methylnaphthalene (< 2 percent). Petroleum-derived naphthalene is usually purer than that derived from coal tar. Where required, crude naphthalene can be further purified by recrystallization from any of a variety of solvents, resulting in 99 percent naphthalene by weight, referred to as 80°C (melting point) [12,13].
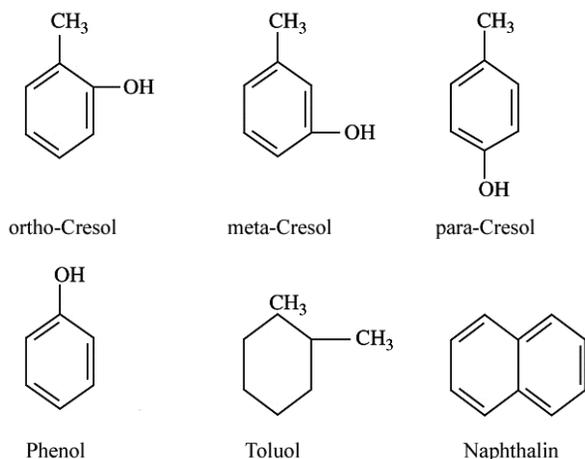
Fig. (3). Chemical structures of the main components of phenols [7].

Toluol (toluene) is another member of phenol frothers which occurs naturally at low levels in crude oil and is usu-

ally produced in the processes of making gasoline *via* a catalytic reformer, in an ethylene cracker or making coke from coal. Final separation (either *via* distillation or solvent extraction) takes place in a BTX plant [12]. Xylenol also belongs to the aromatic alcoholic type frothers. This frother is a mixture of xylenol isomers. The chemical structures of xylenol isomers are shown in Fig. (**4**). The methyl groups can assume six different arrangements. The 3,4- position is the most abundant. Xylenols are obtained from coal by distillation. Similar to phenols, these frothers also have a variable composition. Phenols and xylenols can be added to tall oil fatty acids to improve selectivity as well as power [7].
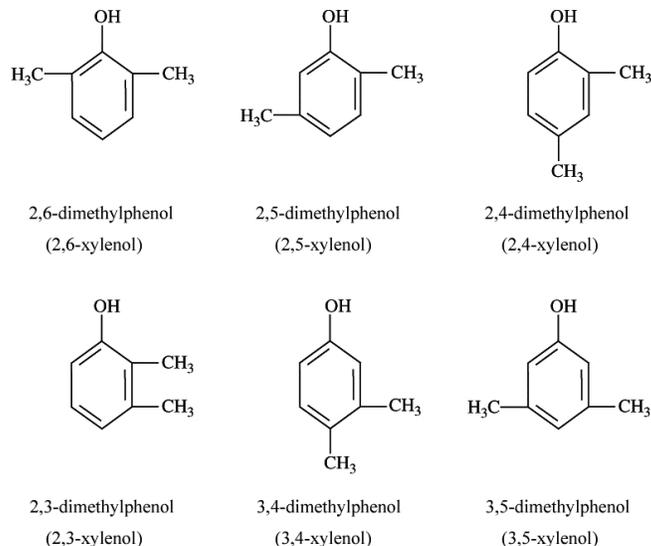
Fig. (4). Chemical structures of xylenol isomers [12].

The most typical frother from phenol type frothers is cresylic acid (actually not an acid), consisting of a mixture of phenols containing varying amount of the three isomers of cresol (see Fig. **3**), xylenols, and other high-boiling fractions. Cresols are acidulation products of toloul. The three isomers of cresol have strong collecting properties. Their popularity declined when acid circuit mills went out of fashion; however, they are still popular in coal flotation because of their availability from coking ovens. The froths produced by cresylic acids are generally similar in structure to those of pine oil, but of a somewhat larger bubble size. An increase in frother dosage decreases froth volume and produces a tendency to effervesce. The lower boiling fractions produce a more fragile froth and are somewhat more selective [7, 14]. Typical specifications for flotation grade cresylic acids were distillation range 190-235°C, with no more than 2 percent below 190°C, no less than 75 percent distilling below 235°C, density of 1.01 to 1.04 g/ml, and 1.7 g/l water solubility. Today's commercial grade has not less than 50 percent distilling over 204°C. If it boils below 204°C it is called cresol. A typical commercial cut boils between 220-250°C, and has as typical compositions meta, para-cresols 0-1 percent, 2,4- and 2,5-xylenols 0-3 percent, 2,3- and 3,5-xylenols 10-20 percent, 3,4-xylenols 20-30 percent, and C_9 phenols 50-60 percent [14].

Froth characteristics and collector properties of cresylic acids are very dependent on the *m*-cresol and phenol content,

Table 2.   Physical and Chemical Properties of Phenols [7,12,14]

	Formula	Mw, g/mol	Density, g/ml	Solubility, g/l	Freezing Point, °C	Boiling Point, °C	State
Phenol	C_6H_5OH	94.11	1.07	83	40.5	181.7	white crystalline solid
Toluol	$C_6H_5CH_3$	92.14	0.87	0.47	-93	110.6	colorless liquid
Naphthalene	$C_{10}H_8$	128.17	1.14	0.03	80.55	218	white solid crystals
Xylenols (~ dimethylphenols):							
2,6-xylenol	$(CH_3)_2C_6H_3OH$	122.16			43-45	203	
2,5-xylenol	$(CH_3)_2C_6H_3OH$	122.16	0.971		63-65	212	
2,4-xylenol	$(CH_3)_2C_6H_3OH$	122.16	1.011		22-23	211-212	
2,3-xylenol	$(CH_3)_2C_6H_3OH$	122.16			70-73	217	
3,4-xylenol	$(CH_3)_2C_6H_3OH$	122.16			62-68	227	
3,5-xylenol	$(CH_3)_2C_6H_3OH$	122.16			61-64	222	
Cresols:							
o-cresol	$CH_3C_6H_4OH$	108.14	1.05	25	29.8	191	colorless crystals
m-cresol	$CH_3C_6H_4OH$	108.14	1.03	24	11.8	202	thicker liquid
p-cresol	$CH_3C_6H_4OH$	108.14	1.02	19	35.5	201.9	greasy-looking solid

so specifications of cresylic acid purchases should be rigorous if froth control problems are able to be avoided in the concentrator. The purer cresylic acids are ruptured to give a more fragile froth and to require a stronger collector for good flotation. Impure cresylic acids contain pyridines and sulfur impurities, which were much sought after 70 to 90 years ago in flotation mills when the frother was also employed as a collector, but in conjunction with selective collectors these cresylic acids can give process control problems. Today, a mixture of tall oil fatty acids and cresol has been successfully used for flotation of spodumene and phenacite [14]. Table **2** shows some physical and chemical properties of phenol frothers.

B) Alkyl Sulfonates

Alkyl (alkylaryl) sulfonate can be described as an anionic frother with a structure that is composed of an aromatic hydrocarbon and aliphatic radical. In spite of the fact that these frothers have good frothing properties, their application was limited, likely because most alkylaryl sulfonate frothers contain traces of sulfur, which interfere with flotation [7]. Fig. (**5**) shows the chemical formula of these frothers.

R = aliphatic radical

M = metal

Fig. (5). Chemical structure of alkylaryl sulfonates [7].

3.1.2. Basic Frothers

These frothers are represented by pyridine and homologs, recovered as byproducts from coal tar distillation. They are used for flotation of base-metal ores. In Europe, a similar product was used to produce a collector applied in the flota-

tion of oxide lead minerals. The following two structures are used as frothers [7]. Fig. (**6**) shows the chemical formulas of these frothers.


Pyridine oxychloride

Pyridine sulfotrioxide
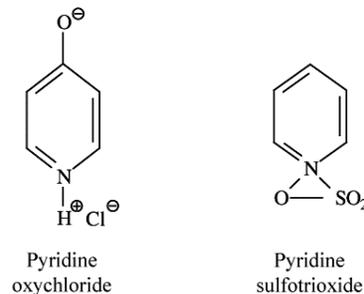
Fig. (6). Chemical structures of two basic frothers used commercially [7].

3.1.3. Neutral Frothers

This is the most important group of frothers widely used in flotation of base-metal ores, oxidic minerals and industrial minerals. They are functional in both acidic and alkaline pulps. These frothers are divided into six sub-groups, with wide differences in chemical composition.

A) Aliphatic Alcohols

These frothers are mixtures of alcohols containing 6-8 carbon atoms. They were at one time marketed by DuPont and still are by Cyanamid, as tailored frothers for specific ore types. The best-known frother from this group is methyl isobutyl carbinol (MIBC or 4-methyl-2-pentanol) and 2-ethyl hexanol (4-heptanol). Cyanamid Company produces MIBC under the trade name AF70 [7,14]. Fig. (**7**) shows the extended formulas of aliphatic alcohol frothers.

$$H_3C-CH-CH_2-CH-CH_3$$
$$\quad\quad | \quad\quad\quad\quad |$$
$$\quad\quad CH_3 \quad\quad\quad OH$$

Methyl isobutyl carbinol
(MIBC)

$$CH_3-CH_2-CH_2-CH-CH_2-OH$$
$$\quad\quad\quad\quad\quad\quad\quad\quad | $$
$$\quad\quad\quad\quad\quad\quad\quad CH_2-CH_3$$

2-ethyl hexanol
(4-heptanol)

$$CH_3-CH-CH-C-CH_2-O-C-CH$$

2,2,4-trimethylpentanediol 1,3-monoisobutyrate
(TEXANOL)

$$CH_3-C-CH_2-O-C-CH_3$$

Diacetone alcohol

n-propanol   *n*-butanol   *n*-pentanol

n-hexanol   2-butanol   *n*-heptanol

n-octanol   *t*-butanol   Isoamyl alcohol
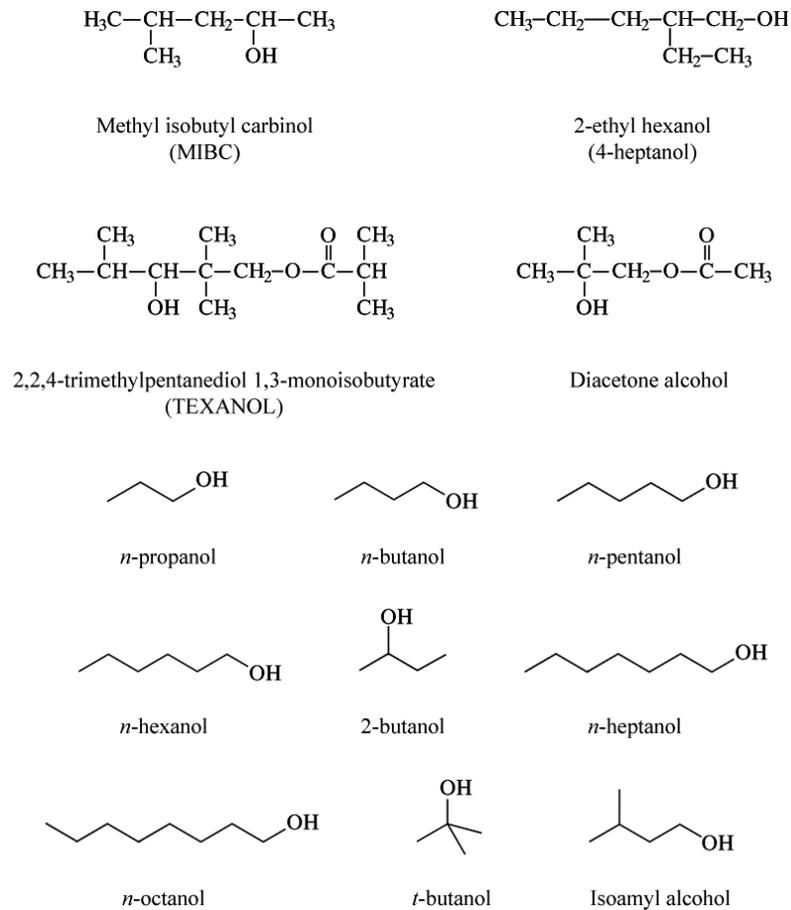
Fig. (7). Chemical structures of aliphatic alcohols [7,14,15].

The properties of aliphatic alcohol frothers are shown in Table **3**. Propanol is manufactured commercially by catalytic hydrogenation of propionaldehyde as follows:

$$H_2C=CH_2 + CO + H_2 \rightarrow CH_3CH_2CH=O \qquad \ldots(1)$$

$$CH_3CH_2CH=O + H_2 \rightarrow CH_3CH_2CH_2OH \qquad \ldots(2)$$

Butanol is produced industrially from the petrochemical feedstock propylene. Propylene is hydroformylated to butyraldehyde (i.e. Oxo process) in the presence of a rhodium-based homogeneous catalyst similar to Wilkinson's catalyst. The butyraldehyde is then hydrogenated to produce *n*-butanol. 2-butanol is produced by the hydration of 1-butene or 2-butene:

$$H_3CHC=CHCH_3 + H_2O \rightarrow CH_3CHOH(CH_2)CH_3 \qquad \ldots(3)$$
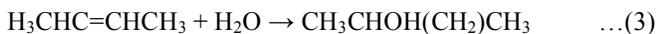
Sulfuric acid is used as a catalyst for this conversion. *t*-Butanol is derived from isobutene as a co-product of propylene oxide production. It can also be produced by the catalytic hydration of isobutylene [12].

Pentanol can be prepared by fractional distillation of fusel oil. Heavier alcohols are produced industrially by the oligomerization of ethylene using triethylaluminium followed by oxidation of the alkylaluminium products. For example, an idealized synthesis for hexanol and octanol are shown:

Hexanol:

$$Al(C_2H_5)_3 + 6C_2H_4 \rightarrow Al(C_6H_{13})_3 \qquad\qquad \ldots(4)$$

$$Al(C_6H_{13})_3 + 1\tfrac{1}{2}O_2 + 3H_2O \rightarrow 3CH_3(CH_2)_5OH + Al(OH)_3 \ldots (5)$$

Octanol:
$$Al(C_2H_5)_3 + 9C_2H_4 \rightarrow Al(C_8H_{17})_3 \qquad\qquad \ldots(6)$$

$$Al(C_8H_{17})_3 + 1\tfrac{1}{2}O_2 + 3H_2O \rightarrow 3CH_3(CH_2)_7OH + Al(OH)_3 \ldots(7)$$
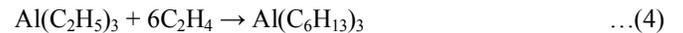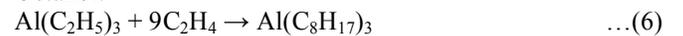
The process generates a range of alcohols that are separated by distillation [12,16].

Aliphatic alcohol frothers are also used as mixtures of different carbon lengths and as a mixture of hydrocarbon oils. The following mixtures are common in mineral flotation [7, 14]:

- Mixture of C_6-C_9 alcohols: a specific gravity of 0.856, viscosity of 5 cps, low water solubility, and flash point of $52^{\circ}C$. These frothers are regarded as highly selective.

- Mixtures of C_4-C_7 alcohols and hydrocarbon oil: an amber liquid with a specific gravity of 0.82, viscosity of 4.5 cps, water solubility of 5 g/l, and flash point of $44^{\circ}C$. These frothers are usually used during copper-molybdenum or molybdenum flotation, and are also recommended for flotation of minerals such as talc, graphite, sulfur and coal. Mixed C_4 to C_7 alcohols produce a livelier froth than MIBC.

- Mixtures of C_5-C_8 carbon alcohols: a specific gravity of 0.81-0.83, viscosity of 6.9 cps, water solubility of 10 g/l,

Table 3.   Physical and Chemical Properties of Aliphatic Frothers [6,7,12,15,17-19]

	Formula	Mw, g/mol	Density, g/ml	Solubility, g/l	Freezing Point, °C	Boiling Point, °C	State
n-propanol	$CH_3(CH_2)_2OH$	60.1	0.8	total	-126.5	97.1	clear, colorless liquid
n-butanol	$CH_3(CH_2)_3OH$	74.12	0.81	77	-89.5	117.2	colorless liquid
n-pentanol	$CH_3(CH_2)_4OH$	88.15	0.8144	27	-77.6	138	colorless liquid
n-hexanol	$CH_3(CH_2)_5OH$	102.17	0.8136	5.9	-46.7	158	colorless liquid
n-heptanol	$CH_3(CH_2)_6OH$	116.2	0.8187	1.8	-34.6	175.8	clear, colorless liquid
n-octanol	$CH_3(CH_2)_7OH$	130.23	0.824	0.3 mg/l	-16	195	colorless liquid
2-butanol	$CH_3CHOH(CH_2)CH_3$	74.12	0.806	125	-114.7	99	colorless liquid
tert-butanol (~ *t*-butanol)	$CH_3C(CH_3)_2OH$	74.12	0.781	very soluble	25	82	colorless liquid or white solid*
Isoamyl alcohol	$(CH_3)_2CHCH_2CH_2OH$	88.17	0.809	25	-117.2	132	clear, colorless liquid
MIBC (~ methyl isobutyl carbinol)	$(CH_3)_2CHCH_2CHOHCH_3$	102.17	0.808	17	-90	132	light brown liquid
4-heptanol (~ 2-ethyl hexanol)	$CH_3(CH_2)_2CH(CH_2)_2OHCH_3$	116.23	0.8183	4.5	-41.2	161	liquids
Diacetone alcohol	$C_6H_{12}O_2$	116.16	0.938	total	-47	166	clear, colorless liquid
TEXANOL (~ 2,2,4-trimethylpentanediol 1,3-monoisobutyrate)	$C_{12}H_{24}O_3$	216.32	0.95	20	-50	244	liquid

*depending on the ambient temperature.

boiling range 135-140°C, and flash point of 55°C. These frothers gave less persistent froth than the other alcohol mixtures.

B) Cyclic Alcohols and Natural Oils

These frothers are basically mixtures of different cyclic alcohols, ethers, terpineols, and ketones, which can be produced as synthetic mixture or form the pine resins. The basic structures of different components of cyclic alcohol frothers and natural oil members are shown in Fig. (**8**). The most abundant cyclic alcohols in the frother mixtures are terpineols (i.e. 90 percent) followed by borneol and pinene. The physical and chemical characteristics of cyclic alcohol frothers are shown in Table **4**. Terpineol is naturally occurring monoterpene alcohol that has been isolated from a variety of sources such as cajuput oil, pine oil, and petitgrain oil. In addition, terpineols are commonly manufactured from the more readily available *α*-pinene. Borneol can be synthesized by reduction of camphor by the Meerwein-Ponndorf-Verley process [12]. Fenchyl alcohol can be prepared by reduction of fenchone during its purification [20]. Pinene, as the name suggests, both forms are important constituents of pine resin. They are also found in the resins of many other conifers, and more widely in other plants. *α*-Pinene is produced from geranyl pyrophosphate, *via* cyclisation of linaloyl pyrophosphate followed by loss of a proton from the carbocation equivalent [12].

The cyclic alcohol frothers are less sensitive to the presence of clay minerals than other types of frothers and they are then extensively used in mixtures with aliphatic alcohol frothers for flotation of base metals and copper porphyry ores containing clay minerals. They are also used as additives to tall oil fatty acid in fatty acid flotation to improve froth stability [7].

The major problem in the use of natural oils and cyclic alcohol frothers derived from natural sources is that their composition is not always constant, and consequently frothing properties are variable. In the early days of flotation, eucalyptus oil was a popular frother cum collector. Later, pine oil became the dominant natural oil frother, because of its greater availability in the western world. Essentially all the pine growing countries such as Canada, USA, Finland, China, etc., have supplied different grades of pine oils at one time or another, but from the flotation point of view the problems that mill operators have faced is the difficulty in specifying a particular grade and obtaining the same frother performance from different suppliers. This problem, and the fact that the natural oils all have collector properties, have made them less popular with modern mill operators who now prefer MIBC and synthetic non-collecting soluble frothers. Those using pine oils emphasize on its small-bubble, closely knit, froths that do not allow excessive particle fall-out, but break down readily in the launder. The close-knit pine oil froth makes recovery better but lowers the grade of concentrate. Increasing the amount of pine oil fed to the cells tends to flatten the froth, decrease its volume, and cause surface spatter. An emergency supply of pine oil can be very useful at mills with ores which tend to have periods of over-frothing. It can also be used in blends with MIBC to regulate the characteristics of the froth and compensate for changes in ores which may affect selectivity and rougher recovery. Typical specifications for pine oil to be used as a frother are

alpha-terpineol   beta-terpineol   gama-terpineol

alpha-pinene   Borneol   Fenchyl alcohol

alpha-camphor   Piperitone   Fenchone

Eucalyptol
(1,8-cineole)   Anethol(e)
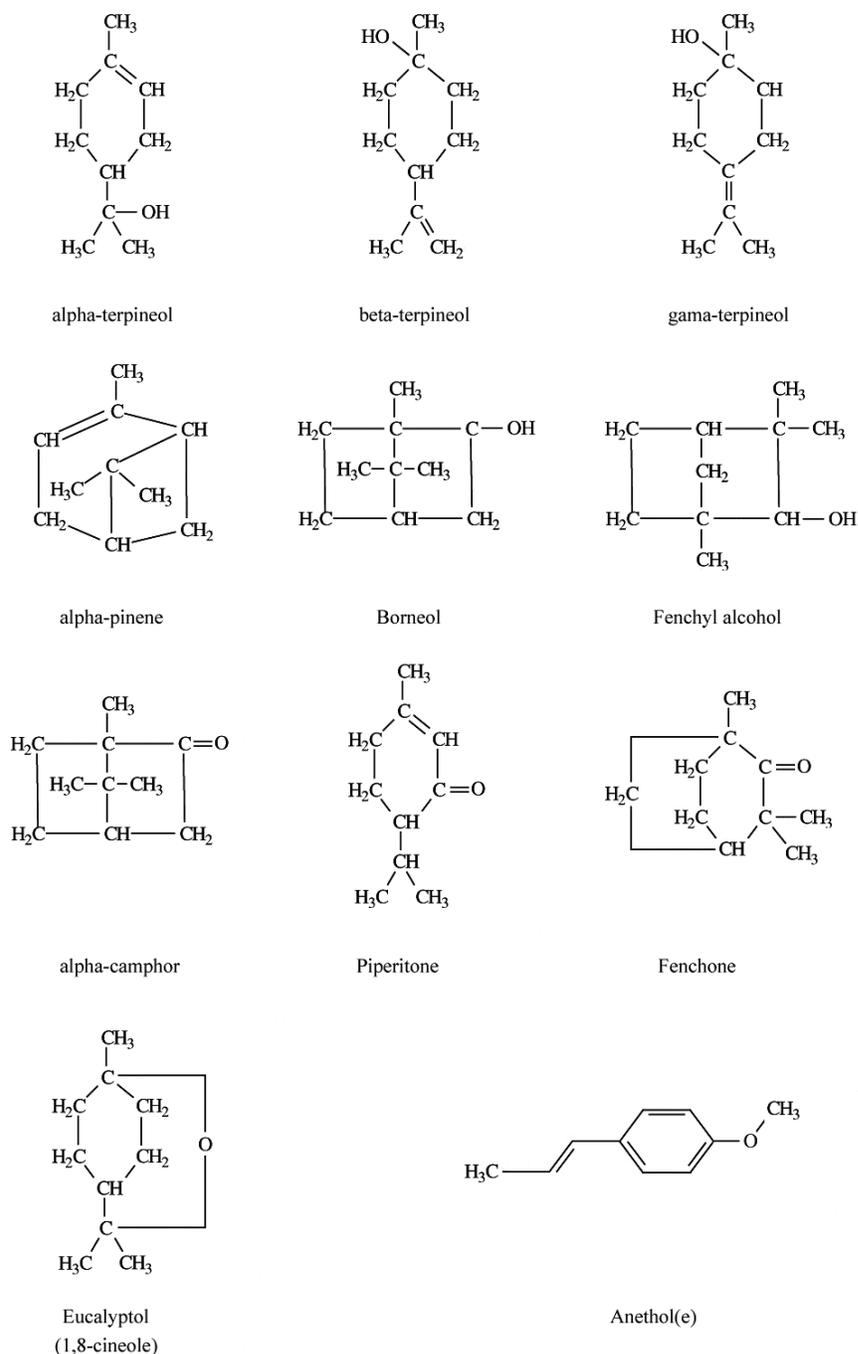
Fig. (8). Chemical structures of different components of cyclic alcohols and natural oil [7,12,14].

clear, yellow oil, with a typical smell, that boils between 170 and 228°C, with density of 0.915 to 0.935 g/ml. At least 44 percent by weight of the composition should be alcohols (expressed as terpineols). At least 78 percent must distil between 170 and 220°C. Its average solubility in water should be approximately 2.5 g/l. For example, a typical assay of commercial pine oil is α-terpineol 60-70 percent, tertiary alcohols 10 percent, borneol and fenchyl alcohol 10-15 percent, and camphor 10-15 percent. Typical properties are a specific gravity of 0.927-0.940, distillation range 200-235°C, and flash point of 172°C. The eucalyptus oils have greater collector action because they are richer in ketones than the pine oils, which contain primarily camphor, while eucalyptus

oil ketones are cineoles and piperitones rather than camphor, and borneols and piperoteols, as well as terpenes. Their main odorous component is the ether 1,8-cineole rather than the ketone, camphor. Typical eucalyptus oils available today have a specific gravity of 0.921-0.923, distillation range 174-177°C, and typical water solubility of 1.4 g/l [14].

Table **4** also shows the physical and chemical characteristics of the main components of natural oils. Anethol(e) is commercially prepared from some essential oils, including anise, star anise, and fennel. Eucalyptol or 1,8-cineole comprises up to 90 percent of the essential oil of some species of the generic product eucalyptus oil, hence so name. It is also found in camphor laurel, bay leaves, tea tree, mugwort,

Table 4.   Physical and Chemical Properties of Cyclic Alcohol Frothers and Natural oil Components [7,12,14,21,22]

	Formula	Polar Group	Mw, g/mol	Density, g/ml	Solubility, g/l	Freezing Point, ºC	Boiling Point, ºC	State
Cyclic alcohols:								
α-terpineol	$C_{10}H_{18}O$	–OH	154.25	0.919	2.2	33	219	clear liquid
β-terpineol	$C_{10}H_{18}O$	–OH	154.25	0.935	1.98	35	220	clear liquid
γ-terpineol	$C_{10}H_{18}O$	–OH	154.25	0.925	2.09	36	222	clear liquid
Borneol	$C_{10}H_{18}O$	–OH	154.25	1.011	0.64	204	213	white solid
Fenchyl alcohol (~ fenchol)	$C_{10}H_{18}O$	–OH	154.25	0.992	insoluble	37	202	oily liquid or white colorless solid*
Ethers:								
Anethol(e)	$C_{10}H_{12}O$	O–C	148.2	0.998	insoluble	20	234	clear, colorless liquid
Eucalyptol (~ 1,8-cineole)	$C_{10}H_{18}O$	O–C	154.25	0.923	insoluble	1.5	176-177	colorless liquid
Terpenes:								
α-pinene	$C_{10}H_{16}$	–	136.24	0.86	insoluble	-65	155	liquid
Ketones:								
α-camphor	$C_{10}H_{16}O$	C=O	152.23	0.99	1.2	179.75	204	white or colorless solid
Piperitone	$C_{10}H_{16}O$	C=O	152.23	0.933	insoluble	-20.20	233-235	clear, light yellowish to yellow liquid
Fenchone	$C_{10}H_{16}O$	C=O	152.23	0.948	slightly soluble	6.1	193.5	colorless oily liquid

* depending on the ambient temperature.

sweet basil, wormwood, rosemary, sage and other aromatic plant foliage. Eucalyptol with purity from 99.6 to 99.8 percent can be obtained in large quantities by fractional distillation of eucalyptus oil. Camphor can be produced from α-pinene. With acetic acid as the solvent and with catalysis by a strong acid, α-pinene readily rearranges into camphene, which in turn undergoes Wagner-Meerwein rearrangement into the isobornyl cation, which is captured by acetate to give isobornyl acetate. Hydrolysis into isoborneol followed by dehydrogenation gives camphor. In biosynthesis camphor is produced from geranyl pyrophosphate, *via* cyclisation of linaloyl pyrophosphate to bornyl pyrophosphate, followed by hydrolysis to borneol and oxidation to camphor. Piperitone is a natural monoterpene ketone which is a component of some essential oils [12].

Fenchone is a constituent of absinthe and the essential oil of fennel. For its purification, the accompanying substances found in fraction 190 to 195ºC are removed by oxidation with either concentrated nitric acid or permanganate solution. Fenchone, being very stable toward oxidizing agents, is affected but little. Having thus been purified in a fair measure, it congeals in the cold and can be further purified by crystallization. However, small amounts of camphor, resulting from the oxidation of borneol esters, can not be removed in this manner. Artificially fenchone is obtained by the oxidation of fenchyl alcohol [20].

C) Alkoxy Paraffins

This group of frothers was developed in 1951 by Dr. Powell of South Africa. In recent years, a number of frothers were produced based on two main structures of TEB (1,1,3-triethoxybutane) and Powell accelerator, so named because it has a strong effect on the flotation rate (Fig. **9**). The Powell accelerator is a more powerful frother than TEB, but otherwise has similar characteristics, i.e. low water solubility, good stability, and a strong effect on flotation rate. Only limited information is available on the chemistry and properties of these frothers, although they are extensively used for flotation of base metals and oxidic mineral ores. Their frothing properties are much different from those of aliphatic and cyclic alcohols with respect to froth stability and sensitivity to the presence of clay minerals. The froths these reagents produce are similar to those of pine oil, except that overfeeding does not affect the froth character as much. They are selective and in many cases, improve rates of flotation of copper and zinc minerals. These frothers are highly effective during the flotation of oxide copper minerals using the sulfidization method [7,14].

D) Polyglycol Ethers

Tveter [23] of Dow Chemicals Company and Booth [24] of American Cyanamid laboratories first developed the polyglycol ether frother series which are completely miscible in water. These frothers are manufactured from synthetic brake fluid and they are methoxy polypropylene glycols or polypropylene glycol methyl ethers. There are several variations of polyglycol ethers produced by different manufacturers, such as Dow Chemical Company under the name Dowfroths (DF#), by Union Carbide as Ucon frothers, by Cyanamid as Aerofroths (AF#), ICI as Tecfroths, etc. With MIBC they

$$H_3C-CH-CH \begin{matrix} O-CH_2-CH_3 \\ \\ O-CH_2-CH_3 \end{matrix}$$
$$H_3C-H_2C-O$$
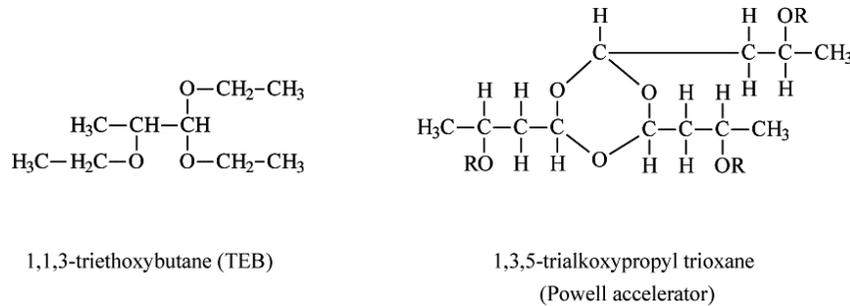
1,1,3-triethoxybutane (TEB)

1,3,5-trialkoxypropyl trioxane
(Powell accelerator)

Fig. (9). Chemical structures of two main alkoxy paraffins [7].

account for nearly 90 percent of all frother use in metallic ore flotation. The three basic structures of these frothers are shown in Fig. (**10**) [7,14].

(a) $\quad H-\left[O-C_3H_6\right]_n-OH$

(b) $\quad CH_3-\left[O-C_3H_6\right]_n-OH$

(c) $\quad CH_3-\left[O-C_3H_6\right]_n-OH + adduct$
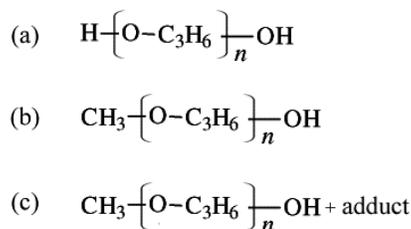
Fig. (10). Different structures of polyglycol ether frothers [7].

The Dowfroths are usually methoxy polypropylene glycols, with the general structure (a), e.g. DF-200, DF-250 and DF-1012. The Dowfroth 250 is one of the most common used ether frothers, which can be made from the reaction of methanol and propylene oxide. Dowfroth 1400 is a diol of 400 molecular weights, with the structure (b). The American Cyanamid products are condensations of propylene oxide with propylene glycol. Aerofroth 65 (AF-65) is an example of such products, which is prepared by the reaction of propylene oxide with water. Union Carbide supplies similar products based on polypropylene glycols and polyethylene glycols, under the trademarks of PPG and Ucon. Some polyglycol ethers are also produced by condensation with butanol or ethylene oxide (structure (c)) or result as a reaction product of butanol and caustic soda. Dowfroth 1263 is an example of these ethers, which is made by reacting DF-250 with butylenes oxide [7,14,24-29].

The molecular weight and carbon length of polyglycol ether frothers determine their power and performance. A higher molecular weight frother gives more persistent froth and less selective than a lower molecular weight frother. The physical and chemical characteristics of polyglycol ether frothers are shown in Table **5**. Unfortunately, the polyglycol ethers from different manufacturers act differently. For example, Hoechst (Germany) polyglycol ether frothers gave more selective froth than those produced by Dow Chemical Company. Fig. (**11**) shows another example for DF-250 produced by two different American and Canadian manufacturers, in term of surface activity. In experience, polyglycol ethers produced from butanol and ethylene oxide are more selective and have better carrying power than similar frothers produced from butanol and caustic soda [7,30].

E) Polypropylene Glycol Ethers

These non-ionic ether frothers are partially soluble in water, and are a mixture of monomethyl ethers of polypropylene glycols, which were first offered by Dow Chemical as DF-4082 and Union Carbide as R17 and R48. These frothers are normally used in base-metal flotation. They produce persistent froth and have relatively high carrying power [7,14]. Fig. (**12**) shows the formula of these frothers.

F) Polyglycol Glycerol Ethers

Originally, these frothers were developed in the former Soviet Union under the trademark of Frother E1, and in 1985 Dow Chemical, under the trade names XK35004.00L, XK35004.01L and XK35004.02L, produced similar frothers. An example of the second family is the reaction product of glycerol with propylene oxide to a 450 molecular weight [7,14]. The general formula of these frothers is shown in Fig. (**13**).

These frothers produce relatively strong froth with a fine texture. XK35004.01L and XK35004.02L can be blended with other polyglycol ethers to fine tune froth properties. They are stable in the range pH 3.5 to 12.3, and usually employed in alkaline flotation [14]. The physical and chemical characteristics of polyglycol ether frothers are shown in Table **6**.

3.2. Solubility Based Classification

Crozier [14] has divided the frothers into slightly soluble in water, and those that are completely miscible. Partially soluble frothers include aliphatic alcohols, natural oils, cresylic acids, alkoxy paraffins and non-ionic polypropylene glycol ethers. The solubility data of these frothers is listed in Tables **2** to **4**. In the case of aliphatic alcohols, the alcohols with lower solubility are more effective than those with higher solubility. Completely water miscible frothers are polyglycol and polyglycol glycerol ethers. These frothers produce compact, lasting froth structures that break down readily in the launders. Unlike the froths from slightly soluble frothers, these frothers produce more tightly knit, more selective froths, that do not spatters on over-feeding the reagent.

3.3. Frothing/Collecting Ability Based Classification

The ability of compound to demonstrate frothing properties has been associated with chemical groups such as hydroxyl (–OH), carboxyl (–COOH), ester (–COOR), carbonyl (–CO), nitrogen-containing (NH$_2$ and N), and sulfur-containing (–SO$_3$–) groups. Considering such a behavior, the

Table 5.   Physical and Chemical Properties of Polyglycol Ether Frothers[*] [7,14,27,29,31,32]

	Formula	Mw, g/mol	Viscosity at 25ºC, cps	Density, g/ml	Solubility, g/l	Freezing Point, ºC	Boiling Point, ºC
Dow Chemical:							
DF-200	$CH_3(C_3H_6O)_3OH$	206.29	7	0.97	total	-50	243
DF-250	$CH_3(C_3H_6O)_4OH$	264.37	12	0.98	Total	-50	252
DF-1012	$CH_3(C_3H_6O)_{6.3}OH$	397.95	27	0.988	32%	-50	293
DF-400	$H(C_3H_6O)_{6.5}OH$	395.61	71	1.007	total	-50	180
DF-1400	$H(C_3H_6O)_6OH$	366.56	75	1.007	total	-45	
DF-1263	$CH_3(C_3H_6O)_4OH(C_4H_8O)$	336.53	19	0.978	very good	-41	> 250
Union Carbide:							
Ucon 200		400	75	1.009	total	-45	
Ucon R55				0.9735	total	-50	
PPG-192	$H(C_3H_6O)_3OH$	192[a]					
PPG-400	$H(C_3H_6O)_{6.5}OH$	420[a]					
PPG-725	$H(C_3H_6O)_{12.8}OH$	762[a]					
PPG-1000	$H(C_3H_6O)_{16.5}OH$	950[a]					
PPG-2000	$H(C_3H_6O)_{34}OH$	1940[a]					
Cyanamid:							
AF-65	similar to DF-400						
AF-67	similar to DF-250						
AF-68	similar to DF-1012						

[*] These frothers all are in liquid state.
[a] These data are characterized by reversed-phase high performance liquid chromatography (HPLC) as reported by Tan *et al.* [31].

compounds commercially used as frothers in mineral/coal froth flotation today can be classified into two general categories. The first category is the group that acts in a flotation system as both collector and frother and is normally associated with non-sulfide mineral flotation. The compounds be-

longed to this category consist of carboxylic, nitrogen- and sulfur-containing groups. Typical members are long-chain amines and amine salts which have chain lengths up to C_{18} (used, for example, as cationic collectors in the flotation of silica), the long-chain sulfates (e.g., petroleum sulfonates), and long-chain fatty acids (which generally include, in varying ratios, C_{18} fatty acids, oleic, linoleic, and linolenic acids). The above materials are ionic and highly surface-active and can result in the formation of stable and persistent froths if overdosed. Because of the soluble metal ion sequestration and the adsorption of most of these dual collector/frother compounds on the substrate to be recovered, the actual chemical equilibrium concentration in the system is relatively low. Thus, reasonable froth action is exhibited in most practical systems by dual functions compounds. However, because of the high surface activity related to the ionic character of these dual function compounds, if the concentration available for frother action becomes too high, very stable and difficult to handle froths will result [33,34].

Fig. (11). Variation of surface tension with concentration of American (A) and Canadian (C) DF-250 [30].
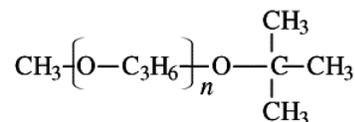
Fig. (12). Chemical structure of polypropylene glycol ethers [7].

$$R-O-\left(\begin{array}{c} CH-CH_2-OH \\ | \\ CH_3 \end{array}\right)_n$$

R = 4 to 6 carbon atoms
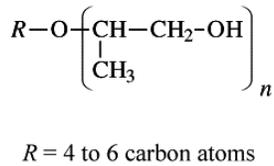
Fig. (13). Chemical structure of polyglycol glycerol ethers [7].

The second category is frothers containing the hydrophilic group OH. The OH group has strong hydrophilic properties and is very weakly-adsorbed on minerals (while the exception of coal and probably other naturally hydrophobic minerals). Therefore, frothers containing this group possess comparatively weak collecting action. The properties of different frothers containing OH group depend on the structure of the hydrophobic group, the number of OH groups in the molecule of frother and their disposition in relation to the hydrophilic portion. Phenols, terpineols, alcohols, alkoxy-type materials, and polypropylene glycol ethers are the main members of this category [33].

3.4. Selectivity/Frothing-Power Based Classification

Based on direct experimental observations in both batch laboratory and continuous large scale flotation cells, the use of a frother significantly increases first, the possibility of a particle-bubble contact, and second, the efficiency of sticking after such a contact. Thus, a major role of a frother is to significantly increase the rate of flotation [34]. With respect to this role, two terms of "selective" and "powerful" are used to characterize frothers. The former refers to the attachment of a hydrophobic particle to an air bubble, which can be used in flotation of very fine particles, whereas the latter which indicates the frothing capacity of the frother, will provide higher recoveries and better performance in floating of coarser particles [2,14,32].

There are two diagrams to characterize the selectivity and power of a frother. The first is the HLB-Molecular weight diagram (HLB stands for hydrophile-lipophile balance) shown in Fig. (**14**). As seen, the frothers which fall on the left side of this diagram are known to be selective in flotation, while the ones which are situated far to the right from this line are known to exhibit properties of strong flotation frothers [32].

Based on the laboratory experiences and literature findings broadly emerge that frothers belonging to alcohol and ketone family are selective for ultrafine particle size fraction and polyglycol frother and aldehyde are effective to float coarse fraction. Branched and water soluble alcohol and ketone molecules produce mono and finer bubble size which enhance the separation efficiency of finer particle size fraction. Polyglycol ether and aldehyde molecules are more sur-

face active and produce more stable and viscous froth compared to alcohol frothers, which leads the recovery of coarse particle size fraction of flotation feed. Therefore, it is difficult to use a single frother that will effectively give good overall flotation performance for wide particle size distributed flotation feed [35-37]. This suggests potential benefits of blending frothers for improved overall valuable recovery. For example, Laskowski *et al.* [38] tested a series of frother blends prepared by mixing MIBC with different polyoxypropylene alkyl ethers, including DF-200, DF-250 and DF-1012, through the determination of dynamic frothability index (DFI) and critical coalescence concentration (CCC), as will be discussed later. Table **7** shows CCC and DFI values for individual frothers and their blends. As seen, the blends shows better frothing behavior compared to MIBC but less effective than Dowfroth frothers.
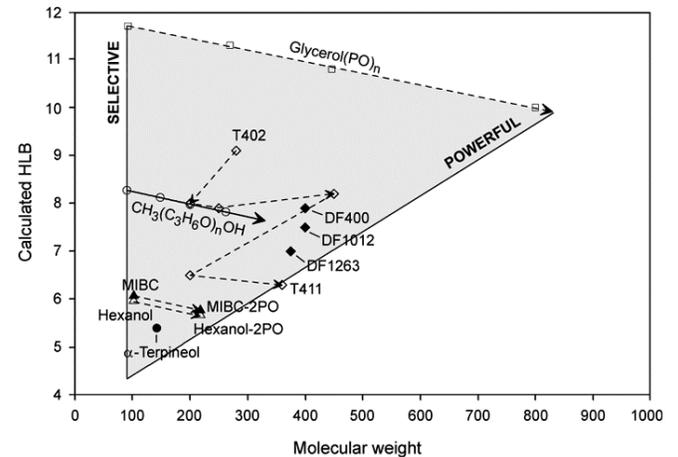

Fig. (14). The HLB-Molecular weight diagram for flotation frothers [32].

Gupta *et al.* [37] conducted a research program to determine the effects of the frother mixture on the froth flotation performance for a wide size distributed coal flotation feed. In this regard, three mixed frother systems were prepared as frother "x" composed of alcohol and ketone, frother "y" consisted of alcohol and aldehyde group chemicals, and frother "z" a blended product of alcohol and polyglycol ether. The following conclusions were drawn from their work:

- Alcohol and polyglycol ether mixed frother "z" was clearly superior compared to mixed frother "x" of alcohol and ketone and mixed frother "y" of alcohol and aldehyde in terms of selectivity and kinetics.

- In terms of ash reduction and recovery, frother "z" was efficient for coarse and ultrafine particle size fractions. It could be described by the presence of short chain alcohol

Table 6.   Physical and Chemical Properties of Polyglycol Glycerol Ether Frothers [14]

	Ave. Mw, g/mol	Specific Gravity	Viscosity at 25°C, cps	Solubility, g/l	Flash Point, °C
XK35004.00L	450	1.05	510	total	205
XK35004.01L	250	1.09	600	total	199
XK35004.02L	700	1.03	220	total	260

Table 7.   DFI and CCC Values for Individual Frothers and Their Blends Investigated by Laskowski *et al.* [38]

	Mole Fraction		CCC, mmol/dm^3	DFI, s.dm^3/mol
	MIBC	Dowfroth		
MIBC	1	–	0.11	34,000
MIBC/DF-200	0.56	0.44	0.094	106,000
MIBC/DF-250	0.78	0.22	0.067	108,000
MIBC/DF-1024	0.89	0.11	0.049	94,000
DF-200	–	1	0.089	196,000
DF-250	–	1	0.033	208,000
DF-1024	–	1	0.015	267,000

molecules (which is selective for ultrafine fraction; see Fig. (**14**)) and polyglycol ether molecules (which is stronger frother for coarse size fraction) in frother "z".

- Frother "z", which contains polyglycol ether and alcohol molecule, was more surface active in reducing the surface tension compared to other two frothers.

- Frother "z" was a more surface active and selective frothing chemical. Synergistic effects in flotation performance occurred with polyglycol ether and short chain alcohol mixed chemical system.

In the second diagram, dynamic frothability index (DFI) values are plotted versus critical coalescence concentration (CCC) values as shown in Fig. (**15**). Laskowski [32, 35] compared the DFI-CCC and HLB-Molecular weight diagrams and showed that the DFI-CCC diagram can be used to classify frothers. The frothers which are situated in the upper-left corner of the diagram are very powerful, while those situated in the bottom-right corner are selective. Table **8** shows the HLB, molecular weight, DFI, and CCC values of flotation frothers.
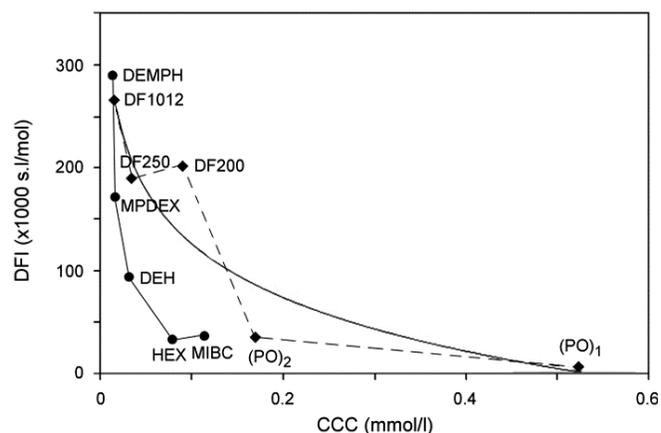

Fig. (15). Relationship between DFI and CCC values for flotation frothers [32].

4. NEW CLASSES OF FROTHERS

Although a new reagent might result in an increase mineral recovery of only about 1 percent over traditional rea-gents, this small improvement is of great economic importance for industrial operations that process thousands tones of ore daily. At such high throughput rates, relatively small improvements in mineral recovery can result in the production of significant additional tones of minerals daily. As is well known, the surface activity of any surfactant is determined by its chemical structure, and incorporating certain functional "group" or "atoms" into the molecular structure of the surfactant will strongly influence its properties [27]. In this regard, several investigators have tried to improve commercially used frothers, in both terms of selectivity and frothing-power.

Keys [43] introduced a new class of frothers which were actually a series of modified alcohol frothing agents, comprising at least one hydroxyl group. These modified frothers were selected from the groups consisting of:

- the reaction product of a C_5-C_{10} diol and a C_1-C_7 carboxylic acid in a ratio of one mole of carboxylic acid per mole of diol and having the predominant structure (**a**) in Fig. (**16**), in which *n* is 5-10 and *x* is 0-6;

- the reaction product of a C_5-C_{10} diol and acrylonitrile in a one to one mole ratio of acrylonitrile to diol such that the reaction product retains at least one hydroxyl group and having the predominant structure (**b**) in Fig. (**16**), in which *n* is 5-10 and *m* is 0-3;

- the reaction product of between about 1 and 10 moles of a C_2-C_3 alkylene oxide per mole of a C_1-C_7 carboxylic acid and having the predominant structure (**c**) in Fig. (**16**), in which *x* is 0-6, *y* is 2-3, and *z* is 1-10;

- the reaction product of a C_2-C_4 alkylene oxide and one mole of C_5-C_{10} diol having the predominant structure (**d**) in Fig. (**16**), in which *n* is 5-10, *y* is 2-3, and *z* is 1-10;

- the reaction product of a C_2-C_4 alkylene oxide and an acrylonitrile; and

- mixtures thereof.

Advantages of these modified alcohol frothers include excellent recovery yields of sulfide particles in the froth flotation and improved flotation kinetics of the particles for increased throughput of ore subjected to the process. Other advantages are the ability of these frothers to operate in harmony with sulfide collectors, and the ability to utilize lower

Table 8.   HLB, Molecular Weight, DFI, and CCC Values for Flotation Frothers

	Mw, g/mol	HLB	DFI, s.dm³/mol	CCC	
				mmol/l	**ppm**
Aliphatic alcohols:					
n-propanol	60.1	7.5[a]			
n-butanol	74.12	7[a]	1,339[b]		
n-butanol[*]	74.12	7[a]	1,271[b]		
2-butanol	74.12	7[a]	826[b]		
t-butanol	74.12	7[a]	1,588[b]		
n-pentanol	88.15	6.5[c]	5,517[b]		
n-hexanol	102.17	6[d]	33,779[b]		
n-heptanol	116.2	5.6[a]	40,867[b]		
n-octanol	130.23	5.1[c]	79,338[b]		
Isoamyl alcohol	88.17	6.5[a]			
MIBC	102.17	6[d]	34,000[f]; 35,020[g]; 36,991[b]; 37,000[h]	0.11[d]	11.2[f,h]; 11.5[e]
2-ethyl hexanol	116.23	5.6[a]	141,147[b]		
Diacetone alcohol	116.16	6.4[e]	12,000[b]		
TEXANOL	216.32				
Cyclic alcohols:					
α-terpineol	154.25	5.4[e]	137,988[g]; 138,000[h]; 138,901[b]		8[g]
Alkoxy paraffins:					
TEB	176.29	6.6[a]	252,589[b]		
Polyglycol ether:					
CH₃(C₃H₆O)OH	90.12	8.3[f]	5,700[f]	0.52[f]	46.8[f]
CH₃(C₃H₆O)₂OH	148.12	8.15[f]	35,000[f]	0.17[f]	25.1[f]
DF-200	206.29	8[f]	196,000[f]	0.089[f]	
DF-250	264.37	7.8[f]	208,000[f]	0.033[f]	
DF-1012	397.95	7.5[f]	267,000[f]	0.015[f]	
DF-400	395.61	9.9[i]			
DF-1400	366.56	10[a]			
DF-1263	336.53	7[e]			
PPG-192	192[j]	10.4[j]			
PPG-400	420[j]	9.8[j]			
PPG-725	762[j]	9.2[j]			
PPG-1000	950[j]	8.4[j]			
PPG-2000	1940[j]	5.6[j]			

[*] Test conducted in distilled water.
[a] Calculated by Davies equation
[b] Cho and Laskowski [39]
[c] Wang and Yoon [40]
[d] Laskowski [32]
[e] Rao [5]
[f] Laskowski [35]
[g] Gupta *et al*. [41]
[h] Melo and Laskowski [36]
[i] Pugh [42]
[j] Tan *et al*. [29]
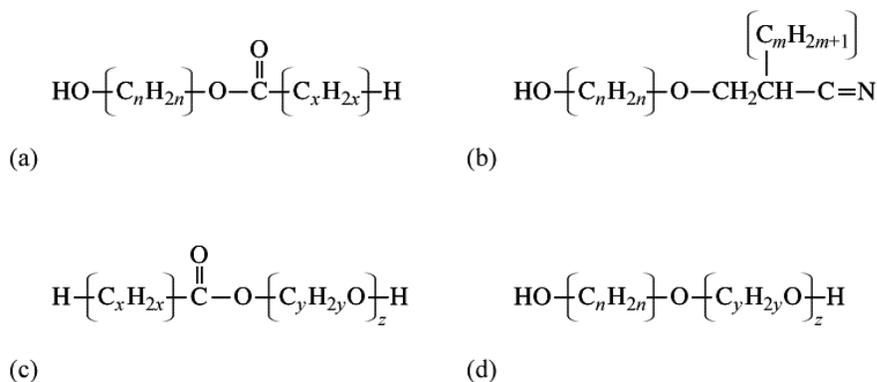
Fig. (16). Chemical structures of modified alcohol frothers [43].

dosages of them compared to conventional frothers while improving selectivity and kinetics in the flotation.

Biermann *et al.* [44] used derivatives of tricyclo-$(5.2.1.0^{2,6})$-dec-3-ene as frothers in the flotation of coal, cassiterite, and sulfide ores (Fig. **17**). These products were surprisingly found to have excellent properties as flotation frothers which make them at least equivalent and even superior to hitherto known flotation frothers. In addition, it has been found that not only are these derivatives compatible with the other constituents of the flotation pulps, a requirement which conventional frothers have to satisfy, they also have a positive effect on the influence of the collector in the flotation pulp, i.e. they enhance or boost the collector effect, and are thus able to contribute toward reducing the quantity in which the compounds added as collectors are used.

Derivatives of tricyclo-$(5.2.1.0^{2,6})$-dec-3-ene have general structure (**a**) shown in Fig. (**17**). In this structure R^1 is hydrogen or a linear or branched C_1-C_8 alkyl radical, such as methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, 2-butyl, *t*-butyl, *n*-pentyl, *n*-hexyl, *n*-heptyl, or *n*-octyl, and isomers thereof. Preferred alkyl radicals are C_1-C_4 alkyl radical. Particularly good frother results are obtained where R^1 is an ethyl radical. R^1 can be an acyl radical of the formula R^2–CO– where R^2 is hydrogen or a linear or branched C_1-C_{18} alkyl or alkenyl radical, such as ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, or octadecyl. R^1 can even

be a hydroxyalkyl radical of the general structure (**b**) (Fig. **17**), in which R^3 and R^4 independently of one another are hydrogen or hydroxyl group, and *m* and *n* are integers of 0 to 5 and the sum $(m+n)$ is an integer of 1 to 5, with the proviso that at least one of the substituents R^3 and R^4 is a hydroxyl group, and/or of mixtures of several isomeric derivatives (structure (**a**)) as frothers in the flotation processes.

Esters of general structure (**a**), in which R^1 has the meaning R^2–CO–, are prepared by reaction of dicyclopentadiene (or tricyclo-$(5.2.1.0^{2,6})$-dec-3,8-diene) corresponding to the structure (**c**) in Fig. (**17**), with carboxylic acids corresponding to the general formula R^2COOH, in which R^2 is as defined above, in the presence of catalytic quantities of mineral acids. Reactants for the dicyclopentadiene are preferably C_1-C_6 carboxylic acids, such as acetic acid, propionic acid or caproic acid, or fatty acids obtainable from natural fats and oils by ester cleavage, preferably lauric acid or oleic acid. Ethers corresponding to structure (**a**), in which R^1 is an alkyl or hydroxyalkyl radical are synthesized by reaction of dicyclopentadiene with monohydric or polyhydric alcohols corresponding to the formula R^1OH or structure (**d**) (Fig. **17**), in which R^1, R^3, R^4, *m* and *n* are as defined above. The monohydric alcohols preferably used contain a C_1-C_4 alkyl radical as the radical R^1. Although it is of particular advantage to use ethanol, polyhydric alcohols may also used for the reaction with dicyclopentadiene. Ethanediol and glycerol are representatives of the polyhydric alcohols particularly suit-
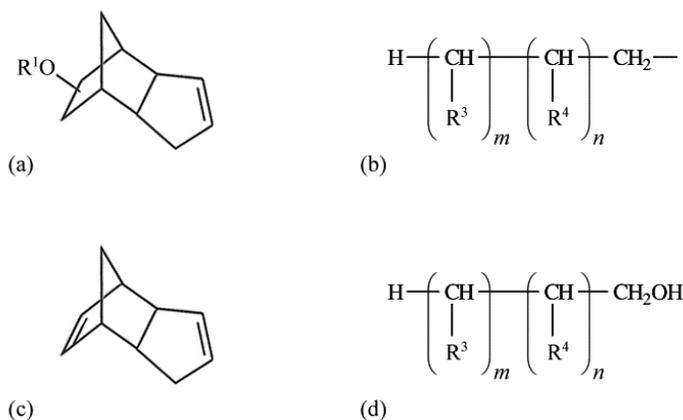

Fig. (17). General structures of derivatives of tricyclo-$(5.2.1.0^{2,6})$-dec-3-ene (**a,b**) and their source chemicals (**c,d**) [44].

able for this purpose. The reaction of dicyclopentadiene with mineral acids alone, such as HCl and H_2SO_4, gives 8(9)-hydroxytricyclo-(5.2.1.0^{2,6})-dec-3-ene, i.e. the compound of general structure (**a**) in which R^1 is hydrogen. This reaction is normally carried out at temperatures in the range of from 20^oC to 150^oC, preferably 40-60^oC, optionally in an organic solvent, such as aliphatic or aromatic hydrocarbons, more especially toluene or xylene or mixtures thereof.

Flotation tests of coal and ores showed that the esters, i.e. compounds in which R^1 is R^2–CO–, show slightly better frother properties than the corresponding ethers, i.e. compounds in which R^1 is alkyl or hydroxyalkyl. Compared with standard flotation frothers, for example 2-ethyl hexanol, a much higher recovery of coal or ores was achieved. In the flotation of coal, there was considerably less residual ash in the concentrate. Accordingly, the selectivity of these derivatives was very good and had a boosting effect on a number of collectors of the type normally used in flotation processes. The result of this booster effect was that the quantities in which the compounds added as collectors were used might be distinctly reduced.

Klimpel and Isherwood [45] have been studied a new class of frothers of general chemical formula, ROH.*n* alkylene oxide units with R in the range 4-6. These frothers are adducts of propylene oxide or butylene oxide, and aliphatic alcohols, such as hexanol•$(C_3H_6O)_2$, methyl pentanol•$(C_3H_6O)_2$, and MIBC•$(C_3H_6O)_2$. The frothers of this family extend the coarse particle range from 20 to 200 μm, but at the expense of recovering fine particles. This makes it desirable to use appropriate blend of frothers of specific chemical structures to give the broadest particle size range recovery. In addition to the increase in coarse particle recovery demonstrated by the alcohol-propylene oxide combination over the same alcohol alone, increasing the branching of the alcohol backbone gradually decreases the effective particle size range floated by the frother-collector combination. A highly branched trihydric alcohol, glycerol, reacted with propylene oxide is a more effective fine particle frother than any of the alcohols alone [5].

Rasheed [46] introduced a series of sulfonates modified by adding an *n*-ethylene oxide chain to the aromatic base, as shown in Fig. (**18**) (**b,c**). The reaction of an ethoxylated alkyl phenol of the formula R–Ph–O$(CH_2CH_2O)_n$H wherein R is a straight or branched alkyl group containing 8-12 carbon atoms, n is 6-10, Ph denotes a phenyl ring and the substituents thereon are in the para-position, with sulfur trioxide forms an intermediate of structure (**a**). By the reaction of this intermediate product with a hydroxide of the formula M–OH

wherein M is lithium, sodium, potassium or ammonium, products of structure (**b**) is formed. Structure (**c**) is obtained by desulfurization of the intermediate (structure (**a**)) through heating the reaction of the intermediate with hydroxide to about 20^oC to 150^oC, preferably about 60^oC. In the presence of tall oil fatty acids as collectors, these frothers gave desirable results in phosphate flotation.

Harris and Jia [27] introduced a new class of frothers by adding a sulfur atom to polyalkoxylated molecule of various configurations. They showed that these frothers increased metal recovery, both copper and molybdenum, in the flotation of porphyry ores. Table **9** shows the chemical structure and flotation results of these frothers, and MIBC and oxygen-bearing polypropylene for comparison purposes.

Recently, Cappuccitti and Finch [47] developed a new class of frothers resulting from the reaction of aliphatic alcohol C_1 (methanol) to C_4 (butanol) and mixtures thereof with between 0.2 moles and 5 moles of ethylene oxide. These ethoxylated alcohols correspond generally to the formula R_1–O–$(CH_2CH_2O)_n$H, where, R_1 is a straight or branched chain, C_1 to C_4 alkyl radical and n is between 0.2 to 5. These frothers have their own set of hydrodynamic and froth properties that depend on the amount of ethylene oxide reacted with the alcohol. The testing of the new frother chemistries led to identifying ethoxylated butanols (ButOH–nEO, n=1.5, 2, 3) as potential equivalents to MIBC. Ethoxylated butanols offered a range of properties; by changing the number of ethoxy groups products could be made slightly weaker (for n=1.5) or stronger (for n=2 and 3) than MIBC but the chemistry could not provide hydrodynamic/froth characteristics similar to frothers like glycols and glycol ethers.

5. BIOFROTHERS

There are two uses of microorganisms in mineral processing: (1) bioleaching, a long-established technique, in which microorganisms assist in the dissolution of metallic ions for metal recovery from ores; and (2) biobeneficiation, in which microorganisms act as surface modifiers, depressants, collectors or dispersing agents to enhance the separation of minerals by either flotation or flocculation [48].

The use of microorganisms in bioflotation processes was first studied by Solojenleen (1976) who announced the possibility of flotation of ores in the presence of sulphate reducing bacteria (SRB) [49]. Solozhenkin and Lyubavina [50] showed that flotation of cerussite was improved by 20-25 percent after pretreatment with SRB. Zajic and Kosaric [51] used a mixture of *Pseudomonas* and *Alcaligenes* as collectors for flotation of scheelite from calcite. *Mycobacterium*
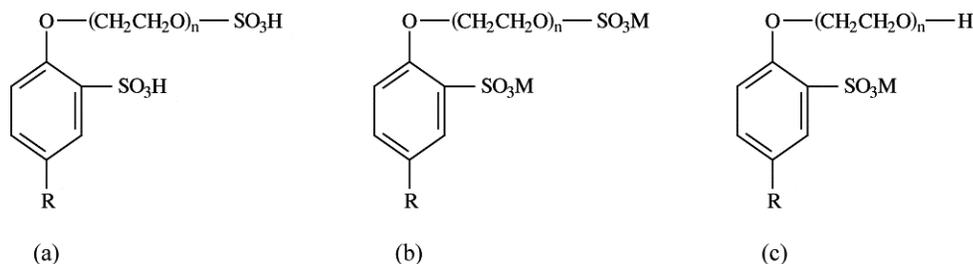
Fig. (18). Chemical structures of modified sulfonates [46].

Table 9.   Formula and Flotation Results of Modified Sulfur-Bearing Frothers [27]

	HLB	Frother Dosage, Kg/Tone	% Cu Recovery	% Mo Recovery
MIBC	6.1	0.105	75.28	72.66
$CH_3S(PO)_5H$	4.4	0.074	76.42	73.58
$CH_2S(PO)_{2.7}H$	1.9	0.110	76.45	74.51
$H(PO)_Xsc_2h_4s(PO)_yh$, X+Y~4	2.7	0.110	77.86	73.55
$CH_3S(PO)_3(BO)H$	4.1	0.099	78.38	78.68
$CH_3S(EO)(PO)_4H$	4.9	0.099	77.81	77.16
$C_4H_9S(EO)(PO)_4H$	3.7	0.084	76.72	72.92
$H(PO)_Xs(PO)_yh$, X+Y~4	5	0.125	76.73	74.64
$H(PO)_Xs(PO)_yh$, X+Y~5	4.9	0.090	77.13	73.81
$H(PO)_Xs(PO)_yh$, X+Y~6	4.7	0.092	78.61	78.39

(EO) : $-CH_2CH_2O-$, (PO) : $-CH_2(CH_3)CHO-$, (BO) : $-CH_2CH_2(CH_3)CHO-$

phlei cells have been used as flotation collectors for hematite [52,53] and as flotation depressants in the anionic flotation of apatite and dolomite [54]. Zheng *et al.* [55] used *Mycobacterium phlei* and *Bacillus subtilis* in order to dolomite depression in anionic flotation. Miettinen *et al.* [56,57] showed that in anionic flotation of apatite and calcite *Staphylococcus carnosus* functions as a depressant for apatite, but as an activator for calcite while freeze dried *Staphylococcus carnosus* can work as a collector for both apatite and calcite. *Staphylococcus carnosus* and *Bacillus firmus* were found to work as collectors for apatite [58]. *Acidithiobacillus ferrooxidans* have been used as cinnabar depressant in cinnabar and antimonite flotation by Lyalikova and Lyubarina [59], and as galena depressant in galena and sphalerite flotation by Rao *et al.* [60,61]. This bacterium has also been used in removing pyrite from mixtures of sulfide minerals [62-65]. *Acidithiobacillus ferrooxidans* have frequently been used as an excellent pyrite depressant in coal flotation [66-69]. *Bacillus polymyxa* was used in the separation of sulfide minerals [70], iron ore flotation [71], for pyrite separation from oxide gangue minerals [72], and in the separation of galena from chalcopyrite [73]. Mesquita *et al.* [74] used *Rhodococcus opacus* as hematite collector in hematite-quartz flotation. This bacterium was later used as a collector of calcite and magnesite by Botero *et al.* [75]. Farahat *et al.* [48] found that *Escherichia coli* can well work as a collector for quartz.

Two points emerging from these works are:

- All researches have focused on using microorganisms as mineral surface modifiers whereas air phase is as important as solid phase;

- Although there is rather a large body of literature on the direct use of microorganisms in flotation, no attention has been made to the use of microbial products in flotation.

It is well known that some microorganisms are able to produce surface-active compounds that can vary in their chemical structure and size. Since the last decade of the past century the concern about environmental protection has lead to an increased interest in the production and properties of these natural products. These surfactants, often called microbial surfactants or biosurfactants, are considered nowadays as potential substitutes of synthetic chemicals from petrochemical origin. The main advantages of biosurfactants over their chemical counterparts are their lower toxicity, better environmental compatibility, biodegradability, and effectiveness in a wide range of temperatures and pH. Last, but not least, their production by renewable resources provides further impetus for serious consideration of biological surfactants as possible alternatives of the commonly used industrial chemicals. The achievements of the microbial production of biosurfactants and various aspects concerning their potential commercial application regarding bioremediation of soils polluted with heavy metals are well documented and summarized in a number of reviews [76,77].

Among the various species of biosurfactants much work has been done on rhamnose containing microbial surfactants produced by *Pseudomonas aeruginosa* strains. This ubiquitous environmental bacterium can be isolated from many different habitats including water, soil and plants. These Rhamnolipids produced by *P. aeruginosa* microorganisms are usually as a mixture of two or four species. They differ by the length of hydrophobic chains (from C_8 to C_{12}) some of which are unsaturated with one double bond. However, under usual growth conditions, two main homologues are primarily obtained: monorhamnolipid (RL-1) and dirhamnolipid (RL-2), as shown in Fig. (**19**). Numerous articles have considered the process of microbial cultivation of rhamnolipid type biosurfactants on different substrates and their properties in terms of film thickness and wettability.

The first investigation on using these biosurfactants in flotation of coal and minerals was done by Fazaelipoor *et al.* [79]. They studied frothing characteristics and flotation applicability of rhamnolipid type biosurfactants as frother. These biosurfactants showed better surface-activity and static frothability, i.e. frother height and half-life, in comparison with MIBC. Fig. (**20**) compares surface tension values from the biosurfactant and MIBC. The results indicate the better ability of the biosurfactant to reduce surface

tension of water compared to MIBC. The height of froth was measured as a function of aeration rate at two different surfactant concentrations. Fig. (**21**) shows the results. The biosurfactant produced higher froth heights compared to MIBC.

(a)

(b)
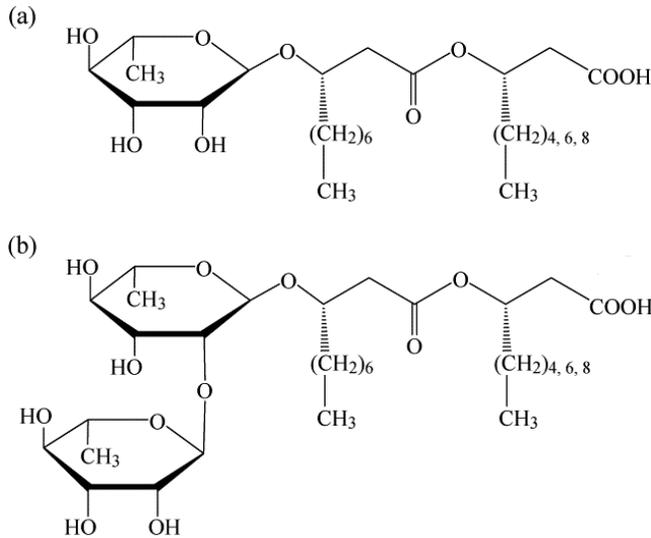
Fig. (19). Monorhamnolipid (RL-1) (**a**) and dirhamnolipid (RL-2) (**b**) produced from *Pseudomonas aeruginosa* bacteria [78].
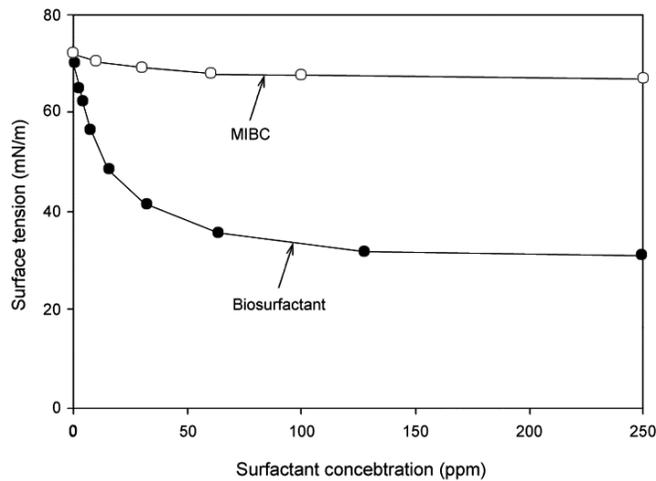
Fig. (20). Comparison of the biosurfactant and MIBC in reducing surface tension of distilled water [79].

There might be two responsible reasons for these results. First, rhamnolipid biosurfactant has a much higher molecular weight (>438 g/mol, depending on the RL-1 and RL-2 ratio) compared to MIBC and this higher molecular weight leads to a more viscous, and hence more stable, froth layer. Second, there is only one –OH group in MIBC and this group will interact with water molecules to form an oriented monolayer at the surface; but in biosurfactant, there are several oxygenated units in the molecular chain and each unit can interact with water molecules through hydrogen bonding, causing the molecules to tend to lie flat at the surface, possibly increasing the viscosity of the froth.
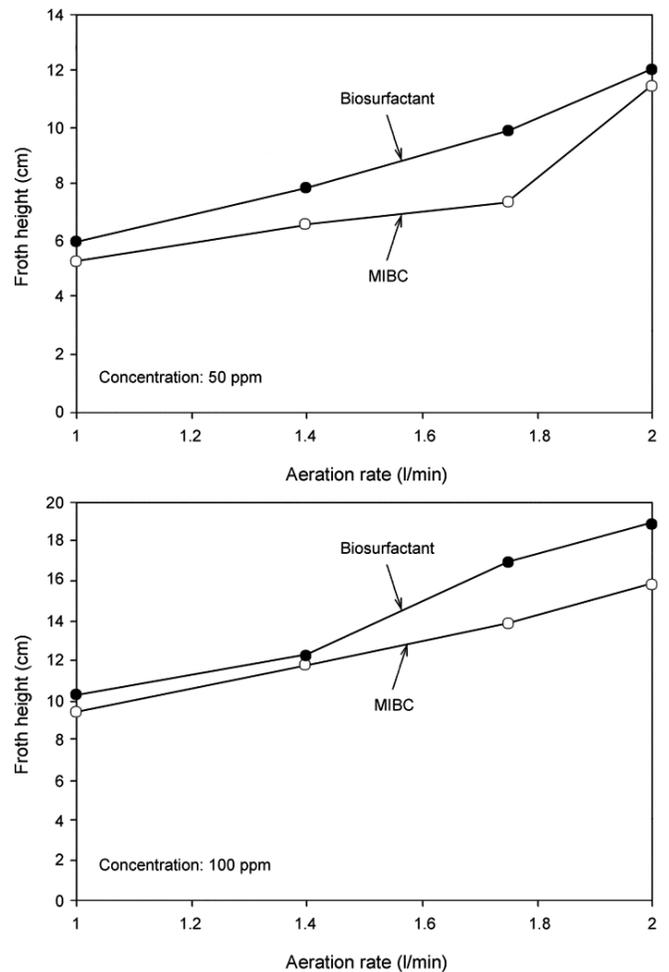
Fig. (21). Froth height as a function of aeration rate [79].

Fig. (**22**) shows the froth half-life values for both surfactants. The results indicate that at the lower concentration MIBC produces more stable froth, while at higher concentration the reverse is true. It seems that at lower concentration the interfacial adsorption density of biosurfactant is less than MIBC due to greater structural and atomic dimensions. At higher concentration the adsorption density of biosurfactant increases by multi-layer adsorption mechanism because of free oxygen and multiple –OH groups.

Coal flotation tests using rhamnolipid biosurfactants as the sole frother of the process yielded products of 72-79 percent recovery with 10-15.5 percent ash content supporting 55-57.5 percent efficiency. These results seem to be promising to introduce rhamnolipid type biosurfactants as a new "biofrother". Rhamnolipids are commercially available from Jeneil Biosurfactant Company, Saukville, Wisconsin, USA, and Urumqi Unite Bio-Technology Co., Ltd., China.

6. SUMMARY

The literature review presented in this article tried to prepare an updated, comprehensive database of frothers regarding to their classifications, properties, and a brief description of their preparation methods. As a summary, the following general remarks can be denoted:
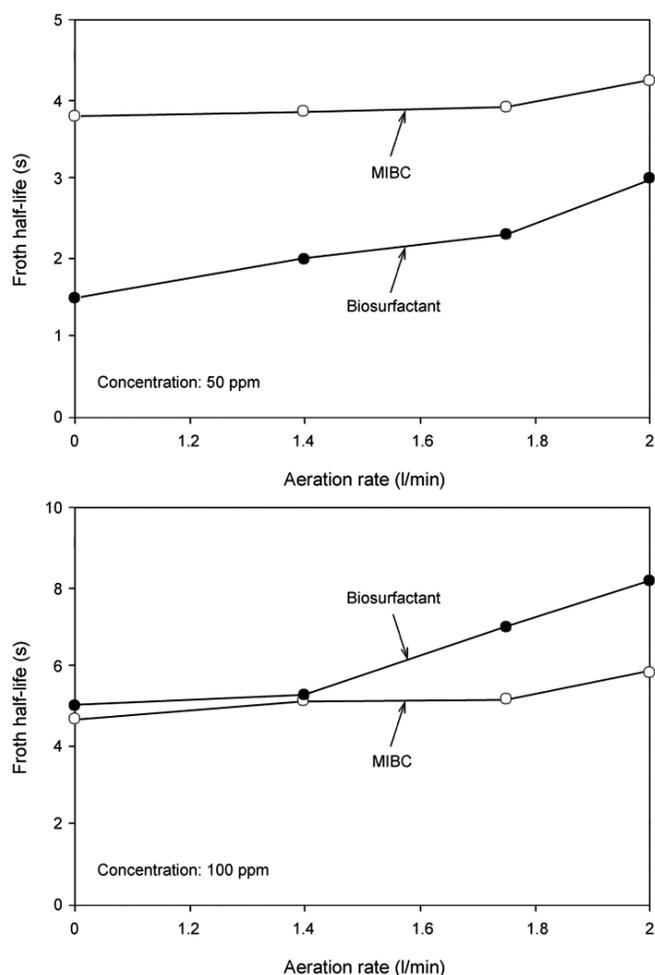
Fig. (22). Froth half-life as a function of aeration rate [79].

- Neutral frothers, specially aliphatic alcohol and ether types, are the most important group of frothers widely used in flotation of base-metal ores, oxidic minerals and industrial minerals, since they are functional in both acidic and alkaline pulps.

- From the practical point of view, the most important characteristics of frothers are molecular weight (Mw), hydrophile-lipophile balance (HLB), dynamic frothability index (DFI), and critical coalescence concentration (CCC). Available data on these parameters were listed in Table **8**, having yet some blank cells which necessitate more researches in this regard.

- Considering selectivity/frothing-power based classification, different mixed frother systems, usually mixtures of aliphatic alcohol and ether frothers are used to support an efficient flotation operation, a wide size distributed feed.

- Different new classes of frothers discussed in this review are actually conventional frothers modified by incorporating certain functional group, specially polyalkoxylated molecules, or atoms into their molecular structure.

- Like particle surface modifiers, frothers are also influenced by biotechnology, leading to introduce a new class of biological frothers, i.e. biosurfactants, so called as "biofrother". A comprehensive research program is being

investigated by the authors to characterize frothing properties and coal and ores flotation applicability of such a biofrother.

ACKNOWLEDEMENT

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