Frother Characterization with Two-Phase Foam System

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Abstract

This paper evaluates frother performance by studying two-phase gas-liquid system. Surface tension, foamability, foam stability and bubble size distribution are measured as a function of frother type, frother dosage, and solution pH. Variation of bubble size with respect to frother concentration is used for predicting the critical coalescence concentration (CCC) of selected alcohol and polyglycol ether family frothers. An inverse relationship is found between critical coalescence concentration and dynamic foamability index (DFI). Df-1012 and PPG are found to be more powerful in terms of stability, foamability and CCC than frothers belonging to alcohol family. Frother effectiveness is found to be relatively better in alkaline pH.

Keywords: *flotation frothers; bubble size; critical coalescence concentration; dynamic foamability index; frother dosage; retention time.*

INTRODUCTION

Coal and coke are the basic energy source as well as reductant for iron and steel making operation. Quality of the coke determines the blast furnace productivity. Low ash metallurgical coal is needed to produce high fuel capacity and porous coke.

Tata Steel coal wahsery treats around 4 million tonnes of coking coal to produce about 2 million tonnes of clean coal having 16% ash. Fine fraction (< 0.5 mm), which is around 20% of the feed to the washery, is treated in the flotation circuit and the rest in the coarse concentrate circuit using dense medium cyclones. The average ash content of the feed, the fine clean coal and the tailings of the flotation circuit are 25, 15 and 38 % respectively. Yield of clean coal from the flotation circuit is about 50%. Although the overall performance of the washery is satisfactory, there is a plenty of scope to improve the recovery and grade of the clean coal. In plant, high-speed diesel (HSD) oil is used as flotation collector for increasing the hydrophobicity and Nalco 8586 as a frothing agent.

The major role of a frother is to provide a stable froth phase, which enables the separation of hydrophobic component from the pulp phase during flotation process. Froth stability depends upon the formation of a froth of relatively consistent character (bubble size and bubble density), the ability to disperse air in the flotation cell, the rate of coalescence of individual bubbles in the cell, and bubble rise velocity to pulp surface.

A successful frother must allow sufficient thinning of the liquid film between the colliding bubble and the particle so that attachment can take place in the time frame of the collision. Thinner liquid film enhances the bubble-particle attachment during collision process but it also increases the bubble-bubble coalescence. Thus a successful frother must achieve a delicate balance between these two competing processes and provide sufficient stability of the bubble/particles moiety and yet allow the

weakly adhering or mechanically trapped particles of unwanted materials to escape with the draining liquid (Laskowski, 2003; Laskowski et al., 2003). Gravity is the main driving force for the drainage in froth phase. The surface gradient along the air/water interface creates the Gibbs-Marangoni effect that acts to retain the film thickness and prevent bubble coalescence. The structure of foams changes with time – on thinning to about 100 nm or less it takes the shape of polyhedrons meeting at 120 degrees at the junction points (Pugh, 2005). The froth stability also depends on, (a) particle size (finer particles stabilize froth) (b) wetting characteristics (particles having contact angle less than 90 degree stabilize froth) (c) shape of particles (Cho and Laskowski, 2002 and Tan et al., 2005a, b).

A common feature of most commercial frothers is their heteropolar nature consisting of nonionic polar group exhibiting hydrophilic character coupled with a hydrophobic nonpolar hydrocarbon chain. This nonionic or neutral character is usually associated with molecules of sufficiently small size so that multiple van der Waals bonding does not occur in the nonpolar portion of the molecule, giving rise to excessively stable froths. It is generally accepted that adding a surface-active agent to water lowers the surface tension of the solution due to heteropolar nature of the reagent molecules. Thus, the surface tension of a solution is an indication of the activity of a frother. Frothers that strongly lower the surface tension produce more stable froths (Klimpel and Hansen, 1988).

While the above conceptual picture is qualitatively correct, the use of surface tension measurements alone to screen frothers for application in flotation is limited. This is due in part to the highly dynamic nature of the froth, especially in the presence of particles and turbulence. The science underlying frother selection and design is not clearly understood. There are general guidelines for this purpose, available in the literature:

- The stability of the froth formed must be such that a further degree of separation of the valuable mineral from the non-floatable (entrained) components is achieved in the froth.
- Once the froth containing the valuable component is removed, it must break readily for further treatment.
- The frother must assist formation of a froth of sufficient volume and stability to act as a medium of separation at low concentrations.
- In case of neutral frother it must have limited collecting properties otherwise it may lead to loss in selectivity.
- It must possess a low sensitivity to changes in pH and dissolved salt concentrations.
- It must be readily dispersible (although not necessarily readily soluble) in the aqueous medium. Frothers can also be added as emulsions.
- It should be relatively inexpensive and abundant for large-scale use.

The prime objective of this study is to characterize different families of frothers based on measurement on two-phase foam system. The following standard techniques have been used to characterize the foaming properties of reagents:

- Surface tension of frother solution
- Foam volume as a function of gas flow rate
- Foam retention time
- Bubble size distribution

MATERIAL AND METHODS

Frothers

Total eight frothers were selected for detailed characterization study in gas-liquid system, which are shown in Table 1.

Table 1: Frothers Samples Selected for the Investigation

Frother family	Name	Chemical formula	Molecular weight	Code
Aliphatic Alcohols	Methyl iso-butyl carbinol		102	MIBC
	2-ethyl hexanol	$CH_3 - CH - CH_2 - CH - CH_3$ CH_3 OH	130	2-et - Hexanol
Cyclic Alcohols	α-terpineol	$CH_3 - CH_2 - CH_2 - CH_2 - CH - CH_2 - OH$ $CH_2 - CH_3$ $CH_3 - CH - CH - C - CH_2 - O - C - CH$	148	Alpha-TP
	Commercial pine oils	Active component: α-terpineol		Pine-C
	Dow froth	$CH_3 (C_3H_6O)_{6.3} OH$	398	DF1012
	Synthetic analytical reagents	$C_7H_{18}O_3$	340	PPG

Methods

Surface Tension

Effect of frother type and concentration on surface tension of water was studied using the Fisher surface Tensiomat, model 21, which is based on the du Nouy method. Frother dosages studied were 5, 15, 30, 50 & 100 ppm.

Foamability and Retention Time

A schematic of the experiment set-up is shown in Fig. 1, which is designed for the measurement of foamability and retention time for all the frother samples. A graduated glass burette of 50 cm height and 1.5 cm diameter is fitted with a glass frit at the bottom and connected to a mercury manometer and air compressor. Experiments were carried out by taking a known volume (15ml) of the reagent solution in the burette and passing nitrogen gas/air to the solution at a fixed flow rate and time period. The increase in the height of the solution as a result of the foam generated by the gas was noted. Since the cross sectional area of the burette is identical in all the tests, the volume of the foam is proportional to the difference in the heights of the solution with and without gas. This difference in height is defined as the foam height. It is a measure of the volume of the foam generated by the gas at a fixed flow rate for a given reagent. Retention time at each airflow rate is measured by stopping air during frothing stage and measuring the time taken by the foam to collapse.

Foamability and retention time have been studied for characterizing the eight frothers as a function of pH, frother dosage and airflow rate. Ranges of parameters are studied as follow:

- Frother dosage: 5, 15, 30, 50 & 100 ppm
- Air flow rate: 10-70 cc/min.
- Solution pH: 3, 7 & 9

Fig. 1: Schematic Diagram of Experimental Setup for Frothability Tests

Bubble Size Distribution:

Foam phase bubble images were captured using a CCD camera, which is connected to a personal computer where the visual information is stored and processed. The same experimental set-up that is shown in Fig. 1 is used for imaging bubbles. Bubbles were generated by passing air at 30 cc/min. Bubble images of all the eight frothers were captured and analyzed by taking five different frother concentration 5, 15, 30, 50 and 100 ppm. These images were analyzed for bubble size distribution manually.

The effect of frothers on bubble size has recently been studied (Comely et al., 2002; Grau et al., 2005). It was found that the effect of frothers on bubble size results from their ability to prevent bubble coalescence. On increasing the frother concentration, the degree of bubble coalescence decrease and at a particular concentration (Critical coalescence concentration, CCC), the coalescence of the bubbles is completely prevented. Further increase of the frother concentration above the CCC value does not affect the bubble size. The primary factors that determine bubble size include the following: bubble generating system (its geometry and hydrodynamics) and superficial gas flow rate. The secondary factor, which practically may be more important that the primary ones, bubble coalescence that is determined by frother concentration.
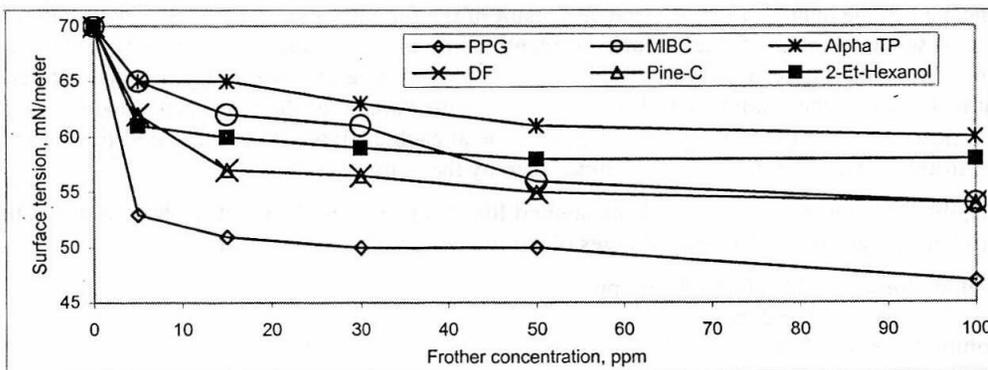
Fig. 2: Surface Tension of Water as a Function of Frother Concentration

RESULTS AND DISCUSSION

Surface Tension

Fig. 2 shows the change in surface tension of water with respect to variation in frother concentration for all eight frothers. Frothers belonging to the polyglycol family showing more surface activity compare to alcohol family frothers. The order of surface activity is given below:

PPG > DF > Pine-C ≈ MIBC > 2-et-Hexanol > Alpha-TP

Frothability/Foamability

Effect of Frother Concentration

A typical plot of foam height vs. airflow rate at 5 ppm and 100 ppm concentration of various frothers are presented in Figs. 3 & 4 respectively. The airflow rate was varied from 10-70 ml/min. There is a linear relationship observed between the foam height (same as foam volume since the cross-section area of the burette is constant) and airflow rate at each concentration of all eight frothers.
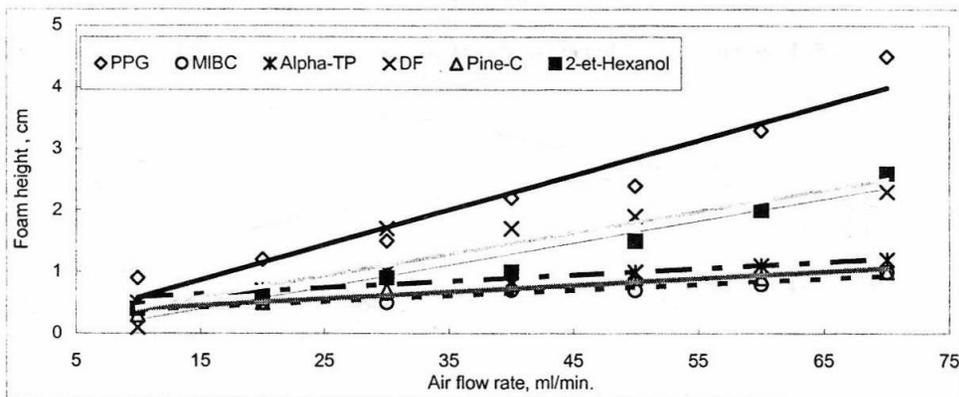
Fig. 3: Foam Height as a Function of Airflow Rate at 5-ppm Frother Concentration
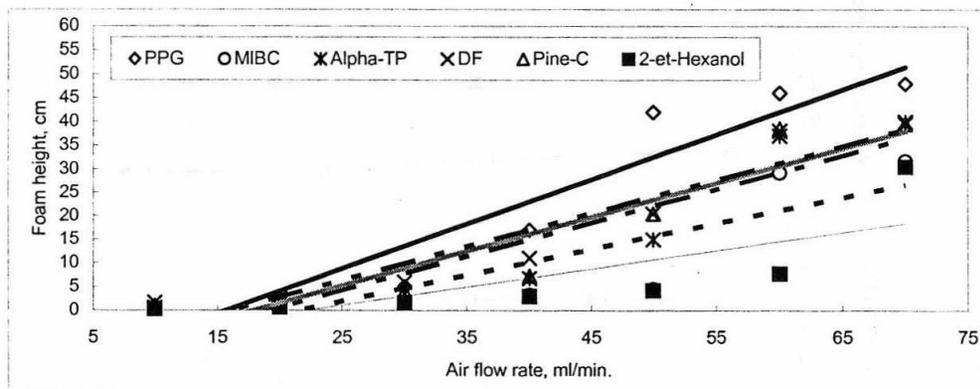
Fig. 4: Foam Height as a Function of Airflow Rate at 100-ppm Frother Concentration

The slope of the foam height vs. airflow rate curve is defined as the foamability of the reagent. This parameter is used as a measure of the intrinsic frothing characteristics of the reagent. The slope of such figures (Figs 3-4) was determined at different frother concentrations. The foamabilities for all frothers are shown in Fig. 5 as a function of frother concentration. The relative frother efficiency in term of foamability is given below:

PPG ≈ Alpha-TP > DF ≈ Texanol ≈ Pine-C > NALCO > MIBC > 2-et-Hexanol
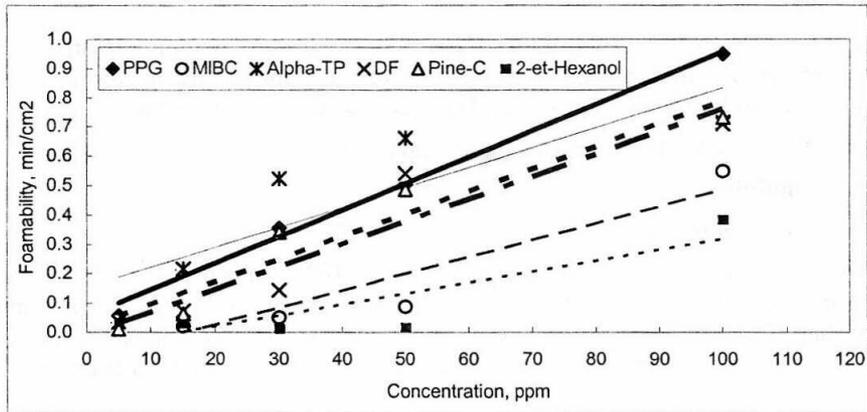
Fig. 5: Foamability As a Function of Frother Concentration for All Frothers
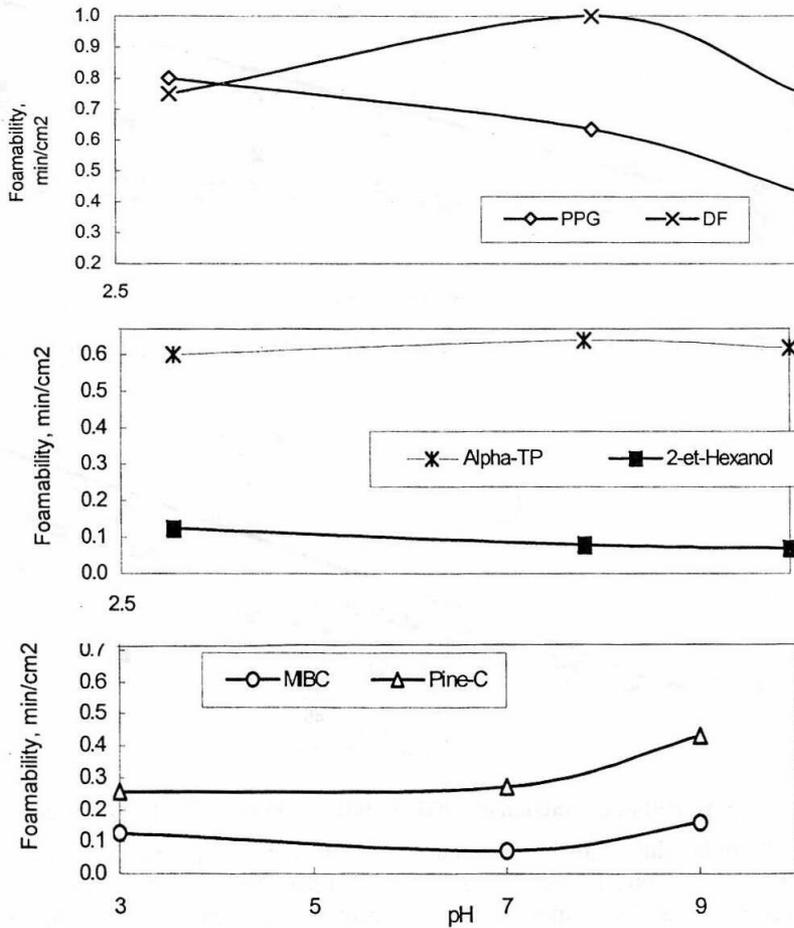
Fig. 6: Effect of pH on Foamability at 50-ppm Frother Dosage

284

Effect of pH

The effect of pH on foamability of frothers belonging to polyglycol ether and alcohol family at 50 ppm dosage is illustrated in Fig. 6. It is clear from Fig. 6 that synthetic frothers belonging to polyglycol ether family namely PPG and DF are most effective at neutral pH with respect to foamability in two-phase systems. Alpha-TP and 2-et-Hexanol do not exhibit any sensitivity to pH and MIBC and Pine-C tend to foam better at alkaline pH. Effect of pH on foamability of different frothers is summarized below:

PPG & DF	Alpha-TP & 2-ethyl hexanol	MIBC & Pine-C
Most effective in neutral pH	Not sensitive to pH	Most effective in alkaline pH

Foam Stability (Retention Time)

Effect of Frother Concentration

The stability of foam of a particular frother solution was measured in the same apparatus under identical conditions as a function of flow rate. The retention time is the time taken by foam to collapse completely after stopping the airflow. Typical plots of retention time vs. airflow rate at frother dosages of 5 ppm and 100 ppm for all frothers are shown in Figs. 7-8. Retention time reaches a plateau with respect to the airflow rate. The retention time value at plateau was taken as the measure of the stability of foam. DF-1012 frother exhibits extraordinarily high retention time, that is, foam is more stable with DF frother. It is interesting to note that foams produced in presence of 2-et-Hexanol are found to be as brittle as those produced by MIBC and Pine-C.
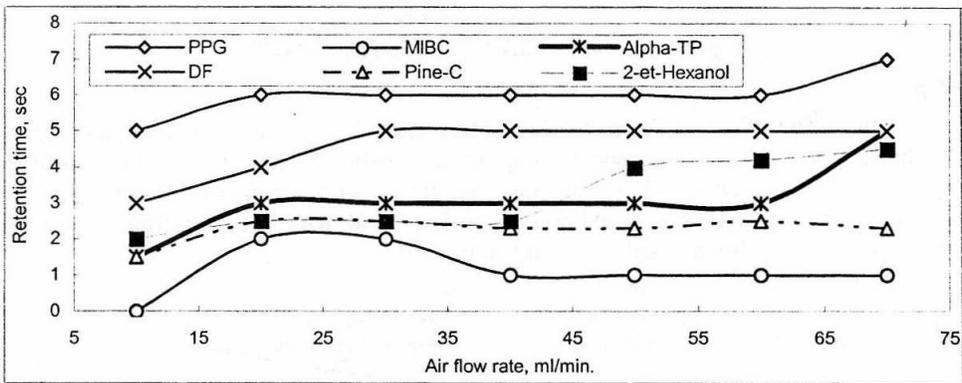
Fig. 7: Retention Time as a Function of Airflow Rate at 5 ppm Frother Dosage
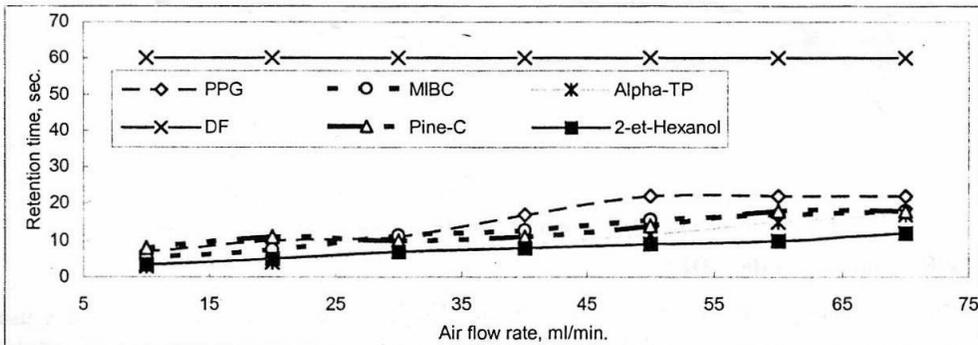
Fig. 8: Retention Time as a Function of Airflow Rate at 100 ppm Frother Dosage

Retention time at plateau (foam stability) is plotted as a function of concentration for each frother, which is shown in Fig. 9. It shows that DF-1012 and Texanol are found to produce more stable foams.

The relative frother efficiency in term of foam stability is given below in decreasing order:

DF >> PPG > MIBC ≈ Pine-C ≈ alpha-TP > 2-et-Hexanol
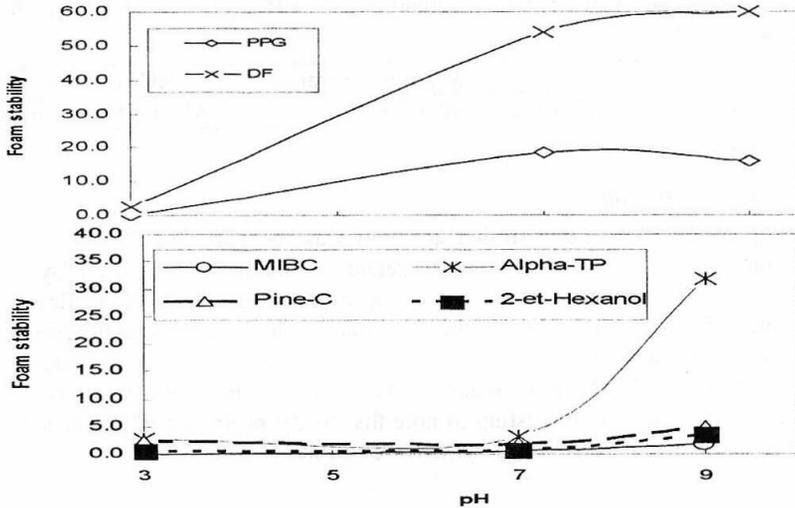
Fig. 9: Effect of Frother Dosage on Foam Stability

Effect of pH

Fig. 10 shows the effect of pH on foam stability of frothers belonging to polyglycol ether and alcohol family. It shows that foam stability tends to improve at alkaline pH and follow the plateau trend at alkaline pH for PPG and DF-1012. It indicates that frothers belonging to alcohol family (MIBC, alpha-TP, Pine-C and 2-et-Hexanol) exhibit increasing trend with pH. All frothers are showing improvement in foam stability at alkaline pH of solution.
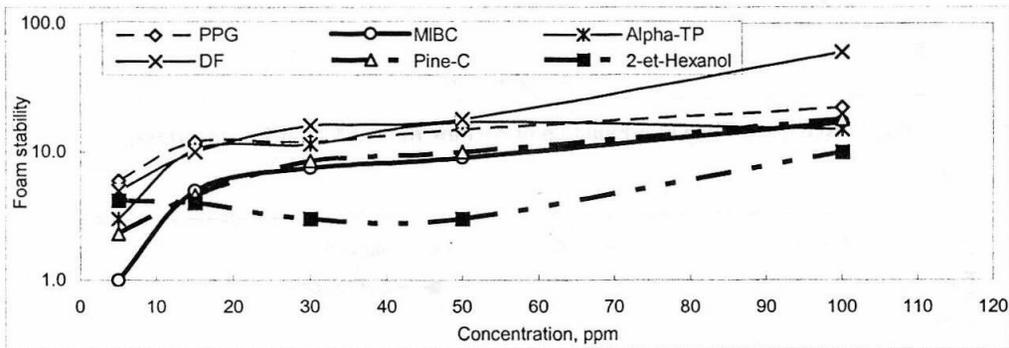
Fig. 10: Effect of pH on Foam Stability at 50-ppm Frother Dosage

Dynamic Foamability Index (DFI)

Many authors (Czarnecki et al., 1982; Malysa et al., 1987; Laskowski et al., 2003b) have used an index called dynamic foamability index (DFI) for characterizing the frother efficiency. DFI is defined as follows

$$DFI = \left(\frac{\partial F}{\partial C} \right)_{c \to 0}$$

Where F is foamability and C is the frother concentration.

DFI value for each frother has been calculated by determining the slope of initial part of the curve from Fig. 11. DFI is representing the initial rate of foaming with respect to lower concentration. DFI values of each frother, which are given below, show that PPG, Texanol and Df-1012 are strong frothing agent.

PPG	DF-1012	2-ethyl hexanol	Alpha-TP	Pine-C	MIBC
1.33	0.86	0.66	0.17	0.17	0.17
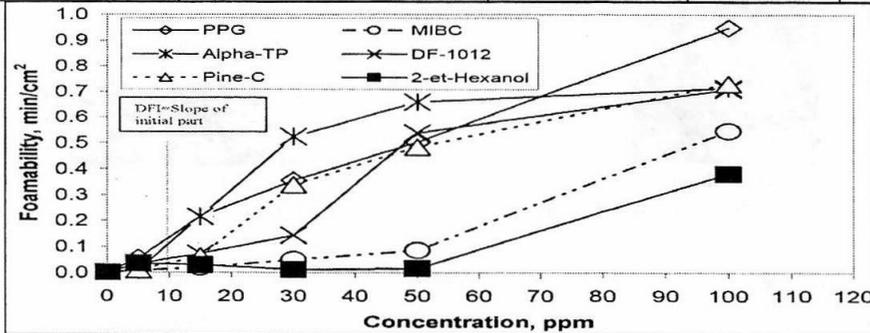
Fig. 11: Foamability Vs. Frother Concentration for DFI Calculation

Bubble Size Distribution (CCC)

Fig. 12 shows the cumulative bubble size distribution at 100-ppm frother concentration and 30-ml/min. airflow rate. DF-1012 curve in Fig. 12 is more steeper than other frothers. It means that DF-1012 is producing more narrow size bubble distribution compare to others.
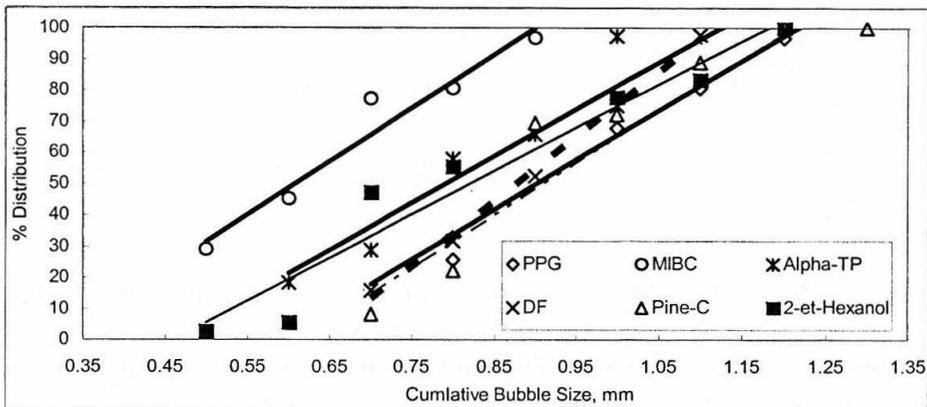
Fig. 12: Cumulative Bubble Size Distribution at 100 ppm Frother
Concentration and 30 Ml/Min. Air Flow Rate

The bubble size distribution, typically represented as D50 (mean diameter of the bubble), is considered to be another measure of the foamability of a reagent. Digital photographs of the foam generated in experiments were taken at 5 ppm, 15 ppm, 30 ppm, 50 ppm and 100 ppm frother dosage at 30 ml/min air flow rate. Some photographs showing bubble size distribution for four different frothers are shown in the Fig. 13.

PPG-100 ppm

DF-100 ppm

MIBC-50 ppm

Alpha-TP-100ppm
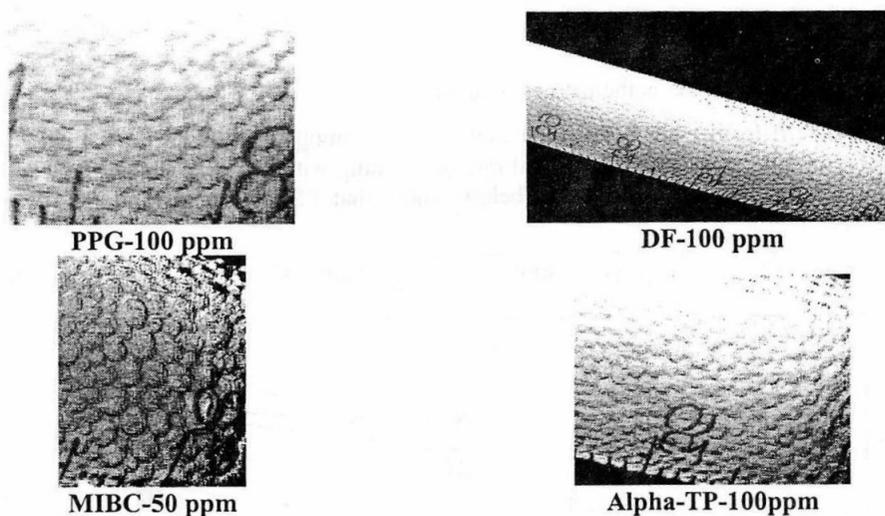
Fig. 13: Photographs Showing Bubble Size Distribution for Different Frothers
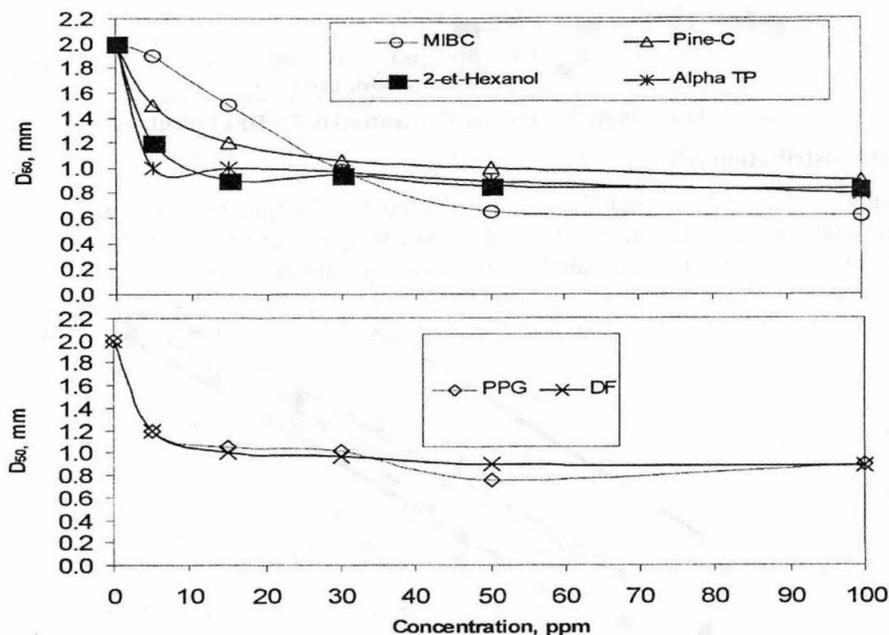
Fig. 14: Bubble Size (D_{50}) as a Function of Frother Concentration at Neutral pH for All Frothers

With the help of these digital photo graphs, the mean diameter of the bubbles (D50) was measured for each frother as a function of concentration. The results are summarized in Fig. 14. As this figure revels, each curve is clearly divided into two concentration ranges, 1) the low concentration range which can be approximated by a steep linear fit and 2) the flat horizontal portion at higher concentration. The intersection of the horizontal asymptote to the D_{50} bubble size-concentration curve with the steep linear portion can easily be determined. This is so called critical coalescence concentration. A clear-cut trend is observed. Bubble becomes smaller on increasing frother dosage but above certain a concentration there is no further decrease observed. Though the equilibrium bubble size for all frothers is in similar range. The dosage at which the bubble size reaches the plateau has

288

been as critical coalescence concentration (CCC). Critical coalescence concentration (CCC) values of each frother based on calculation is given below:

PPG	DF-1012	Alpha-TP	2-ethyl hexanol	Pine-C	MIBC
6	6	8	16	20	36

Frother efficiency is inversely related to critical coalescence concentration (CCC). It means PPG & DF-1012 is more effective frothing agents compare to others. CCC values can be treated as material constants for frothers. The ability of frothers to prevent bubble coalescence is well characterized by CCC. Many authors have tried to correlate CCC and DFI for different frothers. According to them more surface-active frothers are characterized by lower CCC and higher DFI values. Fig. 15 shows the relationship between CCC and DFI values of investigated frothers. It shows that PPG and DF-1012 are powerful frothers compare to others. It is obvious that it should be possible to use such a plot to classify the frothers.
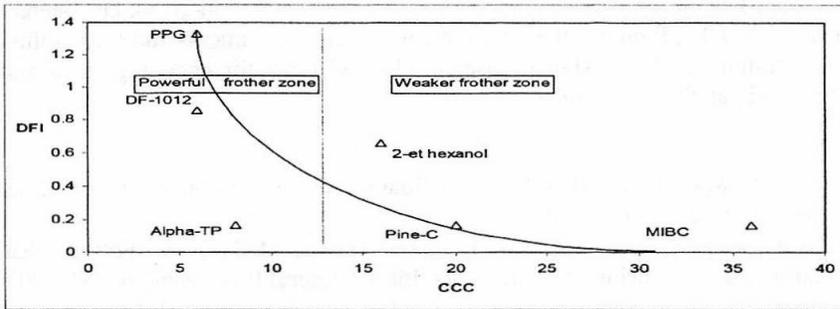
Fig. 15: Relationship between DFI and CCC for Different Tested Frothers

CONCLUDING REMARKS

Performance of different commercial frothers is studied based on two-phase foamabilty, foam stability, surface activity, critical coalescence concentration and dynamic foamability index criteria. The order of frother efficiency as determined by these different investigations are summarized in Table 2.

Table 2: Relative Order of Frother Efficiency

Characterization parameter	Order of the frother efficiency
Surface tension	PPG > DF > Pine-C ≈ MIBC > 2-et-Hexanol > Alpha-TP
Foamability	PPG ≈ Alpha-TP > DF ≈ Pine-C > MIBC > 2-et-Hexanol
Foam stability	DF >> PPG > MIBC ≈ Pine-C ≈ alpha-TP > 2-et-Hexanol
DFI	PPG > DF > 2-et-hexanol > Pine-C ≈ alpha-TP ≈ MIBC
CCC	PPG ≈ DF < Alpha-TP < 2-et-hexanol < Pine-C < MIBC

It is clear from Table 2 that PPG and DF-1012 are strong frothing reagents and MIBC and 2-ethyl hexanol are weaker frothers.

CONCLUSIONS

The following conclusions can be drawn from this two-phase structure-property study of frothers:

- DF-1012 and PPG are found to be better performing frothers in term of foamability and foam stability.
- PPG and DF are showing better foamability in neutral pH. But in other hand, Texanol, MIBC & Pine-C are better in alkaline pH All frothers exhibit higher foam stability at alkaline pH of solution.
- The experimental bubble size-frother concentration curves are clearly divided into two concentration ranges; i) the low concentration range, which can be approximated by a steep linear fit and ii) the flat horizontal portion at higher concentration.
- There is inverse relationship between dynamic foamability index (DFI) and critical coalescence concentration CCC parameters of a frother. DF-1012 and PPG are showing lower CCC.

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REFERENCES

[1] Cho, Y.S., Laskowski, J.S., 2002a. Effect of flotation frothers on bubble size and foam stability. Int. J. Mineral Processing. 64, 69-80.

[2] Comley, B.A., Harris, P.J., Bradshaw, D.J., and Harris, M.C., 2002. Frother characterization using dynamic surface tension measurements. Int. J. Mineral Processing, 64, 81-100

[3] Czarnecki, J., Malysa, K. and Ponianowski, A., 1982. Dynamic frothability index, J. Colloid and Interface Science, 86, 570-572.

[4] Grau, R.A., Laskowski, J.S., and Heiskanen, K., 2005. Effect of frothers on bubble size. Int. J. Mineral Processing, 76 (8), 225-233.

[5] Klimpel, R. R., and Hansen, R. D., 1988. Frothers. Somasundaran, P., Moudgil, B. M. (eds.), Reagents in Mineral Technology. Marcel Dekker, New York, pp 385-409.

[6] Laskowski, J.S., 2003. Fundamental properties of flotation frothers. In: Lorenzen, L., Bradshaw, D.J. (Eds.), Proc. 22nd Int. Mineral Processing Congress, vol. 2. The South African Institute of Mining and Metallurgy, Cape Town, pp. 788-797.

[7] Laskowski, J. S., Cho, Y.S., and Ding, K., 2003a. Effect of frothers on bubble size and foam stability in potash ore flotation systems. The Canadian Journal of Chemical Engineering, 81, 63-69.

[8] Laskowski, J.S., Tlhone, T., Williams, P. and Ding, K., 2003b. Fundamental properties of polyoxypropylene alkyl ether flotation frothers. Int. J. Mineral Processing, 72, 289-299.

[9] Malysa, E., Malysa, K., and Czarnecki, J., 1987. A method of comparison of the frothing and collecting properties of frothers. Colloids and Surfaces, 23, 29-39.

[10] Pugh, R.J., 2005. Experimental techniques for studying the structure of foams and froths. Advances in Colloid and Interface Sci., 114-115, 239-251

[11] Tan, S. N., Fornasiero, D., Sedev, R. and Ralston, J., 2005a. Marangoni effects in aqueous polypropylene glycol films. J. Colloid and Interface Sci., 286, 719-729

[12] Tan, S. N., Pugh, R.J., Fornasiero, Sedev, R. and Ralston, J., 2005b. Foaming of polypropylene glycols and glycol/MIBC mixtures. Minerals Engineering, 18, 179-188